Unit: 3 :
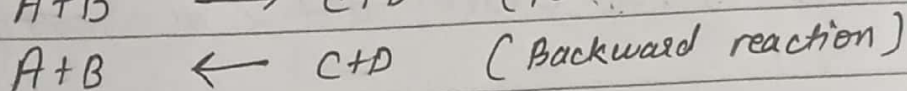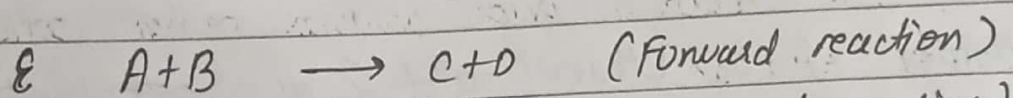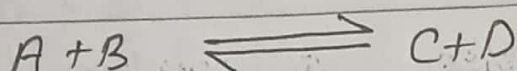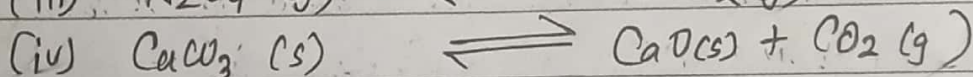## CHEMICAL EQUILIBRIUM
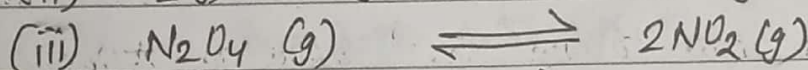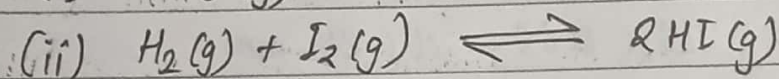
Reversible Reaction

A reaction that goes in forward and background direction simultaneously is called a reversible reaction.

E. $A+B \longrightarrow C+D$ (Forward reaction)

$A+B \longleftarrow C+D$ (Backward reaction)

&o1

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

Eg:

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

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

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

(iv) $CaCO_3 (s) \rightleftharpoons CaO(s) + CO_2 (g)$
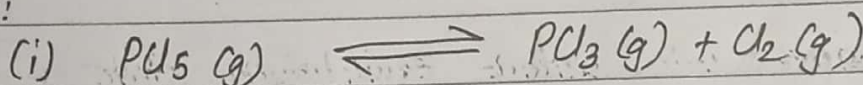
Irreversible reaction:

A chemical reaction that proceeds in only one direction is called irreversible reaction.

Nature of Chemical Equilibrium

Let us suppose a chemical reaction in a closed vessel.

$$H_2O (g) + CO_2(g) \rightleftharpoons H_2 (g) + CO_2 (g)$$

F.r. rate

Equilibrium

Rate →

R.r. rate .

Time →

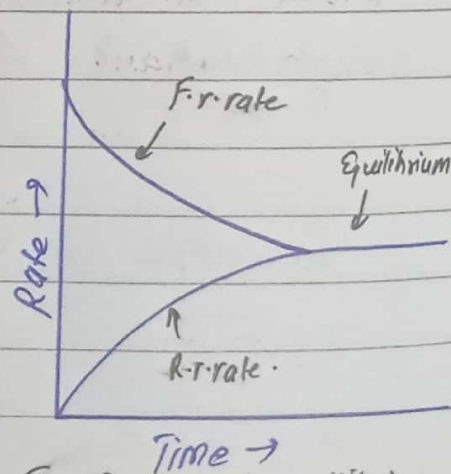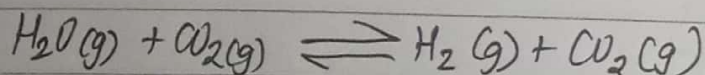for this reaction, after a certain time 't', the rate of forward reaction equals rate of background reaction meaning the system attains equilibrium.

(*): Chemical Equilibrium:

The state of a reversible reaction in which the rates of the forward and reverse reactions are equal and the concentrations of the reactant and products remain constant is called chemical equilibrium.

(*) Characteristics:
(i): It cannot be attained in an open vessel.
(ii) It is dynamic in nature.
(iii) It is reversible and attains equilibrium state spontaneously.
(iv) Chemical equilibrium can be attained from either side.
(v) It represents a compromise bet^o opposing tendencies.
(vi) A catalyst cannot change equilibrium point.

Equilibrium Constant:

*) Active mass: The molar concentration of any substances which determines the rate of chemical reaction is called active mass.

Let us suppose a general reaction;
$$aA + bB \rightleftharpoons cC + dD$$
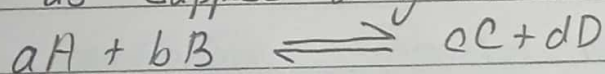
Here, $[A], [B], [C], [D]$ is the molar conc of A, B, C, D at equilibrium point.

(*) Law of Mass Action:

Law of mass Action states that, " the rate of a chemical reaction is proportional to the active masses of the reaction reactants.

Then, according to law of mass action,

rate of forward reaction = $k_f [A][B]^b$ —— (i)
rate of backward reaction = $k_b [C]^c [D]^d$ —— (ii)

Here,

k_f = rate constant for forward rxn
k_b = rate constant for backward rxn.

At equilibrium, both processes proceeds at the same rate. ie,

rate of forward reaction = rate of backward reaction.

ie, $k_f [A]^a [B]^b = k_b [C]^c [D]^d$

or, $\dfrac{k_f}{k_b} = \dfrac{[C]^c [D]^d}{[A]^a [B]^b}$

or $K_{eq} = \dfrac{[C]^c [D]^d}{[A]^a [B]^b}$ —— (iii).

Here, k_f/k_b is a constant called equilibrium constant

and eqn (iii) is equilibrium constant expression or equilibrium law.

(*) Equilibrium constant:

Equilibrium constant is defined as the ratio of product of equilibrium concentrations of the products to the product of equilibrium concentration of the reactants, with each concentration term raised to a power equal to the coefficient of the species in balanced chemical equation.

(*) Characteristics:

(i): K_{eq} doesn't depend upon the use of catalyst.
(ii) K_{eq} depends upon temperature and identity of reactant and products.

(*): Conditions for values of K_{eq}:

(i): If $K_c \gg 1$, equilibrium shifts towards right and reaction mixture mostly contain products.
(ii) If $K_c \ll 1$, equilibrium shift towards left and reaction mixture mostly contain reactants.
(iii) If $K_c \approx 1$, the mixture contains appreciable amount of reactants and products.

Reaction Quotient (Q) and Equilibrium Constant (K_{eq})

Reaction quotient (Q) is the resulting value when we substitute reactant and product concentrations into the equilibrium expression at any instance.

(i): If $Q > K$, reaction goes towards left.

The ratio of products over reactants is too large and the reaction will move towards equilibrium forming more reactants.

(ii) If $Q < K$, reaction goes towards right.

The ratio of products over reactants is too too small and reaction moved towards equilibrium forming more products.

(iii) If $Q = K$, the reaction is already at equilibrium, so no shift occurs.

Equilibrium Constant in terms of partial pressure.

for gaseous reaction, equilibrium constants is expressed in terms of pressure.

for ideal gas equation,
$$PV = nRT$$

on
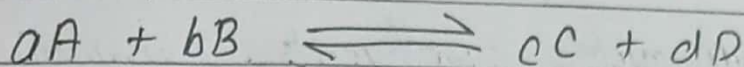$$P = \frac{n}{V} RT$$

or, $P \propto C$

Here, partial pressure of any gas in equilibrium mixture is directly proportional to its molar concentration.

Equilibrium constant in terms of pressure,
$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

(*) **Relation bet^n Kp and Kc...**

for reaction,

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

we know,

$$Kp = \frac{(PC)^c (PD)^d}{(PA)^a (PB)^b} \quad -(i)$$

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

from ideal gas eq^n;

$$P_A \propto C_a, \quad P_B \propto C_B, \quad P_c \propto C_c, \quad P_D \propto C_D$$

So, eq^n (i) becomes.

$$Kp = \frac{(C_c)^c \times (C_D)^d}{(C_A)^a \times (C_B)^d} \times \frac{(RT)^c \times (RT)^d}{(RT)^a \times (RT)^b}$$

or, $Kp = Kc \times (RT)^{(c+d) - (a+b)}$ [From eq^n (ii)]

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

Here, Δn = difference bet^n total moles of the products and the total moles of the reactants.

if $\Delta n = 0$,

$$Kp = Kc.$$

Equilibrium constant in atm unit can be changed to equilibrium constant in a torr unit.

$$Kp_{(torr)} = Kp_{(Atm)} \times [760]^2$$

Modifying Equilibrium Constant Equilibrium

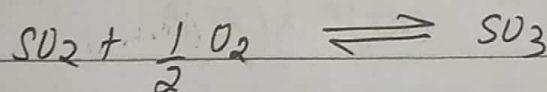**(i): Changing stoichiometric coefficients:**

If a reaction is multiplied by a certain number, its equilibrium constant must be raised to a power equal to that number in order to obtain the new equilibrium constant.

Eg:

for $2SO_2 + O_2 \rightleftharpoons 2SO_3$.
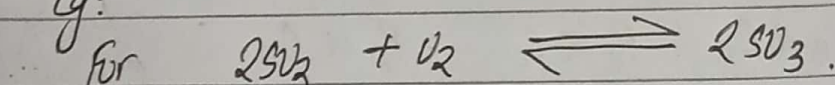
$$K_1 = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \qquad —(i)$$
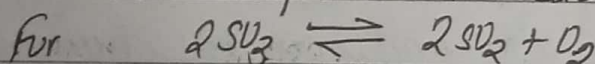
And

$$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$$

$$K_2 = \frac{[SO_3]}{[SO_2] \times [O_2]^{1/2}} \qquad —(ii)$$
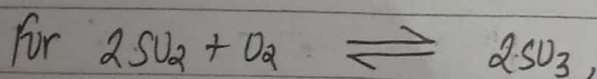
From eq^n (i) and (ii),

$$K_2 = (K_1)^{1/2}.$$

(ii): Reversing the reaction:

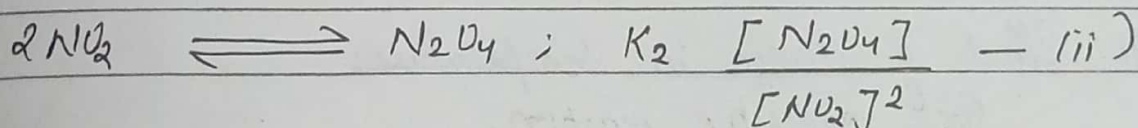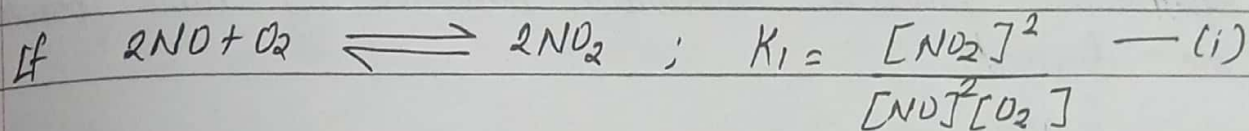The equilibrium constant for a reaction and its reverse are reciprocal to each other.

for $2SO_3 \rightleftharpoons 2SO_2 + O_2$

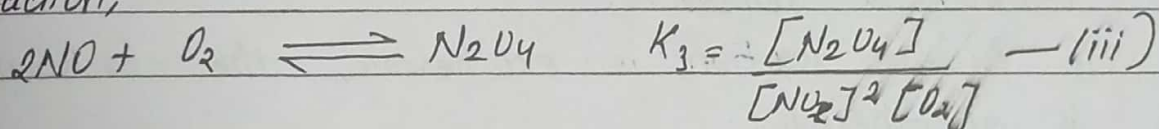$$K_1 = \frac{[SO_2]^2 [O_2]}{[SO_3]^2} \qquad —(i)$$

for $2SO_2 + O_2 \rightleftharpoons 2SO_3$,

$$K_2 = \frac{[SO_3]^2}{[SO_2]^2[O_2]} \qquad —(ii)$$

from (i) and (ii), $K_2 = \dfrac{1}{K_1}$

(iii) Adding the multiple equilibrium reactions to get final reaction

when two or more elementary reactions are added, their equilibrium constants must be multiplied to give equilibrium constant of overall reaction.

If $2NO + O_2 \rightleftharpoons 2NO_2$; $K_1 = \dfrac{[NO_2]^2}{[NO]^2[O_2]}$ —— (i)

   $2NO_2 \rightleftharpoons N_2O_4$; $K_2 \dfrac{[N_2O_4]}{[NO_2]^2}$ —— (ii)

final reaction;
   $2NO + O_2 \rightleftharpoons N_2O_4$ $K_3 = \dfrac{[N_2O_4]}{[NO_2]^2[O_2]}$ —— (iii)

from (i), (ii) and (iii),
   $K_3 = K_1 \times K_2$.

Le-Chatelier's Principle

Le-Chatelier's principle states that, " If a system at equilibrium is subjected to a change of pressure, temperature, or the moles y substance, there will be a tendency for a net reaction in the direction that tends to reduce the effect of this change.
   Equilibrium shifts left or right to minimize the change.

(i): Effect of change in concentration:

Increase in concentration of any of reactants shifts the equilibrium towards forward direction ie,. more products are formed.

Increase in concentration of any of products shifts the equilibrium towards backward direction ie, more reactants are formed.

(ii) Effect of change in temperature:
For reversible reaction,

if forward reaction is endothermic, the backward reaction is exothermic.

if forward reaction is exothermic, the backward reaction is endothermic.

when temperature of a reaction is increased, the equilibrium shifts in direction were heated is absorbed.

Increase in temperature shifts the equilibrium towards endothermic reaction.

Decrease in temperature shifts the equilibrium towards exothermic reaction.

(ii) ~~Change of Pressure~~ Effect of change in pressure:

a) Addition/Removal of gaseous reactants/products.
        We know,
this is similar to change in concentration.

b) Change the volume of container:

   If P is increased, V decreased is and equilibrium shifts in the direction with less number of gas molecules.

   If P is decreased, V increases and equilibrium shifts in direction with greater number of gas molecules.

   If $\Delta n = 0$ then, change in pressure has no effect on equilibrium condition.

c) ~~Addition of Inert Gas:~~ Addition of Inert Gas:

   At constant volume, if inert gas is added, pressure of system increases but the equilibrium constant is not affected by adding inert gas.

   At constant pressure, if inert gas is added, the volume increases and equilibrium shifts in direction with greater number of gas molecules.
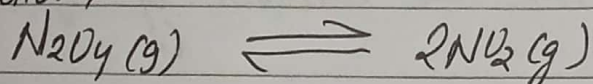
(iv): Effect of catalyst

  Catalyst decreases activation energy which decreases the time taken to reach equilibrium. Catalyst doesn't affect equilibrium constant.
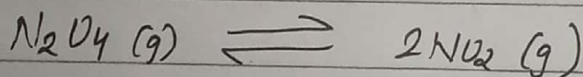
Calculation of the Equilibrium Constant for Gaseous Reaction

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

Here, $K_p = \dfrac{(P_{NO_2})^2}{(P_{N_2O_4})}$

Here,
$$N_2O_4 \, (g) \rightleftharpoons 2NO_2 \, (g)$$
At initial,   1   0
At eq^n $1-f$ $2f$

Total no. of moles present at equilibrium $= 1+f$

$\therefore X_{N_2O_4} = \dfrac{(1-f)}{(1+f)}$ $\therefore X_{NO_2} = \dfrac{2f}{(1+f)}$

Now, partial pressure of N_2O_4 and NO_2 in terms of total pressure

$$P_{NO_2} = X_{NO_2} \cdot P_T = \left(\dfrac{2f}{(1+f)}\right) \times P_T$$

$$P_{N_2O_4} = X_{N_2O_4} \times P_T$$
$$= \frac{2(1-f)}{(1+f)} \times P_T$$

We know,
$$K_p = \frac{(P\,NO_2)^2}{(PN_2O_4)}$$

So,
$$K_p = P_T \times \frac{4f^2}{(1-f^2)}$$

Here, P_T = total pressure of reactant and product.

f = fraction of reactant dissociated.