

Chemical Equilibrium

① Introduction:-

It is a fact that most of the chemical reaction when carried out in a closed vessel, do not go to completion. Under these conditions, a process starts by itself or by inciation continues for some time at a diminishing rate and ultimately appears to stop. The reactants may still be present but they do not appear to change into products anymore.

① Reversible Reactions:-

A reaction is considered reversible if the composition of reaction reaches equilibrium, irrespective of the initial state of the system

eg.



① Irreversible Reactions:-

These are such reactions which almost go till completion.

eg



① Equilibrium:-

Equilibrium represents the state in nature in which properties like temp, pressure, conc. of mixture do not show any change with the passage of time.

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⇒ Characteristics of Chemical Equilibrium:-

- ① The equilibrium is dynamic i.e. the reaction continues both in forward and backward direction.
- ② The rate of forward reaction equals the rate of backward reaction.
- ③ The observable properties of the system such as pressure, concentration, density remains invariant with time.
- ④ The chemical equilibrium can be approached from either side, starting with any combination of reactants or products.

Note:- A catalyst can faster approach the equilibrium but it do not alter the state of equilibrium.

⇒ Types of Equilibria:-

(a) Homogeneous: Equilibrium is said to be Homogeneous when the reactants and products are in same phase.

eg.



(b) Heterogeneous: Equilibrium is said to be heterogeneous if reactants and products are in different phase.





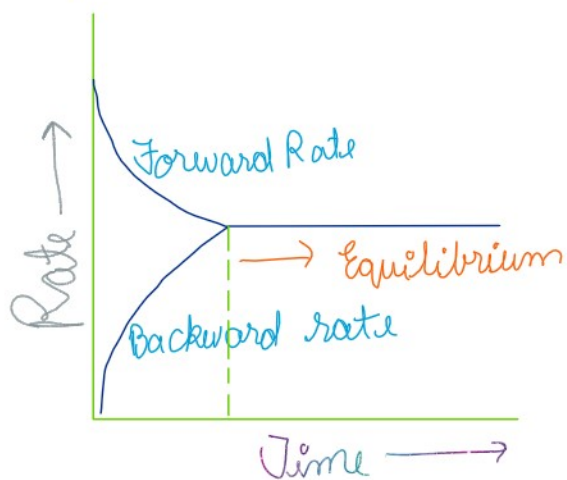
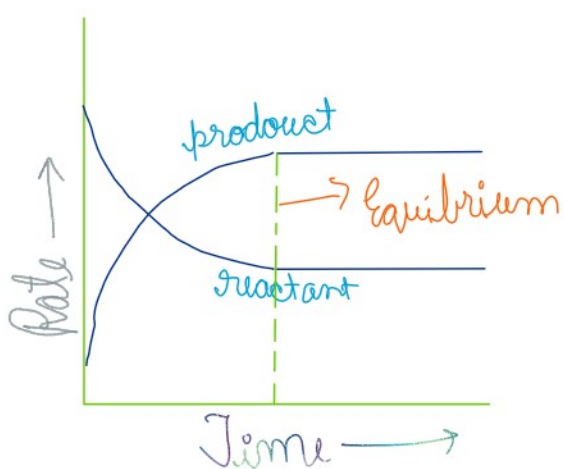
⊙ Law's of Mass Action :-

According to this law the rate of reaction at a given temperature is directly proportional the products of active masses of the reactants, raised to the power equal to stoichiometric coefficient of the balanced chemical equation at particular instant of reaction.



$$\begin{aligned} \text{Rate of reaction} &\propto [A]^a \cdot [B]^b \\ &= K [A]^a \cdot [B]^b \end{aligned}$$

Where K is rate constant or velocity constant of the reaction at that temperature.



⊙ Equilibrium constants (K_p & K_c) and relation between them.





The rate of forward reaction. = $K_f [A]^a [B]^b$

The rate of backward reaction. = $K_b [C]^c + [D]^d$

This ratio $\frac{K_f}{K_b}$ is called equilibrium constant.

For a general equation in which all components are in gaseous phase,



Since for a gas $Pv = nRT$

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

$$\therefore \frac{n}{P} = \frac{P}{RT}$$

$$\therefore [C] = \frac{P_c}{RT}, [D] = \frac{P_d}{RT}, [A] = \frac{P_A}{RT}, [B] = \frac{P_B}{RT}$$

$$\therefore K_c = \frac{\left[\frac{P_c}{RT}\right]^c \left[\frac{P_d}{RT}\right]^d}{\left[\frac{P_A}{RT}\right]^a \left[\frac{P_B}{RT}\right]^b}$$

$$K_c (RT)^{(c+d)-(a+b)} = \frac{P_c^c P_d^d}{P_A^a P_B^b}$$

Since K_c is constant and RT is constant, it implies for this equilibrium the ratio of the partial pressures is also constant.

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

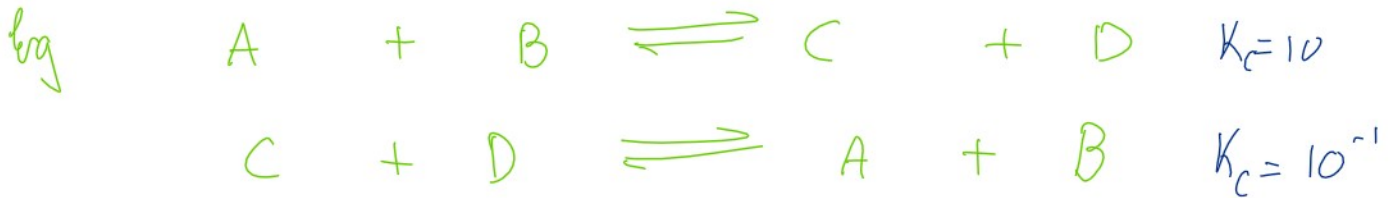
where $\Delta n = \text{Total moles of product gases} - \text{Total moles of reactant gases}$.

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Concentration = mol/dit \propto density

⊙ Important Relationships Involving equilibrium constant.

* If we reverse an equation, K_c or K_p is inverted.



* If we multiply each of the coefficient in a balanced equation by a factor n then the equilibrium constant is raised by same factor.



or if divide it by the n factor, then the equilibrium constant is n^{th} root of the previous value.



⊙ Significance of Magnitude of Equilibrium constant:-

* A very large value of K_c or K_p signifies that forward reaction goes till completion or very nearly so.

* A very small value of K_c or K_p signifies that forward reaction does not occur to any significant extent.

* A reaction is most likely to reach the state of equilibrium when

✓ ✓ ✓

* A reaction is most likely to reach the state of equilibrium when the value of K_c or K_p is neither very large nor very small.

Reaction Quotient (Q) Imp

At each point in the reaction, we can formulate the ratio of concentration terms having the same form as the equilibrium constant expression. This ratio is called the reaction quotient denoted by symbol Q. It helps in predicting the direction of the reaction.

for a general reaction.

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

- If the reaction is at equilibrium $Q = K_c$
- A net reaction proceeds from left to right (forward direction) if $Q < K_c$
- A net reaction proceeds from right to left (backward direction) if $Q > K_c$

Le Chatelier's Principle: V.V Imp

This is based on fundamentals of a stable equilibrium. It states that when a system is in equilibrium subjected to a change in temperature, pressure, concentration of a reacting species, the system reacts in a way that partially offsets the change while reaching a new state of equilibrium.



Let us consider that this reaction is at equilibrium and the moles of Cl_2 , PCl_3 and PCl_5 at equilibrium are a, b and c respectively. and let the total pressure be P_T .

$$V = \frac{(a + b + c) \times P_T}{\dots \times P_T}$$

$$\therefore K_p = \frac{\left(\frac{a}{a+b+c} \times P_T\right) \left(\frac{d}{a+b+c} \times P_T\right)}{\left(\frac{c}{a+b+c} \times P_T\right)}$$

$$\text{Since } P_T = \frac{(a+b+c)RT}{V}$$

$$\therefore K_p = \frac{adRT}{cV}$$

Now if d moles of PCl_3 is added to system, the value of Q would be,

$$= \frac{a(d+d)RT}{cV}$$

We can see that this value is more than K_p . So the system would move reverse to attain the equilibrium.

Some Conditions:-

- (i) If we increase the volume of the system, the Q becomes $\frac{adRT}{cV'}$ where $V' > V$
 $\therefore Q$ becomes less and the system would move forward to attain equilibrium.
- (ii) If we add noble gas at constant pressure the volume of the system will be increased and the reaction will move in forward direction.
- (iii) If we add noble gas at constant volume there will be no change in the expression $Q = \frac{adRT}{cV}$ and the system continues to be in equilibrium.
- (iv) If the pressure of the equilibrium system then reaction will move in the direction where lesser moles are formed.
- (v) If the concentration of the reactant is increased it shifts in the forward direction and if it decreases the reaction moves in the backward direction.

Temperature Effect:-

The equation which is used to predict the temperature effect on equilibrium constant is known as Hoff's Constant and is represented as,

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

* If ΔH° is positive ($T_2 > T_1$) then reaction will move in forward direction and vice-versa

○ Calculation of Degree of Disassociation from Density Measurement:- Imp-

This is the method of calculating degree of dissociation of gas using vapour densities. This method is valid only for those reactions whose K_p exists (meaning reactions having at least one gas and having no solutions)

Since, $PV = nRT$

$$PV = \frac{W}{M} RT$$

$$M = \frac{WRT}{PV} = \frac{PRT}{P}$$

$$\therefore \text{vapour density (VD)} = \frac{PRT}{2P}$$

$$\left\{ \begin{array}{l} \text{molar mass} = \\ 2 \times \text{Vapour Density} \end{array} \right\}$$

Since $P = \frac{nRT}{V}$

$$\therefore VD = \frac{pRT}{2nRT} \times V = \frac{pV}{2n}$$

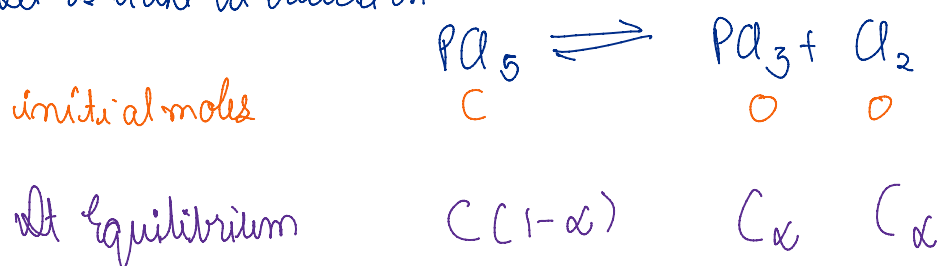
For a reaction at equilibrium, V is constant and p is constant

$$\therefore \text{vapour density} \propto \frac{1}{n}$$

$$\therefore \frac{\text{Total no of moles at equilibrium}}{\text{Initial total moles}} = \frac{\text{vapour density initial}}{\text{vapour density at equilibrium}} = \frac{D}{d}$$

Let us understand this with an example.

Let us take a reaction



$$\therefore \frac{C(1+x)}{C} = \frac{D}{d} ;$$

$$(1+x) = \frac{D}{d}$$

hence, by knowing the value of D and d the value of x can be calculated