Chapter 9 Chemical Kinetics

Day - 1

Ex.1- Calculate the ΔG^o_{rxn} for the following overall reaction of the conversation of

$C_{diamond} \rightarrow C_{graphite}$ $\Delta G^o_{rxn} = ?$

$C_{diamond}(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta G^o_{rxn} = -397$ kJ

$C_{graphite}(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta G^o_{rxn} = -394$ kJ

(a) – 3 kJ

(b) + 3 kJ

(c) – 791 kJ

(d) + 791 kJ

Answer (a) . This proves that conversion of diamond to graphite is spontaneous.

Ex.2 - Combustion of Carbon: at 25oC

$C + O_2 \rightarrow CO_2$; $\Delta H_1 = -393.5$ kJ / mole $\Delta S = 2.986$ J/mole/K

Find ΔG for the reaction

$\Delta G = \Delta H - T\Delta S = -393.5 - (298 \times 2.986)/1000 = -394.39$ KJ/mole

So now two questions

1. Why diamonds are called diamonds for ever
2. Why does wood and paper not catch fire on it's own

Thermodynamics tells us whether the reaction will go forward, backward or is at equilibrium. Thermodynamics does not tell us.

1. how fast or slow the reaction proceeds
2. What is the mechanism of reaction?

Chemical kinetics is the branch of chemistry, which deals with the study of reaction rates and their mechanisms.

Reaction can be classified as

A. Very fast ($t < 10^{-6}$ seconds) ex. $NaOH + HCl \rightarrow NaCl + H_2O$ ($t \sim 10^{-12}$s)

B. Very slow ex. C(diamond) $\rightarrow C_{graphite}$ (t ~ million years)

C. Moderate In between the above two, where rates can be measured experimentally

Ex. $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

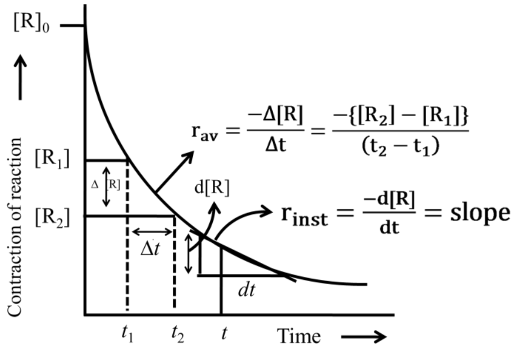
$2FeCl_3 + 6KI \rightarrow 2FeI_2 + 6KCl + I_2$

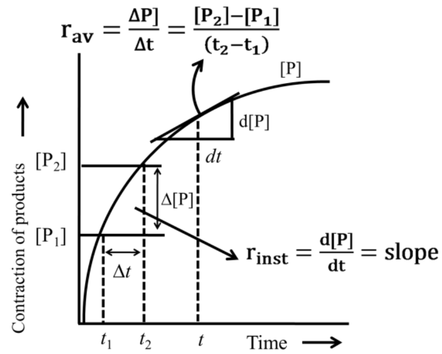
AVERAGE RATE OF REACTION

$$\text{Rate} = \frac{\text{change in concentration}}{\text{change in time}} = \frac{\Delta c}{\Delta t}$$

Instant Rate and Reaction is the rate a particular time = $\frac{dc}{dt}$

Units of Rate of reaction are mole/lit sec or atm/sec





RATE OF REACTION

aA + bB → cC + dD

Rate $= -\frac{1}{a}\frac{1d(A)}{dt} = -\frac{1}{b}\frac{d(B)}{dt} = \frac{1}{c}\frac{d(c)}{dt} = \frac{1}{d}\frac{d(D)}{dt}$

Ex.1: Formation of ammonia from nitrogen and hydrogen if rate of ammonia formation is 2x 10^{-4} mol/lit sec find rate of disappearance of N_2 & H_2

$N_2 + 3H_2 \rightarrow 2NH_3$

Rate $= -\frac{d[N_2]}{dt} = -\frac{1}{3}\frac{d(H_2)}{dt} = \frac{1}{2}\frac{d(NH_3)}{dt}$

given $\frac{d[NH_3]}{dt} = 2 \times 10^{-4}$

As. H_2 & N_2 rate of disappearance is

$\frac{d(N_2)}{dt} = -1 \times 10^{-4}$

$\frac{d(H_2)}{dt} = -3 \times 10^{-4}$

$3 \times 10^{-4}\frac{mole}{litsec}$ and $\frac{10^{-4}mole}{lit\ sec}$

LAW OF MASS ACTION

Law of Mass Action (Goldberg and wage 1864)

"Any given temperature the rate of reaction is proportional to the product of active masses of the power equal to their stoichiometric ratios.

aA + bB →Products

Rate $\propto$ $[A]^a$ and Rate $\propto$ $[b]^b$

Rate = $K[A]^a [B]^b$ K= Rate constant.

The rate constant depends upon

1. Nature of reactants
2. Temperature
3. Catalyst

Unit of rate constant (R) = $\left(\frac{lit}{mol}\right)^{n-1} sec^{-1}$

n = order of reaction

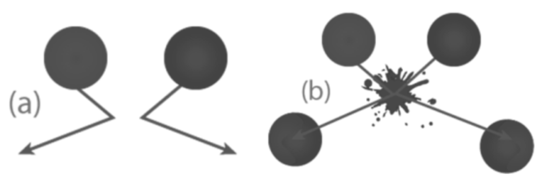
RATE OF REACTION	RATE CONSTANT
Rate of reaction is the change in the concentration of reactions or the change in the concentration of products per unit time	Rate constant is the proportionality constant related to the rate of a particular reaction
Depends on the molar concentrations of reactants and products	Does not depend on the molar concentrations of reactants and products
Depends on the temperature indirectly	Essentially depends on the temperature
Depends on the time taken for the reaction	Does not depend on the time taken for the reaction

Collision theory

A chemical reaction taken place when the molecules of reaction

1. Collide with each other
2. Must possess energy greater than activation energy of the system.
3. The collisions should have proper orientation.

1. Collision of particles



How number of collisions change with concentration