or $t_{1/2} = \frac{2.303 \times}{k}$

$t_{1/2} = \frac{0.693}{k}$

It can be seen that for a first order reaction half life period is constant i.e. it is independent of initial concentration of the reacting species.

Note:- For zero order rkn $t_{1/2} \propto [R]_0$.

For first order rkn $t_{1/2}$ is independent of $[R]_0$.

Pseudo First order Rkn:-

Consider a general equation, $A + B \rightarrow$ Product, in which order with respect to each reactant is 1 so that overall order of reaction is 2. The rate law eqn is:-

$$Rate = k[A][B].$$

However if one of the reactant is present in excess, its concn remains almost constant. In that case the rate of the reaction will depend only on the concentration of reactant present in smaller amount. Thus the reaction becomes a first order rkn.

"Such reactions which are not truly of the first order but under certain conditions become reactions of the first order are called as pseudo first order rxn".

eg. During the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of water, amounts of the various constituents at the begining of the reaction (t = 0) and completion (t) of the reaction are given as under! -

	$CH_3COOC_2H_5$	$+ H_2O$ $\xrightarrow{H^+}$	CH_3COOH	$+ C_2H_5OH$
0	0.01 mol	10 mol	0 mol	0 mol
t	0 mol	9.9 mol	0.01 mol	0.01 mol

The concn of water do not get altered much during the course of reaction.
So in the rate equation:-

$$Rate = k'[CH_3COOC_2H_5][H_2O]$$

the term H_2O can be taken as constant. The equation thus becomes:-

$$Rate = k(CH_3COOC_2H_5)$$

where $k = k'[H_2O]$.

and the reaction behaves as first order

Such reactions are called as pseudo first order.

Inversion of cane sugar is another pseudo first order reaction.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6.$$

Cane sugar.

$$Rate = k[C_{12}H_{22}O_{11}]$$

Temperature Dependence of the Rate of a reaction.

* Concept of Activation Energy of Rxns:-

According to collision theory, a reaction takes place bcoz the reactant molecule collide with each other. However, every collision is not an effective collision i.e. does not result into a chemical reaction. For the collision to be effective, the colliding molecules must have energy more than a particular value.

The minimum energy which the colliding molecules must have in order that the collision between them may be effective is called threshold energy. (23)

At room temp most of the reactant molecules have energy less than the threshold value. However if energy is supplied in the form of heat, light etc, the reactant molecules absorb this energy and their energy becomes equal to or greater than threshold value. Hence they start reacting and change into products.

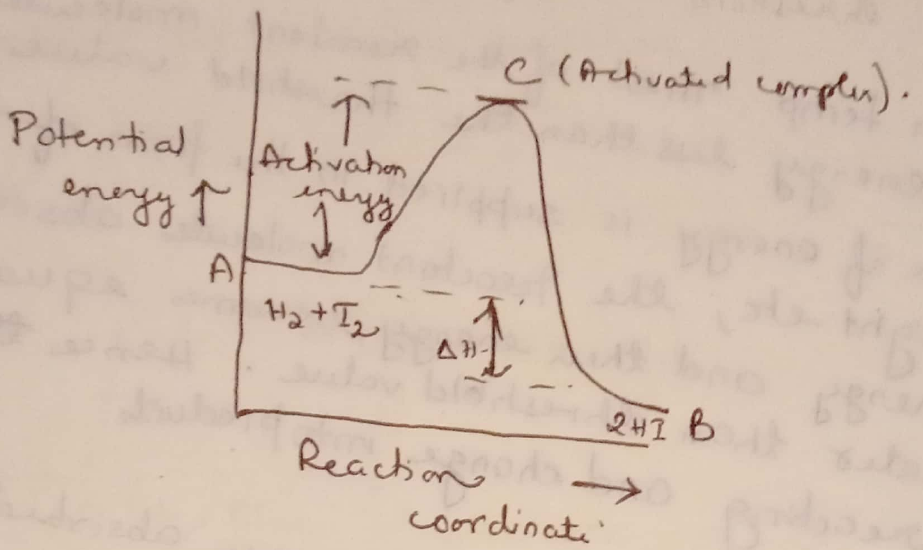
The minimum extra amount of energy absorbed by the reactant molecules so that their energy becomes equal to threshold value is called activation energy.

Evidently, less is the activation energy, faster is the reaction or greater is the activation energy, slower is the reaction.

Reaction Profile (Path followed by a reaction) and concept of activated complex (Transition state)

In order that the reactants may change into products, they have to cross energy barrier corresponding to threshold energy as shown in fig. The fig is obtained by plotting potential energy vs reaction coordinate.

Reaction coordinate represents the reaction profile i.e progress of reaction from reactants to products accompanied by changes in potential energy.

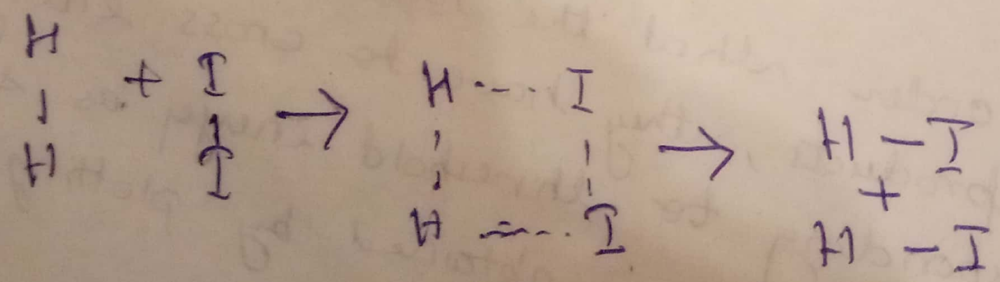


It is believed that when reactant molecules absorb energy, their bonds are loosened and new loose bonds are formed between them.

The intermediate thus formed is called an activated complex or transition state complex. It is unstable and immidiately dissociates to form stable products.

It can be understood easily by using eqn:-

eg:- ~~Fo~~ $H_2 + I_2 \rightarrow 2HI$.



Intermediate.