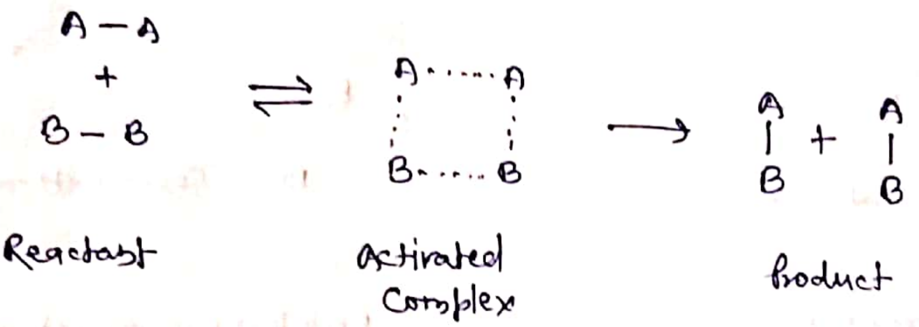
*. Potential Energy diagram and Concept of activated complex :-

A/c to activated Complex theory (ACT), the bimolecular reaction between two molecules A_2 & B_2 progresses through the formation of the so-called activated Complex which then decomposes to yield the product AB —

$$A_2 + B_2 \rightleftharpoons (A_2B_2)^{\#} \longrightarrow 2AB$$

or



Threshold Energy :-

The minimum energy which the reactant molecules should possess so that they may react to produce the product is called threshold energy.

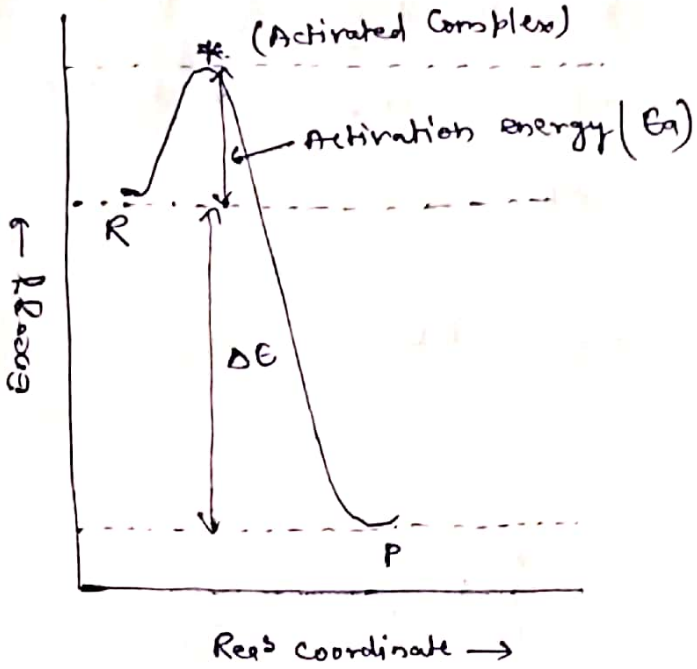
Activation energy :- (Ea)

Reactant molecules possess some energy initially also. The minimum extra energy given to the reactant molecules to make their energy equal to threshold energy is called Activation energy.

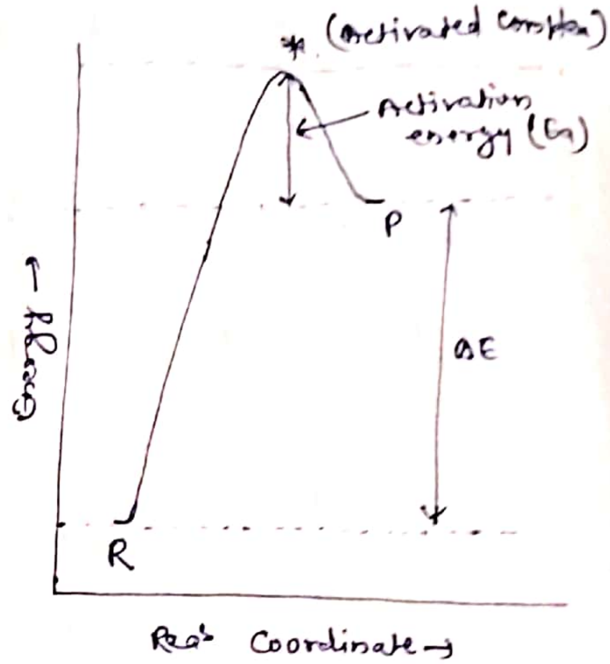
Thus,

Activation energy = Threshold energy − Energy possessed by molecule.

A curve is obtained by potential energy Vs reaction co-ordinate. Reaction coordinate represents the profile energy change when reactants change into products.



Exothermic reaction



Endothermic reaction.

* Rate data and Mechanism of a chemical Reaction :-

For thermodynamic formulation of the activated complex theory, let us consider a simple bimolecular reaction -

$$A + B \underset{}{\overset{K^*}{\rightleftharpoons}} [AB^*] \xrightarrow{k_2} \text{Product}$$

Where, $[AB^*]$ is called Activated Complex

K^* is the equilibrium constant between reactant and activated complex.

From classical mechanics, the energy of vibration is given by - RT/N_A.

and from quantum mechanics, it is given by $h\nu$.

Where,

$$h\nu = RT/N_A$$

or $\nu = RT/N_A h$.

Thus, the reaction rate is given by—

$$-\frac{d[A]}{dt} = k\, K_2\, [AB^*] = k(K_BT/h)\,[AB^*] \quad \text{——} (1)$$

Where, the factor k, called transmission coefficient.

Now, at equilibrium—

$$K^* = \frac{[AB^*]}{[A][B]}$$

or $[AB^*] = K^* [A][B]$ ——— (2)

Now putting this value in eqⁿ — (1)

$$-\frac{d[A]}{dt} = (K_BT/h)\, K^* [A][B] \quad \text{———} (3)$$

thus the rate constant K_2 may be expressed as—

$$K_2 = (K_B T/h)\, K^* \quad \text{———} (4)$$

The equilibrium constant K^* can be expressed in terms of $(\Delta G^\circ)^*$ called the standard Gibb's free energy of activation.

Thus,

$$(\Delta G^\circ)^* = -RT \ln K^*$$

& $(\Delta G^\circ)^* = (\Delta H^\circ)^* - T(\Delta S^\circ)^*$

Thus, we obtained

$$K^{\neq} = e^{-(\Delta G^0)^{\neq}/RT}$$

$$= e^{(\Delta S^0)^{\neq}/R}\, e^{-(\Delta H^0)^{\neq}/RT}$$

Hence, eqn – (4) becomes –

$$K_2 = (K_B T/h)\, e^{(\Delta S^0)^{\neq}/R}\, e^{-(\Delta H^0)^{\neq}/RT} \quad \text{— (5)}$$

eqn – (5) is well known Eyring equation.

& $(\Delta S^0)^{\neq}$ = standard entropy of activation.

$(\Delta H^0)^{\neq}$ = standard enthalpy of activation.

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