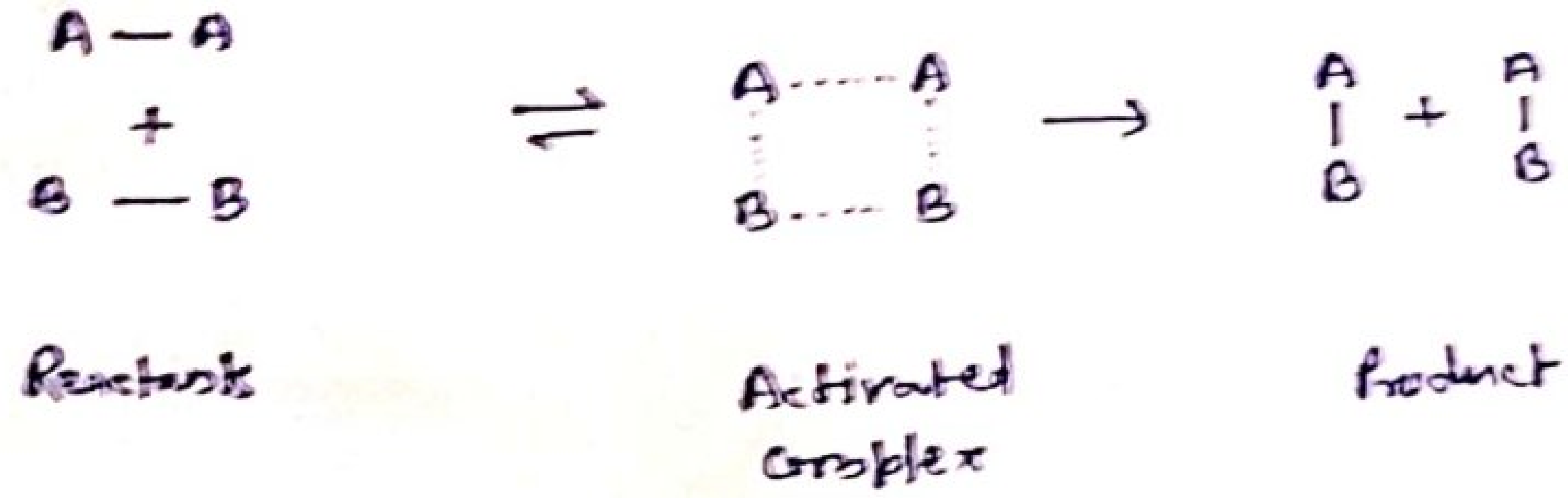
* Activated Complex Theory (ACT) of Bimolecular reactions :-

According to 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, as shown as —

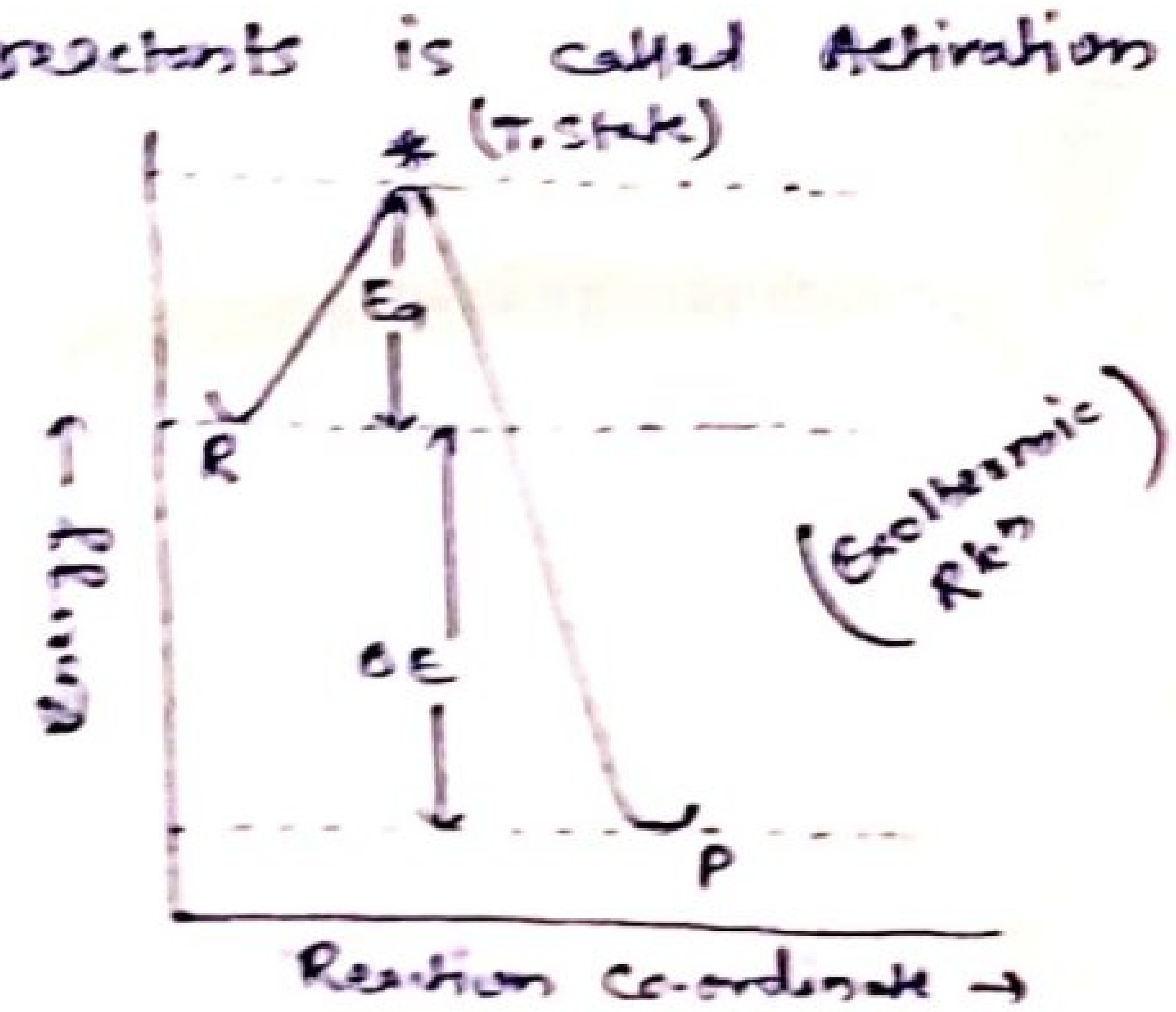
$$A_2 + B_2 \rightleftharpoons (A_2B_2)^* \longrightarrow 2AB$$

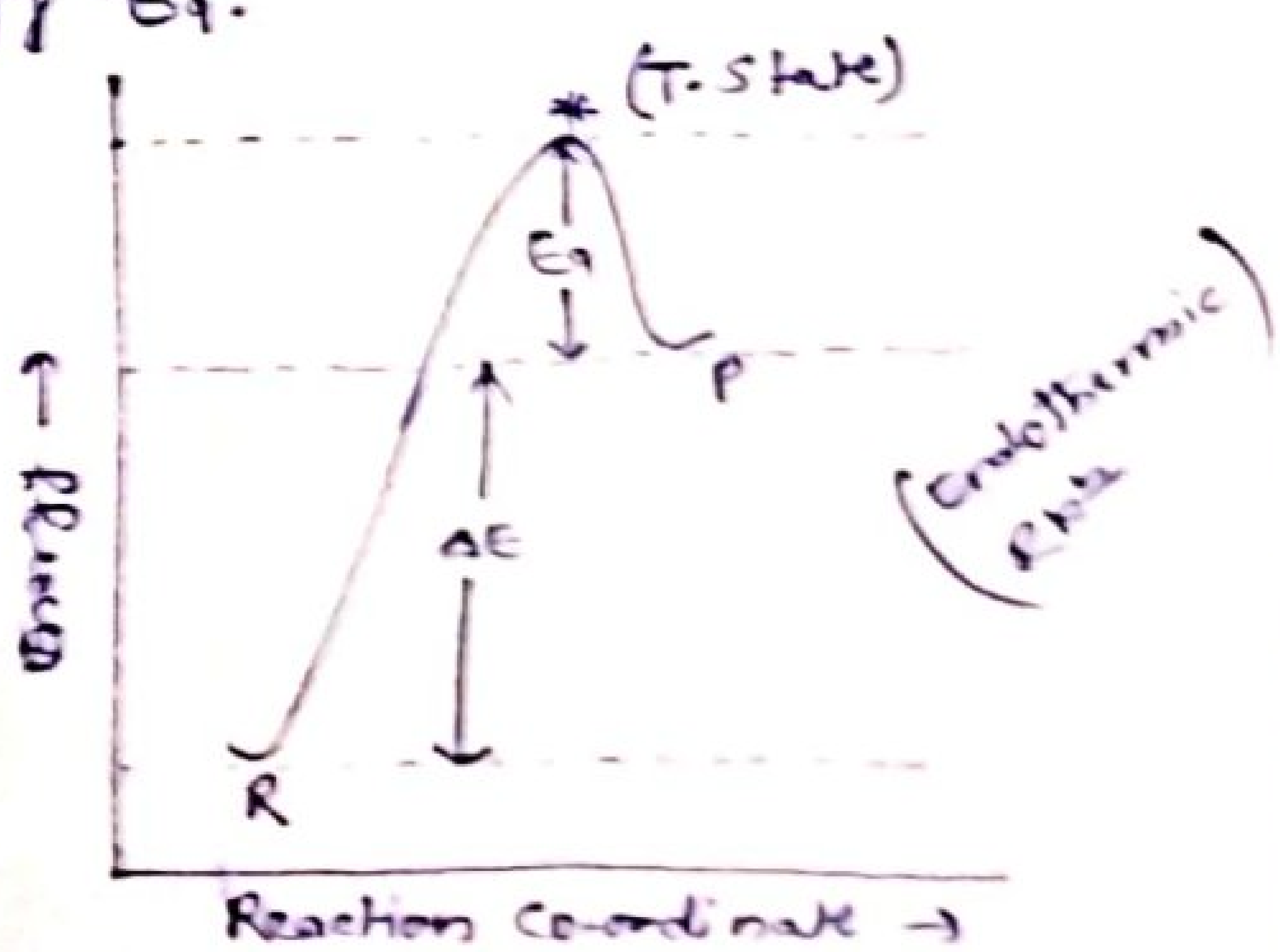
or



The activated complex can be treated as a distinct chemical species in equilibrium with the reactants which then decomposes into Product.

The reaction co-ordinate is a measure of progress of a reaction. The activated complex is not merely an intermediate in the process of breaking or making of chemical bonds. The difference between the energy of activated complex and the energy of the reactants is called Activation energy 'E_a'.





* Thermodynamic formulation of Activated Complex Theory :

Let us consider, a bimolecular reaction —

$$A + B \underset{}{\overset{K^*}{\rightleftharpoons}} (AB)^* \xrightarrow{k_2} \text{Product} \quad \text{—— (1)}$$

Where,

$(AB)^*$ = Activated complex

K^* = equilibrium constant b/n the reactants and activated complex.

In $(AB)^*$, one of the vibrational degree of freedom has become a translational degree of freedom.

The vibrational frequency is given by —

$$\nu = \frac{RT}{N_A h} = \frac{K_B T}{h} \quad \text{—— (2)}$$

The vibrational frequency ν is the rate at which the activated complex molecules moves across the energy barrier.

The rate constant k_2 can be identified with ν.

The rate of this reaction is given by —

$$-\frac{d[A]}{dt} = k\, k_2\, [(AB)^*] = k\,(K_B T/h)\,[(AB)^*] \quad \text{—— (3)}$$

Where the factor k is called transmission coefficient.

The concentration of the activated complex $[(AB)^*]$ is given by —

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

or

$$[(AB)^*] = K^* [A] [B] \quad \text{—— (4)}$$

Thus eqⁿ — (3) becomes,

$$-\frac{d[A]}{dt} = (K_BT/h)\, K^{*}\, [A][B] \qquad (5)$$

The rate constant K_2 is given as—

$$K_2 = (K_BT/h)\, K^{*} \qquad (6)$$

The equilibrium constant K^{*} can be expressed in terms of $(\Delta G^{\circ})^{*}$ as —

$$(\Delta G^{\circ})^{*} = -RT \ln K^{*} \qquad (7)$$

$$\& \quad (\Delta G^{\circ})^{*} = (\Delta H^{\circ})^{*} - T(\Delta S^{\circ})^{*} \qquad (8)$$

Thus we obtained—

$$K^{*} = e^{-(\Delta G^{\circ})^{*}/RT}$$

$$\text{or} \quad K^{*} = e^{(\Delta S^{\circ})^{*}/R}\, e^{-(\Delta H^{\circ})^{*}/RT} \qquad (9)$$

eqⁿ — (9) is called well known Eyring equation.

$(\Delta G^{\circ})^{*}$ = called standard Gibb's free energy of activation.

$(\Delta S^{\circ})^{*}$ = called standard entropy of activation.

$(\Delta H^{\circ})^{*}$ = called standard enthalpy of activation.

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