

SUBJECT - CHEMISTRY

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CLASS - B.Sc (Hons) PART - III

PAPER - V

TOPIC - Entropy of activation

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Q Explain the entropy of activation

Ans Entropy of activation (ΔS^\ddagger): The Standard free energy change (ΔG°) is related with equilibrium constant (K) of a reaction as-

$$\Delta G^\circ = RT \ln K$$

$$\therefore K = e^{-\Delta F^\circ/RT} = e^{-\Delta H^\circ/RT} \cdot e^{\Delta S^\circ/R}$$

where ΔS° = Standard entropy change and ΔH° = Standard enthalpy change. for equilibrium constant (K^\ddagger) we have -

$$K^\ddagger = e^{-\Delta H^\ddagger/RT} \cdot e^{\Delta S^\ddagger/R}$$

where ΔS^\ddagger and ΔH^\ddagger are the difference in the values of Standard entropy change and standard enthalpy change respectively for the activated complex and reactants -

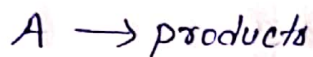
Reactants \longrightarrow Activated Complex \longrightarrow products.

Q Explain unimolecular reactions on the basis of Collision Theory.

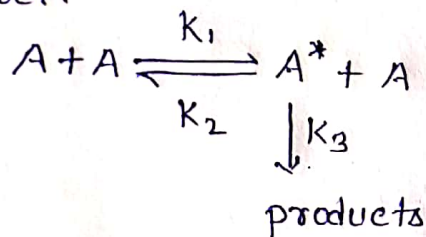
Ans For a reaction to occur, the reactant molecules must come in close contact for collision. For a collision, there must be at least two molecules just like for clapping, there must be two hands and if that is so, then the reaction cannot be truly unimolecular. So, collision theory cannot be applied to unimolecular reactions. For the occurrence of such reactions,

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Lindemann proposed That There is a time-lag between activation by collision and subsequent reaction. During which the activated molecules may lose the excess energy and then they will not react and if they do not lose the excess energy, they will react. Applying Lindemann theory of time-lag unimolecular reaction



We see that the reactant molecules (A) combine firstly to form few activated molecules (A^*). Then there is a time-lag during which the activated molecules may revert to original state by losing the excess energy or the activated molecules may react to form product.



$$\therefore \text{Rate of formation of } A^* = k_1 [A]^2$$

$$\therefore \text{Rate of disappearance of } A^* = k_2 [A^*] [A] + k_3 [A^*]$$

$$= [A^*] (k_2 [A] + k_3)$$

According to Steady State principle, whenever a short lived reaction intermediate is formed its rate of formation can be taken as its rate of disappearance i.e.

$$k_1 [A]^2 = [A^*] (k_2 [A] + k_3)$$

$$\text{or } [A^*] = \frac{k_1 [A]^2}{k_2 [A] + k_3}$$

Since the rate of reaction is proportional to the concentration of activated molecules, hence:

$$-\frac{d[A]}{dt} = k_3 [A^*] = \frac{k_1 k_3 [A]^2}{k_2 [A] + k_3}$$

When $[A]$ is very high, then:

$$-\frac{d[A]}{dt} = \frac{k_1 k_3 [A]^2}{k_2 [A]} = k' [A]$$

Then the reaction will be unimolecular and when $[A]$ is very low, then:

$$-\frac{d[A]}{dt} = \frac{k_1 k_3 [A]^2}{k_3} = k_1 [A]^2$$

Then the reaction will be bimolecular.