$$\frac{dx}{dt} = k_f\,([\mathrm{A}]_0 - x) - k_f\left(\frac{[A]_0 - x_{\mathrm{eq}}}{x_{\mathrm{eq}}}\right)x$$

Integrating this equation between the limits $t = 0, x = 0$ and $t = t, x = x_{\mathrm{eq}}$, we have

$$\int_0^x \frac{dx}{x_{eq} - x} = k_f \frac{[\mathrm{A}_0]}{x_{\mathrm{eq}}} \int_0^t dt$$

$$= -\ln\,(x_{\mathrm{eq}} - x) + \ln\, x_{\mathrm{eq}} = k_f \frac{[\mathrm{A}]_0\, t}{x_{\mathrm{eq}}}$$

or $$\ln \frac{x_{\mathrm{eq}}}{x_{\mathrm{eq}} - x} = k_f \frac{[A]_0}{x_{\mathrm{eq}}}\, t$$

From this equation we can find the value of k_f from the quantities $[\mathrm{A}]_0$, x_{eq} and x at time t. All these quantities can be measured easily. From the value of k_f the value of k_b can be calculated by using the relation.

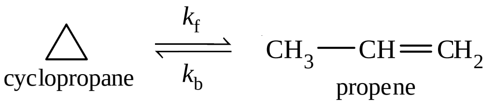
$$k_b = k_f\left(\frac{[\mathrm{A}_0] - x_{\mathrm{eq}}}{x_{\mathrm{eq}}}\right)$$

Examples of Opposing Reactions

(*a*) Dissociation of hydrogen iodides

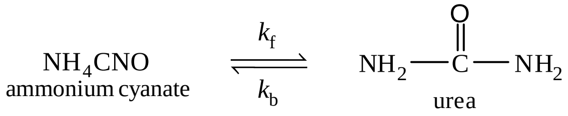
$$2\mathrm{HI} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{H_2 + I_2}$$

(*b*) Isomerisation of cyclopropane into propene



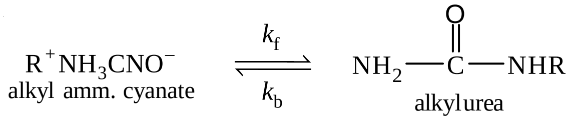
$$\text{cyclopropane} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{CH_3{-}CH{=}CH_2}$$

(*c*) Isomerisation of ammonium cyanate into urea in aqueous solution.



$$\underset{\text{ammonium cyanate}}{\mathrm{NH_4CNO}} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \underset{\text{urea}}{\mathrm{NH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2}}$$

(*d*) Isomerisation of alkyl ammonium cyanate into substituted urea in aqueous solution



$$\underset{\text{alkyl amm. cyanate}}{\mathrm{R^+NH_3CNO^-}} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \underset{\text{alkylurea}}{\mathrm{NH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NHR}}$$

(*e*) Reaction between gaseous CO and NO_2

$$\mathrm{CO(g) + NO_2(g)} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \mathrm{CO_2(g) + NO(g)}$$

Limitations of the Collision Theory

The collision theory of reaction rates is logical and correct. However, it has been oversimplified and suffers from the following weaknesses.

(1) **The theory applies to simple gaseous reactions only.** It is also valid for solutions in which the reacting species exist as simple molecules.

(2) The values of rate constant calculated from the collision theory expression (Arrhenius equation) are in agreement with the experimental values only for simple bimolecular reactions. **For reactions involving complex molecules, the experimental rate constants are quite different from the calculated values.**

(3) There is no method for determining the steric effect (*p*) for a reaction whose rate constant has not been determined experimentally.

(4) In the collision theory it is supposed that only the kinetic energy of the colliding molecules contributes to the energy required for surmounting the energy barrier. There is no reason why the rotational and vibrational energies of molecules should be ignored.

(5) **The collision theory is silent on the cleavage and formation of bonds involved in the reaction.**

The various drawbacks in the simple collision theory do not appear in the modern transition-state theory.

TRANSITION STATE THEORY

The **transition state** or **activated complex theory** was developed by Henry Erying (1935). This theory is also called the **absolute rate theory** because with its help it is possible to get the absolute value of the rate constant. The transition state theory assume that simply a collision between the reactant molecules does not really causes a reaction. During the collision, **the reactant molecules form a transition state or activated complex which decomposes to give the products.**

Thus,

$$\underbrace{A + B\text{—}C}_{\text{Reactants}} \longrightarrow \underbrace{ABC^{\ddagger}}_{\text{Activated complex}} \longrightarrow \underbrace{A\text{—}B + C}_{\text{Products}}$$

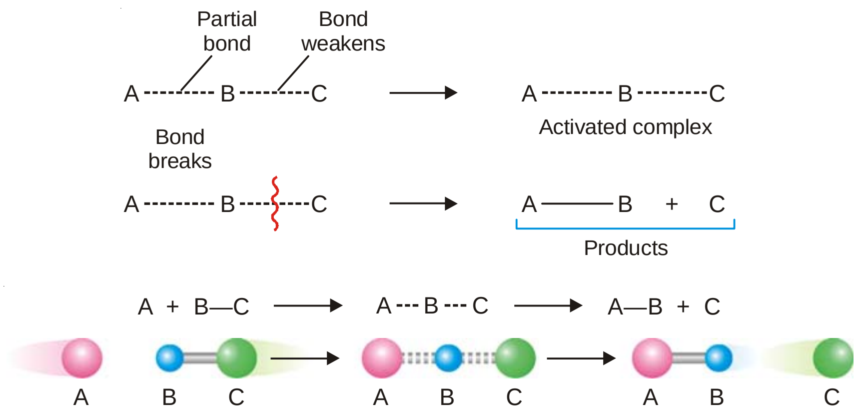
The double dagger superscript ($\ddagger$) is used to identify the activated complex.

The transition state theory may be summarised as follows :

(1) In a collision, the fast approaching reactant molecules (A and BC) slow down due to gradual repulsion between their electron clouds. In the process **the kinetic energy of the two molecules is converted into potential energy.**

(2) As the molecules come close, **the interpenetration of their electron clouds occurs which allows the rearrangement of valence electrons.**

(3) A partial bond is formed between the atoms A and B with corresponding weakening of B – C bond. This leads to formation of an **activated complex** or **transition state.** The activated complex is momentary and decomposes to give the products (A–B + C)



The activated complex theory may be illustrated by the **reaction energy diagram** (Fig. 20.13).

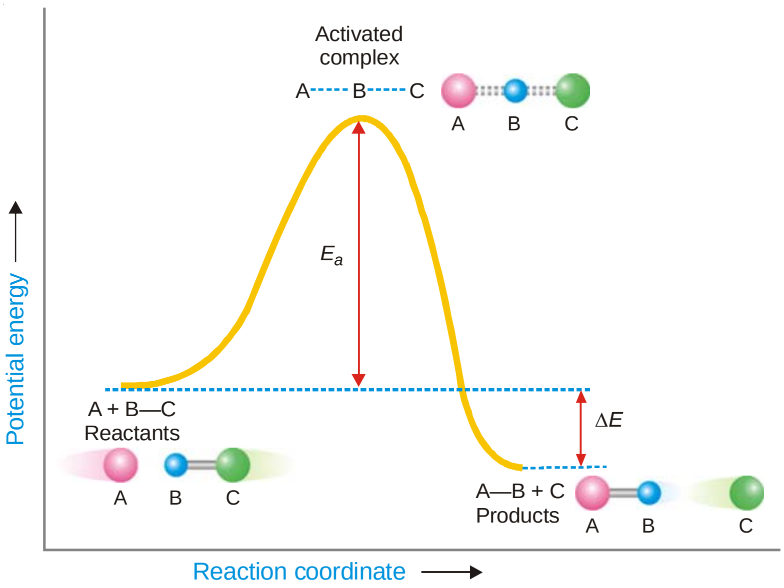


Figure 20.13
Change of potential energy during a collision between the reactant molecules for an exothermic reaction.

Here the potential energy of the system undergoing reaction is plotted against the **reaction coordinate** (the progress of the reaction). The difference in the potential energy between the reactants and the activated complex is the **activation energy,** E_a.The reactants must have this minimum energy to undergo the reaction through the transition state.

As evident from the energy diagram, energy is required by the reactants to reach the transition state. Also, the energy is obtained in passing from the transition state to the products. If the potential energy of the products is less than that of the reactants (Fig. 20.14) the energy obtained in going from the activated complex to products will be more than the activation energy (E_a). Thus such a reaction will be **exothermic.**

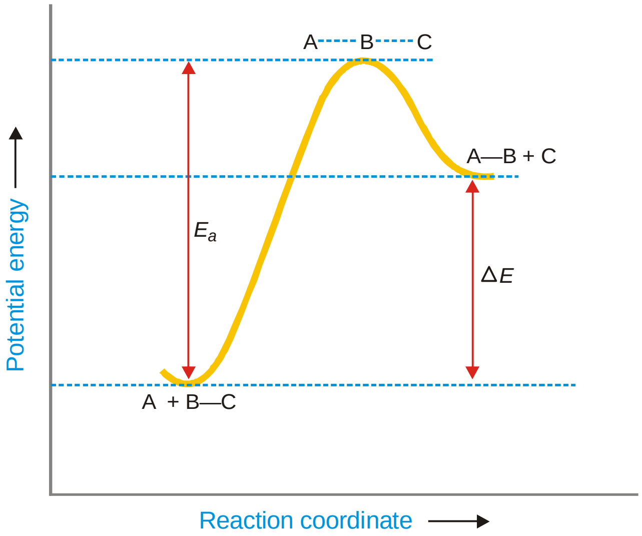


Figure 20.14
A potential energy diagram for an endothermic reaction.

On the other hand, if the potential energy of the products is greater than that of the reactants, the energy released in going from the activated complex to products will be less than the activation energy and the reaction will be **endothermic.**

ACTIVATION ENERGY AND CATALYSIS

We know that for each reaction a certain energy barrier must be surmounted. As shown in the energy diagram shown in Fig. 20.15, the reactant molecules must possess the activation energy, E_a, for the reaction to occur.

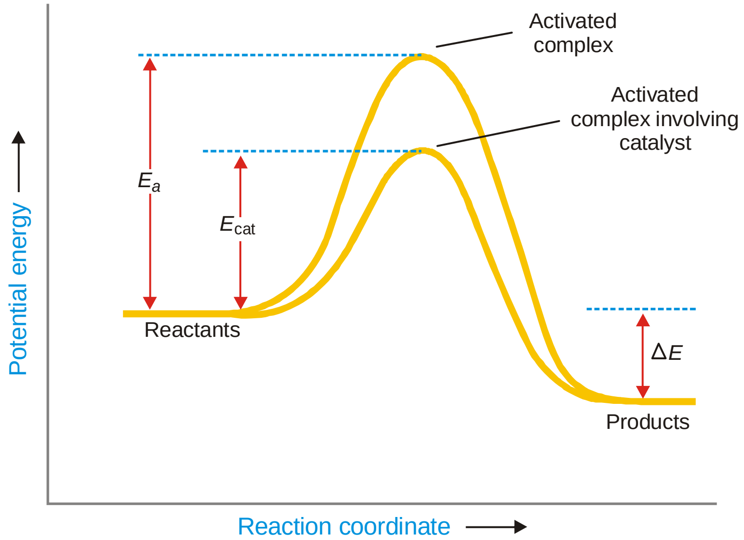


Figure 20.15
Energy diagram for a catalysed and uncatalysed reaction showing a lowering of activation energy by a catalyst.

The catalyst functions by providing another pathway with lower activation energy, E_{cat}. Thus a much large number of collisions becomes effective at a given temperature. Since the rate of reaction is proportional to effective collisions, the presence of a catalyst makes the reaction go faster, other conditions remaining the same. It may be noted from the above diagram that although a catalyst lowers the activation energy, the energy difference, ΔE, between products and reactants remains the same.

LINDEMAN'S THEORY OF UNIMOLECULAR REACTIONS

A number of unimolecular reactions, for example,

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

are found to be of the first order. It is difficult to account for such reactions using the collision theory and the absolute reaction rate theory. If two molecules must collide in order to provide necessary activation energy, a second order rate law should result. In 1922, Lindeman explained this anomaly by assuming that **there existed a time lag between activation and reaction of molecules.** During this time lag, the activated molecules could either react or be deactivated. Thus,

$$A + A \longrightarrow A + A^* \qquad \textit{activation} \; ...(1)$$

$$A + A^* \longrightarrow A + A \qquad \textit{deactivation} \; ...(2)$$

$$A^* \longrightarrow \text{products} \qquad \textit{reaction} \; ...(3)$$

If the time lag is long, step (3) is slow, the reaction should follow first order kinetics. However, if A reacts as soon as formed, step (2) is the slow step, then the reaction should be second order.

The proof of Lindeman's theory is provided by studying the effect of change of pressure on the reaction. At high pressure the rate of deactivation will be dominant. On the other hand, at sufficiently low pressure all the activated molecules will react before they can be deactivated. Therefore the reaction kinetics should change from first order to second order with decreasing pressure. Several gases are known to exhibit this behaviour.

EXAMINATION QUESTIONS

1. Define or explain the following terms :

(*a*)	Rate of reaction	(*b*)	Order of a reaction
(*c*)	Molecularity of a reaction	(*d*)	Rate constant
(*e*)	Half life of a reaction	(*f*)	Arrhenius equation

2. Derive mathematical expression for the rate constant of a reaction (A + B → Products) of the second order.

3. The first order rate constant for the decomposition of N_2O_2 of 0°C is 5.2×10^{-6} min^{-1}. If the energy of activation is 6200 joules per mole, calculate the rate constant at 25°C.

Answer. 7.385×10^{-6}

4. (*a*) Define order of a reaction, molecularity of a reaction and half life period. Show that for first order reactions the half life period is independent of the initial concentration.

(*b*) The rate constant of a reaction is 1.2×10^{-3} sec^{-1} at 303 K. Calculate the rate constant at 313 K, if the activation energy for the reaction is 44.12 kJ mol^{-1}.

Answer. 1.47×10^{-3}

5. (*a*) Explain why the rate of a reaction cannot be measured by dividing the amount of reactants reacted by the time taken.

(*b*) What is activation energy? How is it determined?

6. (*a*) For the kinetics of bimolecular reactions briefly discuss the "Collision Theory".

(*b*) Derive an expression for the half life period of the following reaction:

$A \rightarrow B,\ \text{rate} \propto [A]$

(*c*) With the help of two examples, show that the rate can be independent of initial concentration of the reactants. What is the order of such reactions?

(*d*) If the rate constant at one temperature alongwith the activation energy is given, how can the rate constant at any other temperature be determined?

7. Explain Arrhenius equation. Discuss Arrhenius concept of activation energy. Give graphical representation of activation energy diagram. (*Jiwaji BSc, 2000*)

8. (*a*) Explain, with examples, zero-order reaction. Write rate law expression for it.

(*b*) The reaction, A + B + C → Products, is found to obey the rate law

$$r = \frac{-d[A]}{dt} = k\,[A]^2\,[B]^{3/2}\,[C]^{-1/2}$$

What is the order of overall reaction? (*Purvanchal BSc, 2000*)

9. Derive an expression for rate constant of a bimulecular gaseous reaction on the basis of collision theory. (*Allahabad BSc, 2001*)

10. Distinguish between reaction rate and rate constant of a reaction. Derive the integrated rate law for first order reaction. (*kathmandu BSc, 2001*)

11. (*a*) Explain briefly the collision theory of reaction rates. What are its limitations and how far they are overcome by theory of absoulte reaction rates?