Effect of Temperature on rate of reaction and thermodynamics of rate of chemical reactions

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8 TEMPERATURE DEPENDENCE OF REACTION RATES

Temperature dependence of reaction rates can be studied by plotting a graph between rate constant (k) and temperature (T) for different reactions as shown below in Fig. 4.
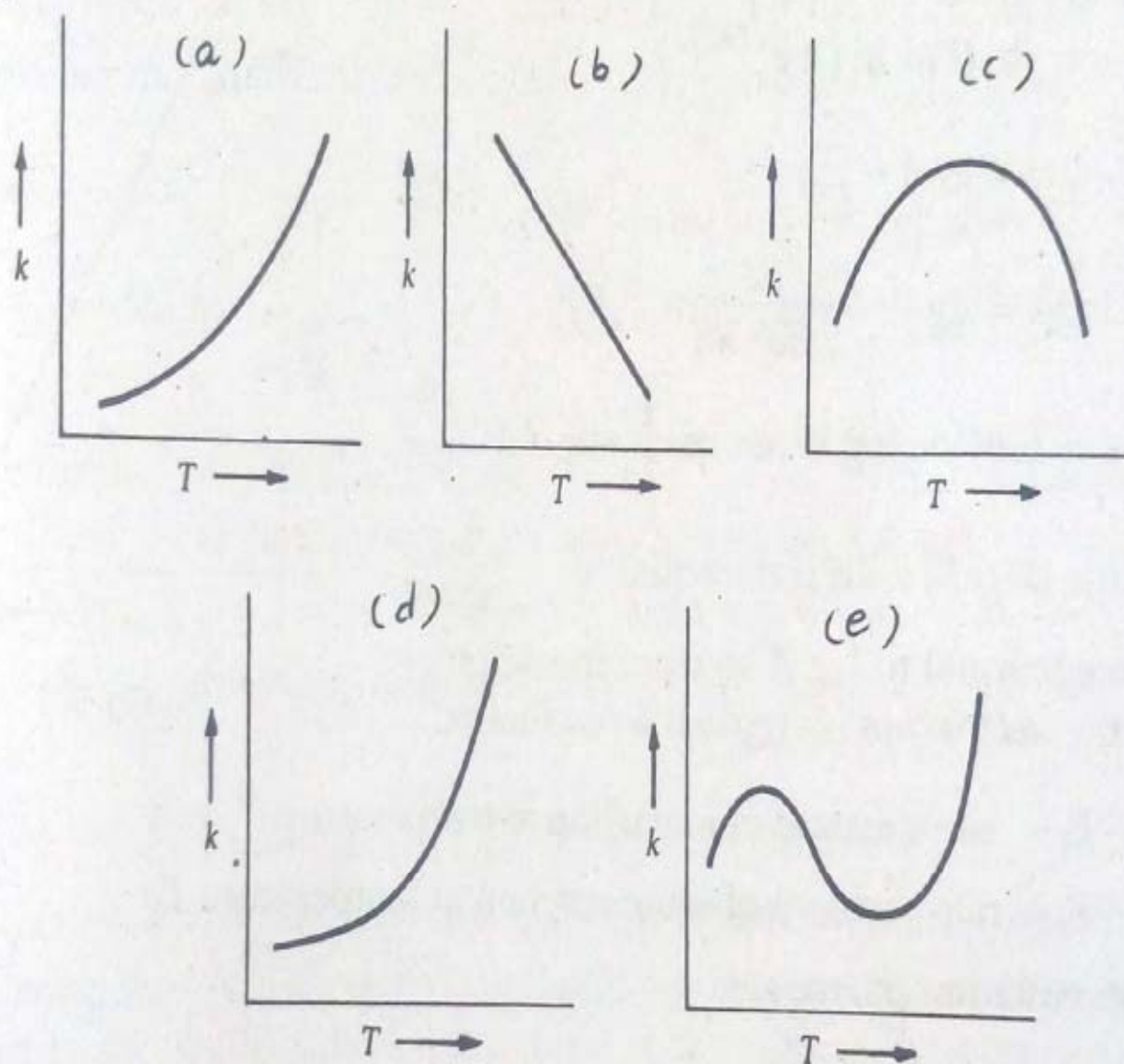

Fig. 4. Temperature dependence of reaction rates for different reactions.

Curve (*a*) is applicable for *most of the reactions* and indicates that rate increases th increase in temperature. This is easy to understand because number of effec- e collisions between the reactant molecules increases with increase in tempera- re. Thus, rate increases.

Curve (*b*) is applicable for *reversible reactions* when effect of temperature is ore on backward reaction.

Curve (*c*) is applicable for *enzyme catalyzed reactions* because enzymes show aximum efficiency at some optimum temperature, beyond which they undergo naturation.

Curve (*d*) is applicable for *explosion reactions*, because at explosion tempera- re, sudden rise in rate occurs.

Curve (*e*) is applicable for *some combustion reactions*.

15.2 Transition State Theory of Reaction Rates

In this theory. two molecules approach and distort as they meet and form an unstable activated complex. This activated complex is a combination of the two reactant molecules. It can either go on to form products or can fall apart into the unchanged reactants. If we follow the potential energy of the two reactant molecules, we see that it rises (at the expense of the kinetic energy they had initially) as they merge to form the activated complex. the potential energy falls again as the product molecules form and separate (Fig. 17).

The entire curve is called the *reaction profile*, and the hump between the reactants and products is the activation barrier. The height of the barrier is the activation energy E_a of the reaction because only reactant molecules that have enough kinetic energy and the correct orientation in the activated complex to cross the barrier can turn into products. The rest molecules just depart unchanged from the collsion encounter.

Reaction rates in this theory are treated from thermodynamic considerations. All the reactions proceed through an activated or transition state which has energy higher than the reactants or products. It is assumed that an equilibrium is established between the reactants and the activated complex.
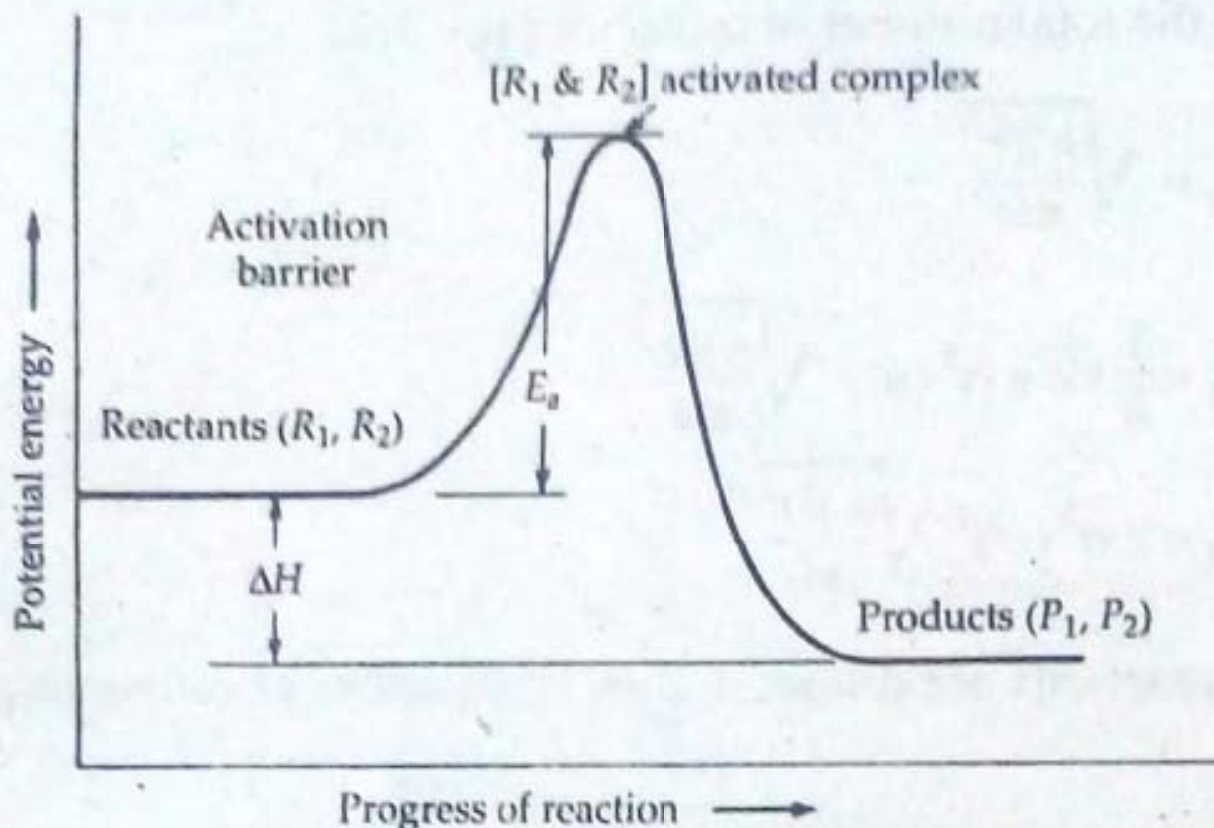

Fig. 17. A reaction profile for an exothermic reaction. In the transition state theory of chemical reactions, it is supposed that the potential energy of the reactant molecules rises as they approach each other, reaches a maximum as they form an activated complex, and then decreases as the product molecules form and separate. Only molecules with enough energy and the correct relative orientation can cross the barrier and react when they meet.

$$R_1 + R_2 \xrightleftharpoons{K_{eq}^{\#}} [R_1 R_2]^{\#} \xrightarrow{K_2} \text{Products} \qquad \ldots(1)$$

Reactants   Activated complex
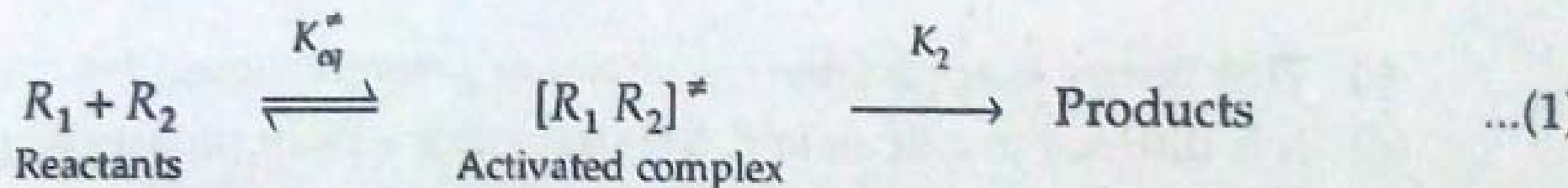
The rate of such a reaction depends on (*i*) concentration of the activated complex molecule and (*ii*) the rate at which it decomposes.

$$\therefore \text{ Rate} = \left(\begin{array}{c} \text{Concentration of the} \\ \text{activated complex molecule} \end{array} \right) \times \left(\begin{array}{c} \text{Frequency of decomposition of} \\ \text{the activated complex} \end{array} \right)$$

As the activated complex is in equilibrium with the reactants.

$$\therefore \qquad K_{eq}^{\#} = \frac{[R_1 R_2]^{\#}}{[R_1][R_2]}$$

$$\Rightarrow \qquad [R_1 R_2]^{\#} = K_{eq}^{\#} [R_1][R_2] \qquad \ldots(2)$$

As the activated complex $(R_1 R_2)^{\#}$ is unstable so at a particular vibration it decomposes to form products. The rate of decomposition of the complex is dependent (proportional) to the frequency of vibration.

$$-\frac{d}{dt}[R_1] = -\frac{d}{dt}[R_2] = k_2[R_1][R_2]$$

$$= [R_1 R_2]^{\#} v = K_{eq}^{\#}[R_1][R_2]\,(v) \qquad \ldots(3)$$

According to Planck's expression, the energy of the molecule associated with frequency v is given by

$$E = h v. \qquad \text{...(4)}$$

Moreover, the average energy of such a vibrational degree of freedom is given by kT, where k is Boltzmann's constant

$$\therefore \qquad v = \frac{E}{h} = \frac{kT}{h} = \frac{RT}{Nh} \qquad \text{...(5)}$$

Substituting this value of v in equation (3), we get

$$k_2 [R_1] [R_2] = K_{eq}^* [R_1] [R_2] v$$

$$\Rightarrow \qquad k_2 [R_1] [R_2] = K_{eq}^* [R_1] [R_2] \frac{RT}{Nh}$$

$$\Rightarrow \qquad k_2 = K_{eq}^* \frac{RT}{Nh} \qquad \text{...(6)}$$

Now, Free energy of activation, ΔG^* is given by

$$\Delta G^* = - RT \ln K_{eq}^* \qquad \Rightarrow \qquad \ln K_{eq}^* = \frac{-\Delta G^*}{RT}$$

Moreover, ΔG^* is related to enthalpy of activation ΔH^* and the entropy of activation ΔS^* by $\Delta G^* = \Delta H^* - T \Delta S^*$.

$$\therefore \qquad \ln k_{eq}^* = \frac{-(\Delta H^* - T \Delta S^*)}{RT}$$

$$\Rightarrow \qquad k_{eq}^* = exp\left(\frac{-\Delta H^*}{RT}\right) exp\left(\frac{\Delta S^*}{R}\right) \qquad \text{...(7)}$$

$$\Rightarrow \qquad k_{eq}^* = exp\left(\frac{-\Delta H^*}{RT}\right) exp\left(\frac{\Delta S^*}{R}\right) \qquad \qquad \text{...(7)}$$

Substituting this value of K_{eq}^* in equation (6), we get

$$k_2 = \frac{RT}{Nh}\left[exp\left(\frac{-\Delta H^*}{RT}\right) exp\left(\frac{\Delta S^*}{R}\right)\right] \qquad \qquad \text{...(8)}$$

Now taking logarithm of equation (6), we get

$$\ln k_2 = \ln T + \ln K_{eq}^* + \ln\frac{R}{Nh}$$

Differentiating w.r.t. temperature, we obtain

$$\frac{d \ln k_2}{dT} = \frac{1}{T} + \frac{d \ln k_{eq}^*}{dT} \qquad \qquad \text{...(9)}$$

As the variation of k_{eq}^* with temperature is given by

$$\frac{d \ln k_{eq}^*}{dT} = \frac{\Delta E^*}{RT^2} \qquad \qquad \text{...(10)}$$

From equations (9) and (10), we get

$$\frac{d \ln k_2}{dT} = \frac{1}{T} + \frac{\Delta E^*}{RT^2} = \frac{RT + \Delta E^*}{RT^2} \qquad \qquad \text{...(11)}$$

Comparing equation (11) with $\dfrac{d \ln k_2}{dT} = \dfrac{E_a}{RT^2}$, we get

$$E_a = \Delta E^* + RT \qquad \qquad \text{...(12)}$$

But
$$\Delta H^* = \Delta E^* + P \Delta V^* \qquad \Rightarrow \qquad \Delta E^* = \Delta H^* - P \Delta V^*$$

and for ideal gases, $P \Delta V^* = \Delta n^* RT$

$$\therefore \qquad \Delta E^* = \Delta H^* - \Delta n^* RT \qquad \qquad ...(13)$$

Substituting the value of ΔE^* from eqn. (13) in eqn. (12), we get

$$E_a = \Delta H^* - \Delta n^* RT + RT \qquad \qquad ...(14)$$

where Δn^* is the change in number of molecules in passing from the initial state to the activated state.

For unimolecular reactions, $R \rightarrow [R^*] \rightarrow$ Product, $\Delta n^* = 0$, as there is no change in the number of molecules as the activated complex is formed.

$$\therefore \qquad E_a = \Delta H^* + RT \qquad \Rightarrow \qquad \Delta H^* = E_a - RT \qquad \qquad ...(15)$$

Substituting this value of ΔH^* from eqn. (15) in eqn. (8), we get

$$k_2 = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{(E_a - RT)}{RT}\right)$$

$$= \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{E_a}{RT}\right) e \qquad \qquad ...(16)$$

For a biomolecular reaction, $\Delta n^* = -1$,

From eqn. (14), $\qquad E_a = \Delta H^* + 2 RT$

$$\Rightarrow \qquad \qquad \Delta H^* = E_a - 2 RT \qquad \qquad ...(17)$$

Thus, the rate equation (8) for bimolecular reaction is

$$k_2 = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{(E_a - 2RT)}{RT}\right)$$

$$\Rightarrow \quad k_2 = \frac{RT}{Nh} e^2 \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-E_a}{RT}\right) \quad \ldots(18)$$

The entropy of activation (ΔS^*) can be calculated from the experimental values
rate constant (k_2) and activation energy (E_a).

Comparing eqns. (16) and (18), with Arrhenius equation

$$k = A e^{-E_a/RT}.$$

We can say that pre-exponential factor A is related to ΔS^* by

$$A = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) z$$

here $z = e$ for unimolecular reactions and $z = e^2$ for bimolecular reactions.

The quantity $\frac{RT}{Nh}$ does not depend on the nature of the reactant or activated
mplex, and therefore, will be same for all reactions at the same temperature.

Example 37. The rate constant of a second-order reaction is $5 \cdot 70 \times 10^{-5}$ dm^3 mol^{-1} s^{-1} at 25°C and 64×10^{-4} dm^3 mol^{-1} s^{-1} at 40°C. Calculate the activated energy and the Arrhenius pre-exponential factor.

Solution : Substituting the given data in Eq. 44, we have

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] \quad \text{or} \quad E_a = R(\ln k_2/k_1) \left[\frac{T_1 T_2}{T_2 - T_1} \right]$$

$$E_a = (8 \cdot 314 \text{ J K}^{-1} \text{ mol}^{-1}) \left[\ln \frac{1 \cdot 64 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}}{5 \cdot 70 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}} \right] \times \left[\frac{298 \text{ K} \times 313 \text{ K}}{313 \text{ K} - 298 \text{ K}} \right]$$

$$= 54478 \text{ J mol}^{-1} = 54 \cdot 48 \text{ kJ mol}^{-1}$$

To calculate the Arrhenius pre-exponential factor A, we incorporate one of the given data in Arrhenius equation, $k = A e^{-E_a/RT}$. Thus,

$$\ln k = \ln A - E_a/RT \quad \text{or} \quad \ln A = \ln k + E_a/RT$$

At $T = 298$ K, $\quad k = 5 \cdot 7 \times 10^{-5}$ dm^3 mol^{-1} s^{-1}

$$\therefore \quad \ln A = \ln (5 \cdot 7 \times 10^{-5} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}) + \frac{54478 \text{ J mol}^{-1}}{(8 \cdot 314 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})}$$

$$\therefore \quad A = 2 \cdot 01 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Note that the units of A are the same as those of the rate constant.