Lecture 24

We will continue to learn about "Chemical Kinetics"

Suggested book: Physical Chemistry by Ira Levine

The response of equilibria to temperature: van't Hoff equation

Le Chatelier's principle states that:

"A system at equilibrium, when subjected to a disturbance, responds in a way that tends to minimize the effect of the disturbance".

We are concerned here about how the chemical reaction will respond to temperature increase as a perturbation/disturbance.

If the reaction is exothermic then increase in temperature will favour the reactants.

Conversely, if the reaction is endothermic then increased temperature will favour the products.

The above statements are qualitative ones. We will see how to express them quantitatively.

From the pressure dependence of chemical potential (vide 2nd law of thermodynamics)

$$\mu = \mu^0 + R\,T\,\ln\left(\frac{p}{p^0}\right) \quad (p^0 = 1 \text{ atm}) \quad \text{[for ideal gas]}$$

$$\mu = \mu^0 + R\,T\,\ln p$$

$$\Delta G_r = \mu_B - \mu_A = (\mu_B^0 + R\ T\ \ln\ p_B) - (\mu_A^0 + R\ T\ \ln\ p_A)$$

$$= (\mu_B^0 - \mu_A^0) + R\ T\ \ln\ \left(\frac{p_B}{p_A}\right)$$

$$= \Delta G_r^0 + R\ T\ \ln\ \left(\frac{p_B}{p_A}\right)$$

At equilibrium, $\Delta G_r = 0$

Then, $\Delta G_r^0 = (-)\ R\ T\ \ln\ \left(\frac{p_B}{p_A}\right)$

If we replace $\dfrac{p_B}{p_A} = K$, then, $\Delta G_r^0 = (-)\ R\ T\ \ln\ K$

Thus, when ΔG_r^0 is (–)ve (i.e. < 0), then $K > 1$ (i.e. $p_B > p_A$)

When ΔG_r^0 is (+)ve (i.e. > 0), then $K < 1$ (i.e. $p_B < p_A$)

So, let us start from $\Delta G_r^0 = (-) \, R \, T \ln K$

$\Rightarrow \ln K = -\dfrac{\Delta G_r^0}{R \, T}$

$\Rightarrow \dfrac{d \ln K}{dT} = -\dfrac{1}{R} \times \dfrac{d \left(\dfrac{\Delta G_r^0}{T}\right)}{dT}$ [K, ΔG_r^0 depends only on temperature and not on pressure]

From Gibbs-Helmholtz equation we know that

$$\dfrac{d \left(\dfrac{\Delta G_r^0}{T}\right)}{dT} = (-) \dfrac{\Delta H_r^0}{T^2}$$ [will learn in 2nd law of thermodynamics class]

Where, ΔH_r^0 is standard reaction enthalpy at temperature T

Thus we get,

$$\boxed{\dfrac{d \ln K}{dT} = (+) \dfrac{1}{R} \times \dfrac{\Delta H_r^0}{T^2}}$$ .... (A)   (in 1884)

This is van't Hoff equation.

Another form of van't Hoff equation can be obtained as follows.

$$\frac{d\left(\frac{1}{T}\right)}{dT} = (-)\frac{1}{T^2} \quad \text{so, } dT = -T^2\, d\left(\frac{1}{T}\right)$$

$$\Rightarrow \frac{d\ln K}{d\left(\frac{1}{T}\right)} = (-)\frac{T^2}{R} \times \frac{\Delta H_r^0}{T^2}$$

$$\Rightarrow \boxed{\frac{d\ln K}{d\left(\frac{1}{T}\right)} = (-)\frac{\Delta H_r^0}{R}} \qquad \ldots\ldots\ldots \text{(B)}$$

$\Rightarrow$ This is another form of van't Hoff equation.

$$\boxed{\frac{d\ln K}{dT} = (+)\frac{1}{R} \times \frac{\Delta H_r^0}{T^2}} \qquad \ldots\ldots\ldots \text{(A)}$$

[Q. How will the plot of ln K vs. T or (–) ln K vs. $\frac{1}{T}$ look like?]

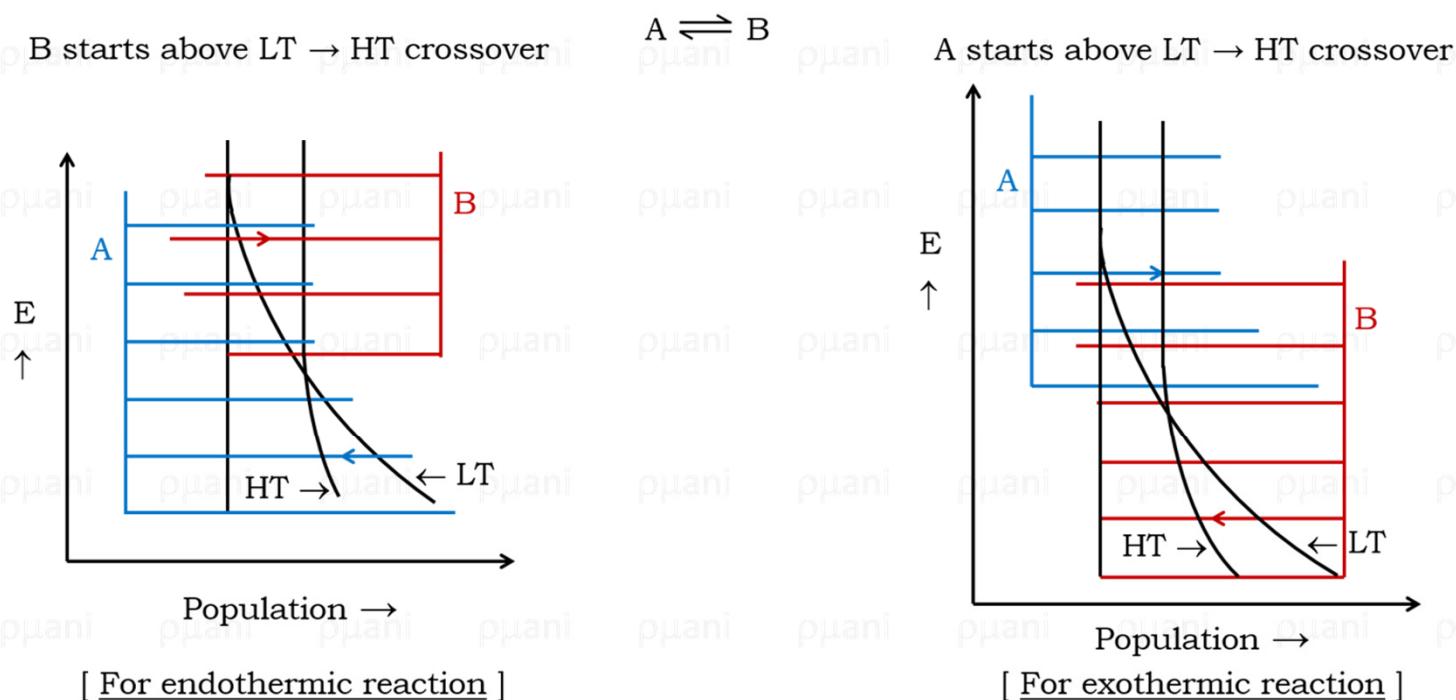From equation (A), for a reaction that is exothermic i.e. $\Delta H_r^0 < 0$, $\frac{d\ln K}{dT} < 0$

This means ln K and therefore K decreases as temperature increases.

Thus, for an exothermic reaction, with increase in temperature the state shifts away from equilibrium.

The reverse happens for endothermic reaction.

Molecular interpretation:

When temperature is increased, the Boltzmann distribution changes as follows:

$$A \rightleftharpoons B$$

B starts above LT → HT crossover

A starts above LT → HT crossover

E ↑

Population →

[For endothermic reaction]

Population →

[For exothermic reaction]

As temperature changes, the change corresponds to an increased population of the higher energy states at the expense of lower energy states. We see that states that arise from B molecules become more populated at the expense of A molecules. So the total population of B state increases and B molecules become more abundant in equilibrium mixture. This is for endothermic reaction. For exothermic reaction, population of A state (which is at higher energy) increases at the expense of B state.

Temperature dependence of reaction rate: Arrhenius equation

It was found experimentally that, for many reactions a plot of ln k against $\frac{1}{T}$ gives straight line.

In 1889, Arrhenius pointed out that rate constant k(T) for many reaction follow the equation,

$$\boxed{k = A \times e^{-\frac{E_a}{RT}}}$$ .... (i)

'A', E_a are constants, characteristics of a reaction. R is molar gas constant.

A $\rightarrow$ pre-exponential factor/Arrhenius factor

$E_a \rightarrow$ Arrhenius activation energy

A has the same unit of k

E_a has the same unit as of RT (i.e. energy (molar), say kJ/mole)

Arrhenius arrived at equation (i) by arguing that temperature dependence of rate constants would probably resemble temperature dependence of equilibrium constant.

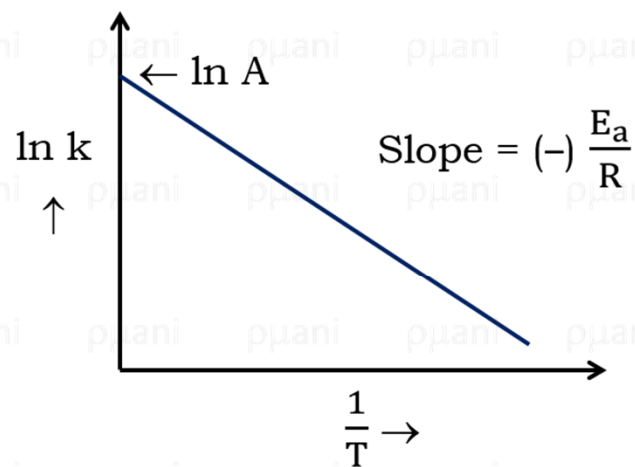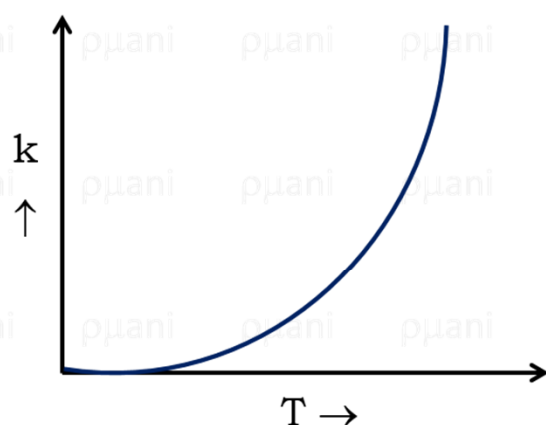Arrhenius wrote, $\dfrac{d \ln k}{dT} = \dfrac{E_a}{RT^2}$

Integrating the above equation we get equation (i)

[assuming E_a is independent of T (mostly true when $\underline{E_a \gg RT}$)]

From equation (i) we can write, $\boxed{\ln k = \ln A - \dfrac{E_a}{RT}}$ .... (ii)

$$\boxed{\begin{array}{l} \text{R T at 25°C} \\ \text{0.6 kCal/mol} \\ \text{2.48 kJ/mol} \\ \text{~25 meV/mol} \end{array}}$$

The plots:

Thus, from the experimental plots E_a, A can be calculated.

Arrhenius equation holds true for simple homogeneous reaction to most complex reactions.

Existence of activation energy can be explained as two colliding molecules require certain minimum kinetic energy (of relative motion) to initiate breaking appropriate bonds and allow new compounds to be formed.

Maxwell-Boltzmann distribution law:

$$\frac{dn_{\varepsilon_{tr}}}{N} = 2\pi \times \left(\frac{1}{\pi\,kT}\right)^{\frac{3}{2}} \times \sqrt{\varepsilon_{tr}} \times e^{-\frac{\varepsilon_{tr}}{kT}} \times d\varepsilon_{tr} \qquad \text{contains the } e^{-\frac{\varepsilon_{tr}}{kT}} \text{ factor.}$$

The fraction of collisions in which the relative kinetic energy of the molecules along the line of collision exceeds the value of ε_{tr} is proportional to $e^{-\frac{\varepsilon_{tr}}{kT}}$ or $e^{-\frac{E_a}{kT}}$

A few relevant points:

➢ A high E_a signifies that rate constant depends strongly on temperature. If a reaction has zero E_a, then its rate is independent of temperature. When E_a is negative, then rate decreases with increase in temperature.

Question: $E_a = R\,T^2 \dfrac{d \ln k}{dT}$ equation is valid. E_a depends on temperature or not?

➢ A low activation energy means a fast reaction and a high activation energy means slow reaction. Rapid increase in k as temperature (T) increases is due to the increase in number of collision where energy exceeds E_a. Slope of ln k vs. $\dfrac{1}{T}$ plot gives E_a. This means higher the E_a, stronger is the temperature dependence of the rate constant (steeper is the plot).

➢ Temperature dependence of some reaction do not follow Arrhenius behaviour i.e. ln k vs. $\dfrac{1}{T}$ plot is not straight line in those cases. However, even for non-Arrhenius type of reaction $E_a = R\,T^2 \dfrac{d \ln k}{dT}$ holds.

➢ Non-Arrhenius behaviour is a sign that quantum mechanical tunnelling is playing a significant role in the reaction.

➢ Activation energy of common reaction lie in the range of 0–100 kCal/mole.

➢ Value of 'A' depends on the molecularity of the reaction. For uni-molecular reaction 'A' has a typical value of 10^{12} to 10^{15} sec^{-1}, for bi-molecular reaction 'A' has a typical value of 10^{8} to 10^{12} dm^{3} mol^{-1} sec^{-1}.

Temperature dependence of rate constants : Examples

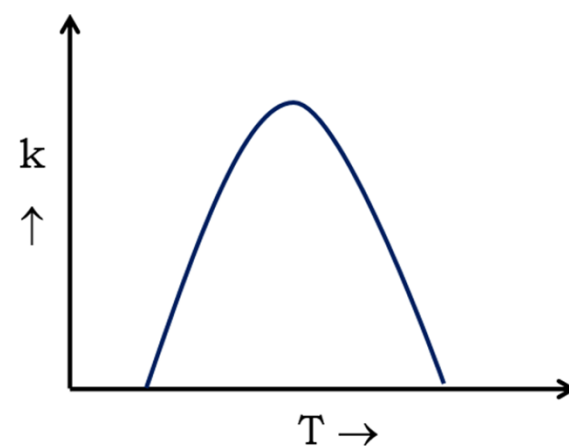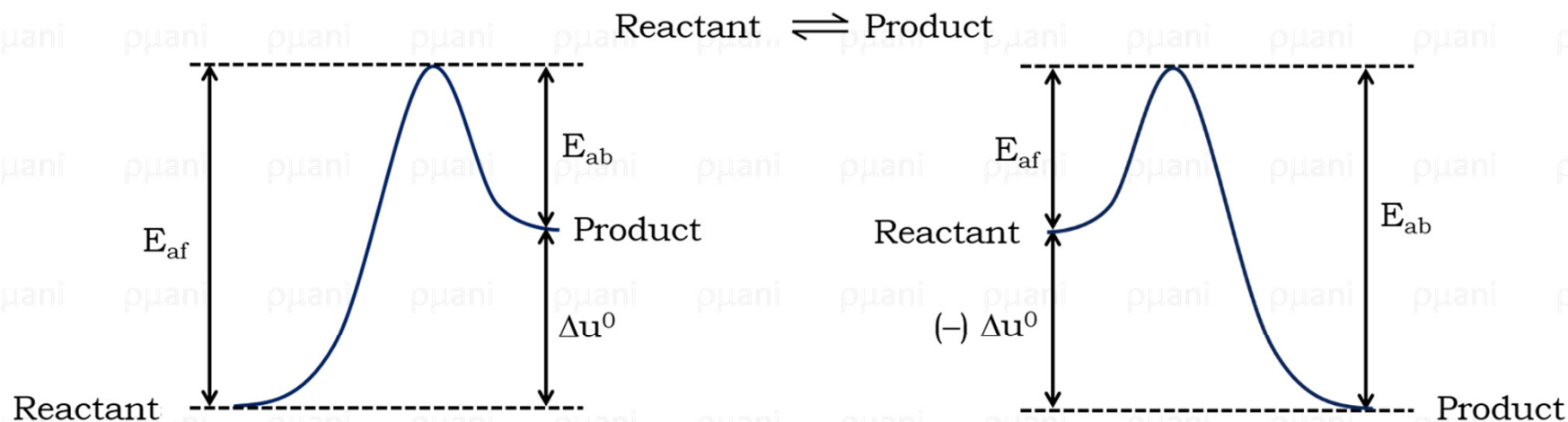[For normal reaction]

k
↑

T →
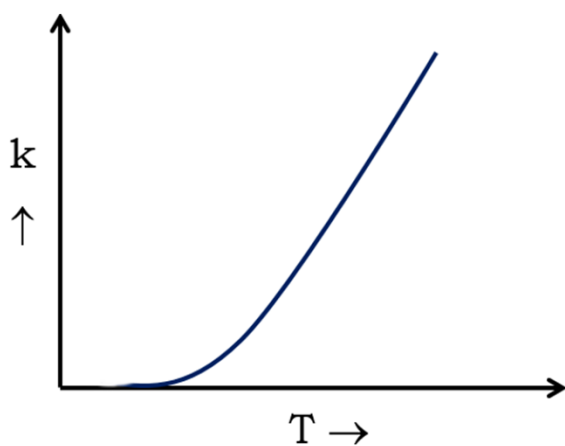
[For explosion reaction]

k
↑

T →
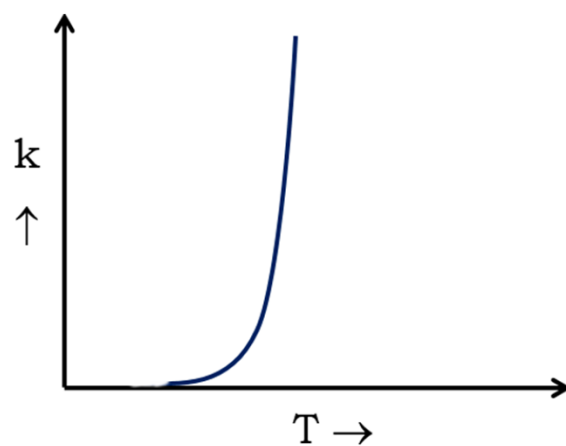
[For enzyme-catalyzed reaction]

k
↑

T →

Reactant $\rightleftharpoons$ Product

E_{af} = Activation energy for forward reaction

E_{ab} = Activation energy for backward reaction

Δu^0 = Change in standard-state molar internal energy (for the reaction)

$$\Delta H_T^0 = \Delta u_T^0 + \Delta n_g R T$$

$\Delta u^0 = E_{af} - E_{ab}$, for ideal gas, elementary reaction

Thus, Δu^0 can have (+)ve and (–)ve values.