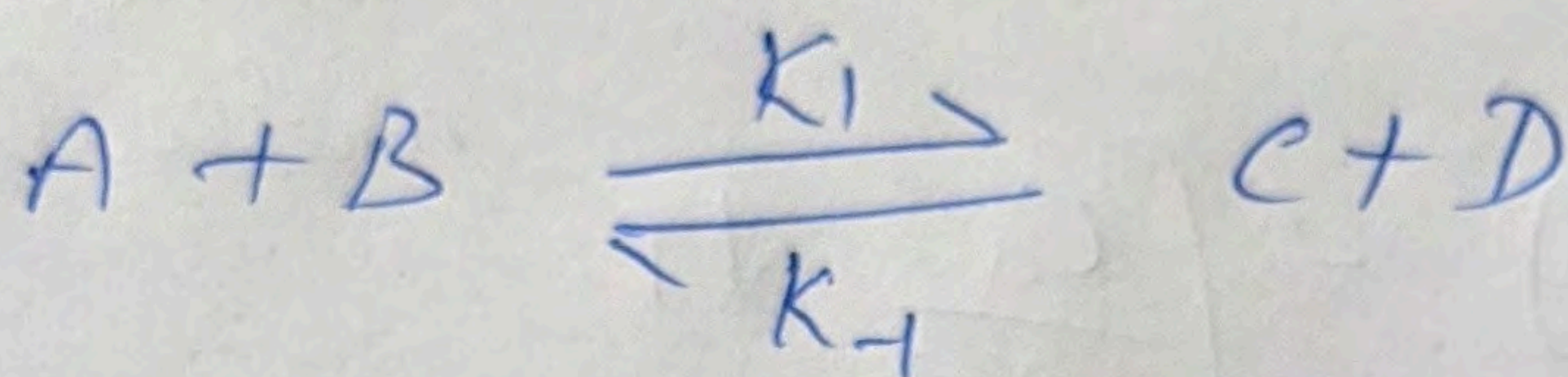


Arrhenius Equation

The dependence of rate constant of a reaction can be studied using Arrhenius Equation. We can derive the relation b/w rate constant and temperature by using Van't Hoff Equation (already studied in thermodynamics), which is applicable to a reaction at Equilibrium.



k_1 → rate constant for forward reaction

k_{-1} → for backward reaction

$$K_{eq} = \frac{k_1}{k_{-1}} \quad \text{--- (1)}$$

K_{eq} → Equilibrium Constant

Van't Hoff Equation is

$$\frac{d \ln K_{eq}}{dT} = \frac{\Delta E}{RT^2} \quad \text{--- (2)} \quad [\Delta E \rightarrow \text{Energy change of the reaction}]$$

Using relation (1), (2) becomes

$$\frac{d \ln (k_1/k_{-1})}{dT} = \frac{\Delta E}{RT^2}$$

$$\frac{d \ln (k_1/k^0)}{dT} - \frac{d \ln (k_{-1}/k^0)}{dT} = \frac{\Delta E}{RT^2} \quad [k^0 \rightarrow \text{unit rate constant}]$$

$$\Delta E = E_1 - E_{-1}$$

$$\frac{d \ln (k_1/k^0)}{dT} - \frac{d \ln (k_{-1}/k^0)}{dT} = \frac{E_1}{RT^2} - \frac{E_{-1}}{RT^2} \quad \text{(4)}$$

$$\text{or } \frac{d \ln (k_1/k^0)}{dT} = \frac{E_1}{RT^2} + I \quad \text{(3) and } \frac{d \ln (k_{-1}/k^0)}{dT} = \frac{E_{-1}}{RT^2} + I$$

(Equation separation) (I - integration constant)

I can have any value including a value of zero. 96
we take ($I=0$), then relation (3) & (4) can be
written as

$$\frac{d \ln(k/k^0)}{dT} = \frac{E_a}{RT^2} \quad (5)$$

$E_a \rightarrow$ activation Energy which is defined as the minimum Energy required to activate the reactant molecules of a reaction.

Integrate Eq. (5)

$$\int d \ln(k/k^0) = \int \frac{E_a}{RT^2} dT$$

$$\ln(k/k^0) = -\frac{E_a}{RT} + \text{Constant} \quad (6)$$

Take antilog of relation (6)

$$k = A \exp(-E_a/RT) \quad (7)$$

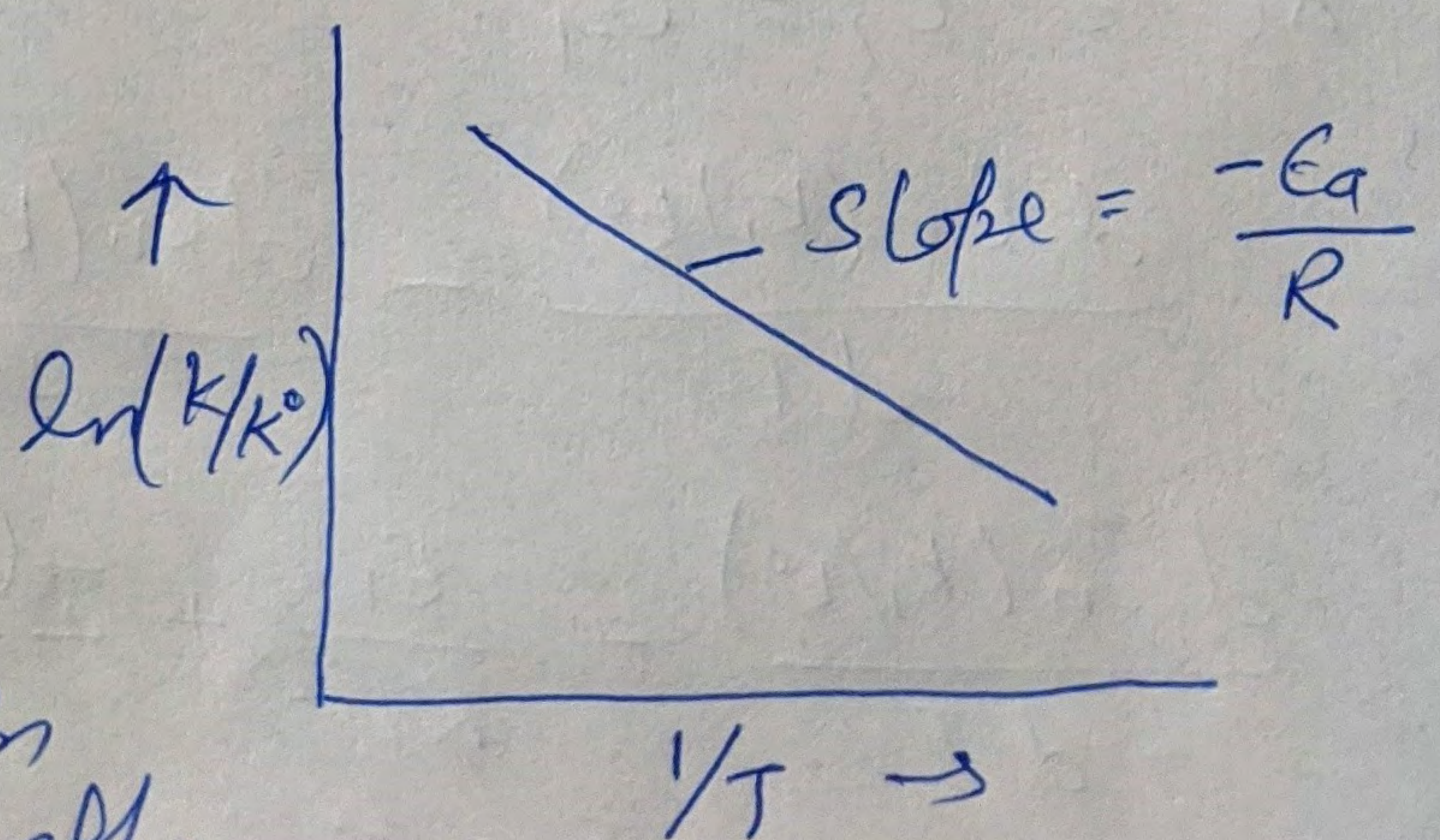
Eq. (6) & (7) are the alternative forms of
Arrhenius Equation

According to Eq. (7) \rightarrow rate constant increases exponentially with temperature.

$A \rightarrow$ is known as Pre-exponential factor or Arrhenius constant.

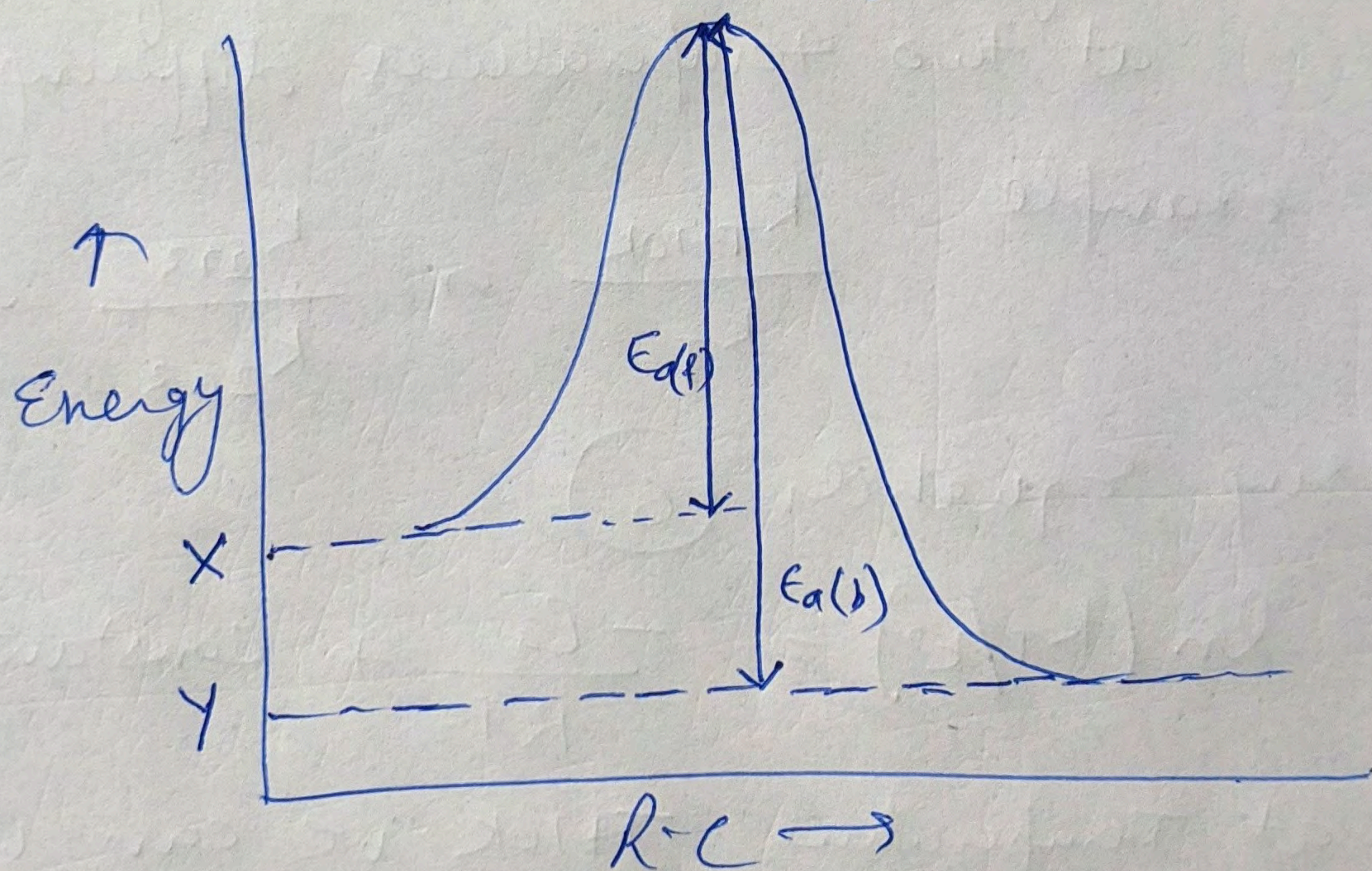
Plot a graph of Eq. (6)

If we have the values of rate constant at different temperatures, we can calculate the activation energy by plotting the graph.



Physical Significance of Activation Energy (E_a) (3)

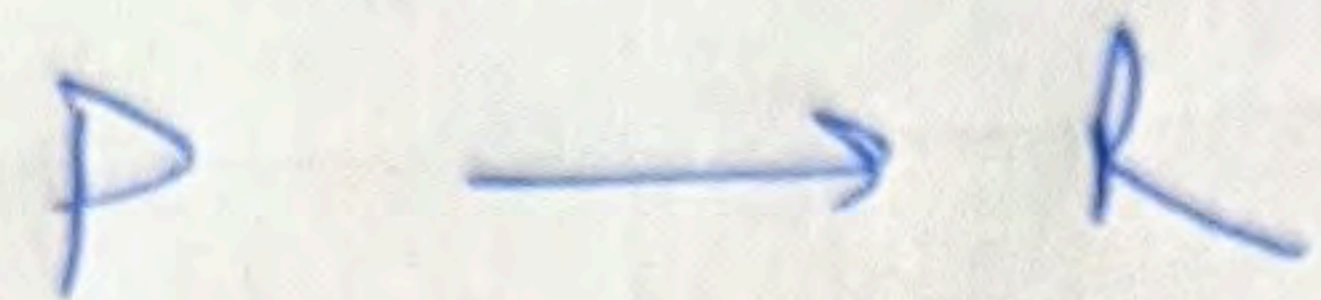
As we have already studied that products formed when reactant molecules come close and collide each other. During these collisions, molecular rearrangement takes place which involve, breaking of old bonds and formation of new bonds. Molecular rearrangement or breaking of bonds can take place only when the colliding reactant molecules have energy which is equal to greater than some minimum energy. This we can understand easily by following graph



$E_a(f)$ \rightarrow activation energy for forward reaction
 $R \rightarrow P$

The reactant molecules already have X amount of energy. When reactant molecules collide they should at least have $E_a(f)$ more energy to convert into the products.

Similarly, for the backward reaction (4)



~~It~~ $E_a(b)$ is the activation energy
 γ is the amount of energy that the product molecules already have, they need $E_a(b)$ to convert into the reactant molecules and.

$$\Delta E = E_a(f) - E_a(b)$$

Temperature Coefficient of Reaction Rates

Definition :- Temperature coefficient of a reaction is defined as the ratio of rate constants at two temperatures differing by 10 K.

for example $\frac{k_{T+10K}}{k_T}$ or $\frac{k_{273}}{k_{263}}$ or $\frac{k_{313}}{k_{303}}$

Using Equation (6)

$$\ln(k_T/k^0) = \frac{-E_a}{RT} + \text{constant} \quad (7) \text{ and}$$

at Temperature $T+10K$ we can write it as

$$\ln(k_{T+10K}/k^0) = \frac{-E_a}{R(T+10K)} + \text{constant} \quad (8)$$

$$(8) - (7)$$

$$\ln(k_{T+10K}/k^0) - \ln(k_T/k^0) = \frac{-E_a}{R(T+10K)} - \left(\frac{-E_a}{RT} \right)$$

$$\ln(k_{T+10K}/k^0) - \ln(k_T/k^0) = \frac{E_a}{R} \left(\frac{10K}{T(T+10K)} \right)$$

$$\ln \left(\frac{k_{T+10K}}{k_T} \right) = \frac{E_a}{R} \left(\frac{10K}{T(T+10K)} \right)$$

Take antilog

$$\frac{k_{T+10K}}{k_T} = \exp \left(\frac{(10K)E_a}{RT(T+10K)} \right)$$

Usually, when calculated the value of temperature coefficient at ordinary temperatures, it comes b/w 2-3 which means on increasing the temperature of a reaction by 10K - the rate of reaction increases by 2 to 3 times.

After studying the above notes try to solve the following numericals:

Q1 For the first-order reaction $A \rightarrow B$
The value of pre-exponential factor A is $4.3 \times 10^{13} \text{ s}^{-1}$ and E_a is 105.89 kJ/mol . What is the value of rate constant (k) at 298 K ?

$$\text{Hint: - } k = A \exp \left(-\frac{E_a}{RT} \right)$$

Q2 For the reaction
 $2 \text{NOCl (g)} \rightleftharpoons 2 \text{NO (g)} + \text{Cl}_2 \text{ (g)}$
the rate constant at 300 K is $3.6 \times 10^{-4} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and at 350 K is $6.0 \times 10^{-1} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. What is the energy of activation for the reaction?