

→ CALCULATION OF ACTIVATION ENERGY

Arrhenius equation

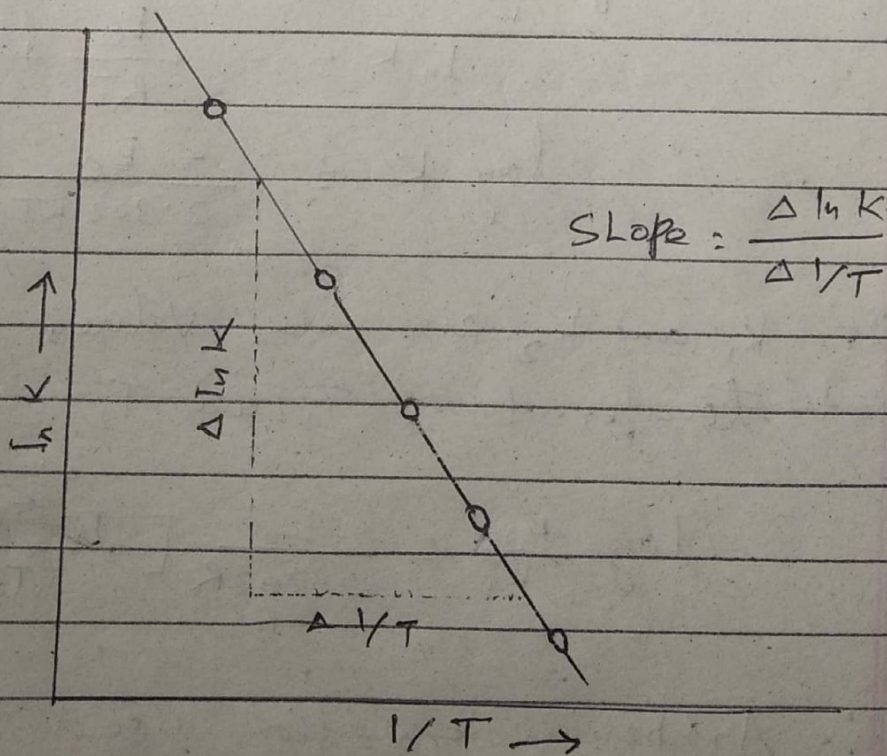
$$\ln K = - \frac{E_a}{R} \left(\frac{1}{T} \right) + \ln A$$

$$\begin{array}{ccc}
 \uparrow & & \uparrow \\
 \uparrow & & \uparrow \\
 y = mx + b & &
 \end{array}$$

Arrhenius equation is $y = mx + b$
(straight line)

Plot the natural logarithm of K against $1/T$, get a straight line. From the slope of line, u

$$\therefore \text{Slope} = - \frac{E_a}{R}$$



The plot of $\ln K$ versus $1/T$ gives a straight line. The slope of line $\Delta \ln K / \Delta 1/T$ gives E_a .

(7)

→ CALCULATION OF E_a FROM THE VALUES OF k AT TWO TEMPERATURES :

The rate constant k is measured at two temperature

AT Temperature T_1 , where rate constant k_1 ,

$$\ln k_1 = -\frac{E_a}{RT_1} + \ln A \quad \text{--- (i)}$$

AT Temperature T_2 , where rate constant k_2

$$\ln k_2 = -\frac{E_a}{RT_2} + \ln A \quad \text{--- (ii)}$$

Subtracting the eqⁿ. (i) from eqⁿ. (ii)

$$\begin{aligned} \ln k_2 - \ln k_1 &= \left[-\frac{E_a}{RT_2} + \ln A \right] - \left[-\frac{E_a}{RT_1} + \ln A \right] \\ &= -\frac{E_a}{RT_2} + \frac{E_a}{RT_1} \end{aligned}$$

$$\text{or, } \ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

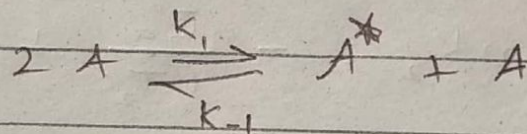
$$\text{or, } \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Thus, the values of k_1 and k_2 measured at T_1 and T_2 use to find E_a .

LINDEMANN THEORY of Unimolecular

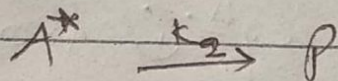
A bimolecular reaction can be easily understood with collision theory. But in case of unimolecular reaction, molecules has to be activated collide with another molecule. So, it must follow second order kinetic but some unimolecular reaction are also first order.

Linderman accounted for this by considering a 2 step mechanism as follow.



A → Reactant

P → Product



A* → activated reaction

According to s.s.A (steady state Approximate),

Rate of formation of A* = Rate of decomposition of A*

$$k_1 [A]^2 = k_{-1} [A^*] [A] + k_2 [A^*]$$

$$k_1 [A]^2 = [A^*] [k_{-1} [A] + k_2]$$

$$[A^*] = \frac{k_1 [A]^2}{k_{-1} [A] + k_2}$$

$$\text{Rate} = k_2 [A^*]$$

$$= k_2 \frac{k_1 [A]^2}{[k_{-1} [A] + k_2]}$$

Case i, Reactant concentration High ↑↑

$$k_{-1} [A] \gg k_2$$

$$\text{rate} = \frac{k_1 k_2 [A]^2}{k_{-1} [A]}$$

$$= k [A]^1$$

first order kinetic

Case ii, Reactant ^{conc.} ↓ product ↑

$$k_2 \gg k_{-1} [A]$$

$$\text{rate} = \frac{k_2 k_1 [A]^2}{k_2}$$

$$= k_1 [A]^2$$

second order kinetics