Effect of Temperature on Rate of Reaction

→ "Arrhenius Equation"

For Most of the chemical reactions, it is found that on increasing Temperature by 10°C Rate of Reaction doubles (or nearly doubles)

Approx Dependency:

$$\text{Temp coeffecient} = \frac{K_{(t+10)^\circ C}}{K_{t^\circ C}}$$

(Rate ∝ K)
K → Rate Constant

$$\text{Temp Coeffecient} = \frac{(\text{Rate})_{t+10^\circ C}}{(\text{Rate})_{t^\circ C}}$$

To find Temp coeffecient (how many times K increases on 10°C rise in temperature), taken any value of t. (Most commonly t = 25°C)

Temp Coeffecient ≃ [2, 3]

Q1) If Temp. Coeffecient for a reaction rate is 2, find the Rate of Reaction at 60°C if rate at 20°C is x.

Solution

Rate	x	$2x$	$4x$	$8x$	$16x$
Temp	20	30	40	50	60

Exact Dependency :

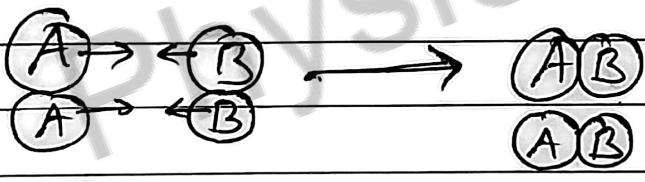
Arrhenius Equation

$$K = A \cdot e^{-Ea/RT}$$

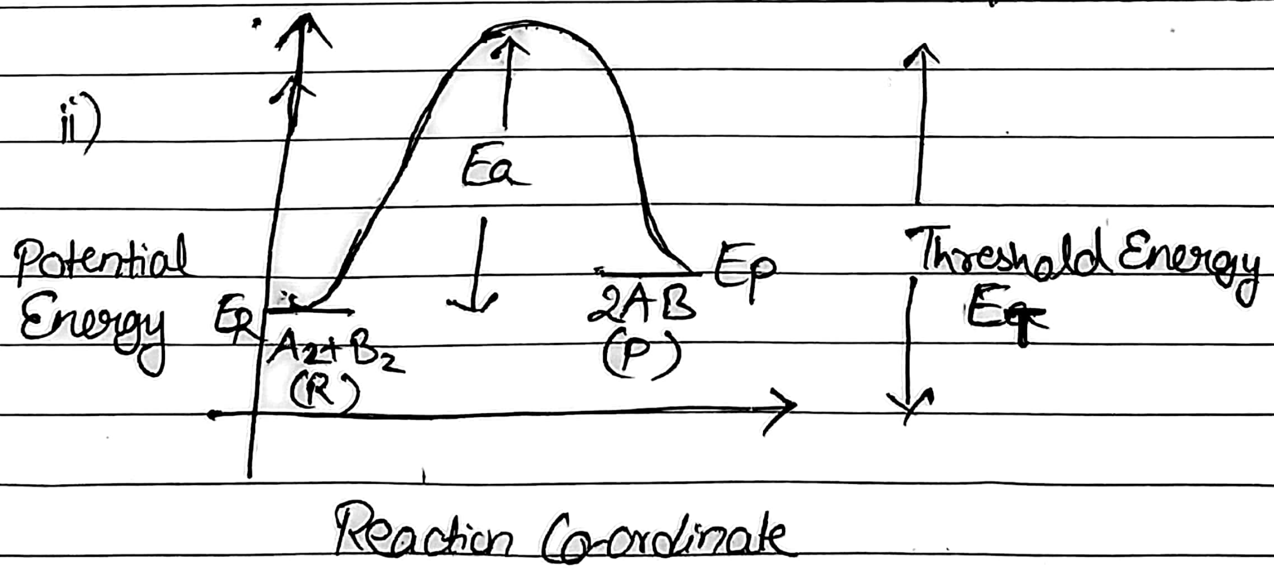
$K \rightarrow$ Rate Constant
$A \rightarrow$ Arrhenius factor / frequency facter
Pre - exponential facter
$e \rightarrow$ exponential constant
$Ea \rightarrow$ Activation Energy (Joule / mole)
$R \rightarrow$ Universal Gas Constant = 8.314 J / mole K
$T \rightarrow$ Temperature in kelvin

Collision Theory Explanation:

$$A_2 + B_2 \longrightarrow 2AB$$

i) 

proper orientation
(Head-on collision)

ii) 

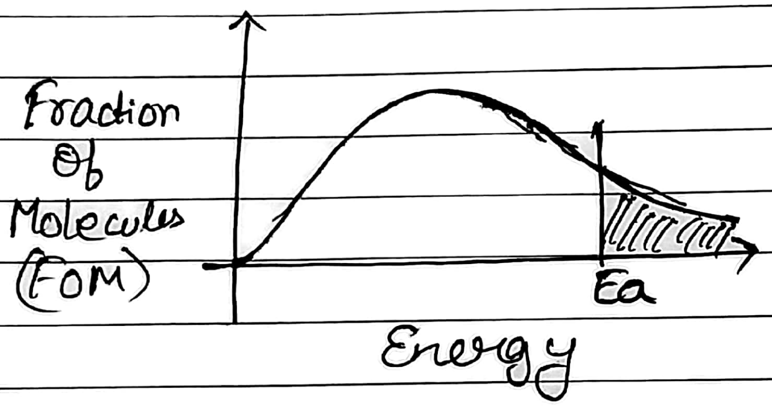
$$Ea = E_T - E_R$$

$Ea \rightarrow$ Activation Energy
$E_T \rightarrow$ Threshold Energy
$E_R \rightarrow$ Energy of Reactant

Activation Energy $(E_a) = E_T - E_R$

↳ Extra Energy required by Reactant Molecules to cross Energy barrier (Threshold) to cause effective collision.

⇒ Note: All the Molecules do not have same Kinetic Energy during collisions



FOM having energy greater than Ea $= e^{-E_a/RT}$

These molecules can cause effective Collision (if orientation is also proper)

⇒ Rate $\propto e^{-E_a/RT}$

Rate $= K[\text{Conc}]^n$

Rate $\propto K$

$K \propto e^{-E_a/RT}$

$\boxed{K = A.e^{-E_a/RT}}$ Arrhenius Equation

Taking log on both sides

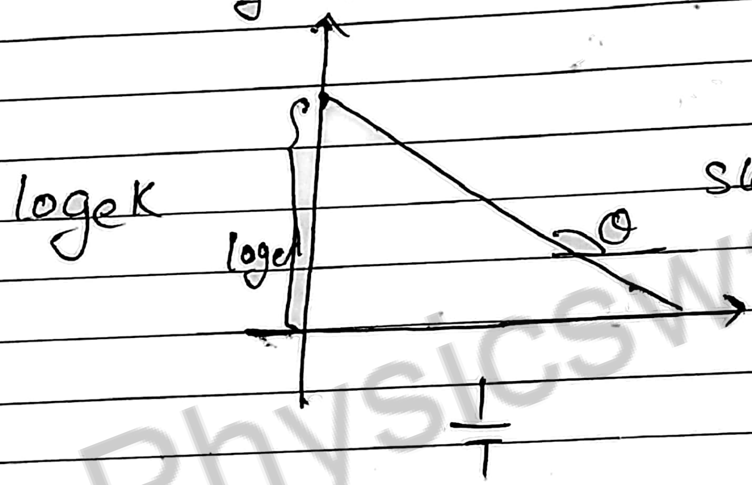
$$\log_e K = \log_e (A \cdot e^{-Ea/RT})$$

$$\log_e K = \log_e A + \log_e e^{-Ea/RT}$$

$$\log_e K = \log_e A - \frac{Ea}{RT} \log_e e$$

$$\boxed{\log_e K = -\frac{Ea}{RT} + \log_e A}$$

$$y = -mx + c$$



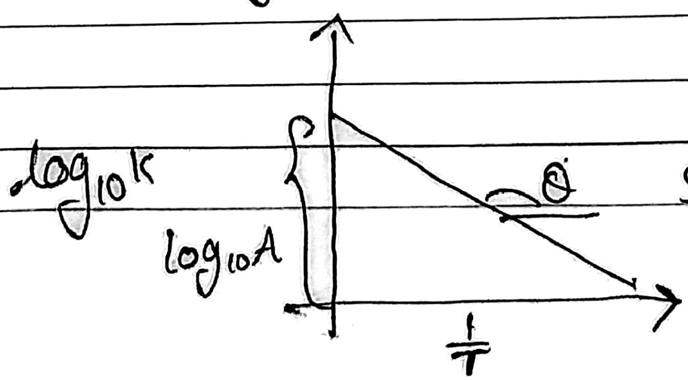
$$\text{Slope} = \tan\theta = -\frac{Ea}{R}$$

OR

$$2.303 \log_{10} K = -\frac{Ea}{RT} + 2.303 \log_{10} A$$

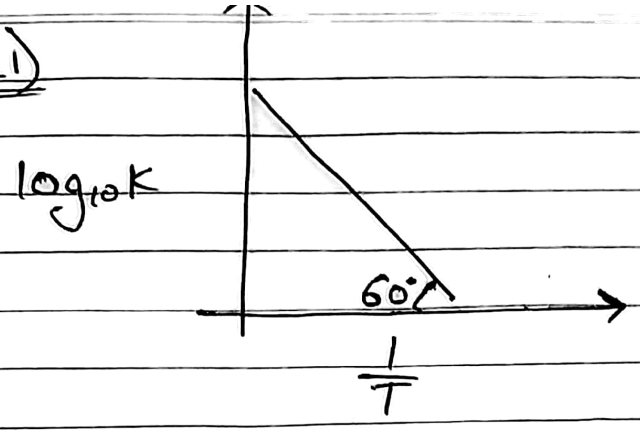
$$\boxed{\log_{10} K = -\frac{Ea}{2.303RT} + \log_{10} A}$$

$$y = -mx + c$$



$$\text{Slope} = \tan\theta = -\frac{Ea}{2.303R}$$

Q1)



Find Activation Energy

$$\text{Slope} = \tan 120^\circ = -\sqrt{3} = \frac{-E_a}{2.303R}$$

$$E_a = \sqrt{3} \times 2.303 \times 8.314 \text{ J/mole}$$

Q2) For a n^{th} order reaction, the value of frequency facter is 100 and the value of E_a is 19147 J/mole at 727°C. Find Rate Constant K

a) 1 b) 10 c) 100 d) 1000

Solution

$$\log_{10}K = \frac{-E_a}{2.303RT} + \log_{10}A$$

$$= \frac{-19147}{2.303 \times 8.314 \times 1000} + \log_{10}100$$

$$= -1 + 2$$

$$\log_{10}K = 1$$

$$K = 10^1$$

(min⁻¹)

Q3) The rate constant for a first order reaction is given as

$$\log_{10} K = 10 - \frac{1.2\times10^4}{T}$$

Find i) value of Arrhenius factor 'A'
ii) Temperature at which half life of reaction is 70 mins

Solution

i) $\log_{10} A = 10$

$A = 10^{10}$

ii) $K = \frac{0.693}{t_{1/2}}$ (first order)

$= \frac{0.693}{70} \approx \frac{0.70}{70} = 10^{-2}$

$$\log_{10}(10^{-2}) = 10 - \frac{1.2\times10^4}{T}$$

$$-2 = 10 - \frac{1.2\times10^4}{T}$$

$$\frac{1.2\times10^4}{T} = 12$$

$$T = \frac{1.2\times10^4}{12\times10} = 10^3 = 1000K$$

Ratio of Rate Constant at two diff Temperature

$K_1 \longrightarrow T_1$ Let $T_2 > T_1$

$K_2 \longrightarrow T_2$

$$\log_{10} K_1 = \frac{-E_a}{2.303RT_1} + \log_{10} A \quad \text{(i)}$$

$$\log_{10} K_2 = \frac{-E_a}{2.303RT_2} + \log_{10} A \quad \text{(ii)}$$

(Assumption: Ea & A do not change with Temperature)

(i) − (ii)

$$\log_{10} K_1 - \log_{10} K_2 = \frac{E_a}{2.303RT_2} - \frac{E_a}{2.303RT_1}$$

$$\log_{10}\left(\frac{K_1}{K_2}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\log_{10}\left(\frac{K_2}{K_1}\right) = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log_{10}\left(\frac{K_2}{K_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\boxed{\log_{10}\left(\frac{K_2}{K_1}\right) = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)}$$

Q4) The decomposition of A into products has rate constant $1.5 \times 10^4 s^{-1}$ at 27°C and $1.5 \times 10^5 s^{-1}$ at 127°C. Find the activation energy.

Solution

$$\log_{10}\left(\frac{K_2}{K_1}\right) = \frac{Ea}{2.303\,R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log_{10}\left(\frac{1.5\times10^5}{1.5\times10^4}\right) = \frac{Ea}{2.303\times8.314}\left(\frac{400-300}{400\times300}\right)$$

$$1 = \frac{Ea}{2.303\times8.314} \times \frac{100}{400\times300}$$

$$Ea = 3\times400\times2.303\times8.314 \text{ J/mole}$$

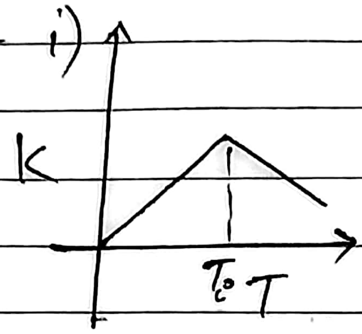
Note: Remember Rate $\propto$ K

So if relation between two Rates is given $\Rightarrow$ relation between K

Note: K does not always follows Arrhenius Equation

Note: K does not always increase with Temperature

example i)

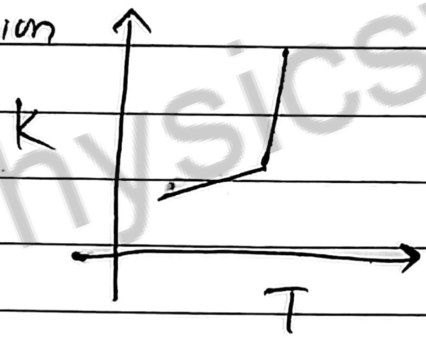


• Bacterial reaction

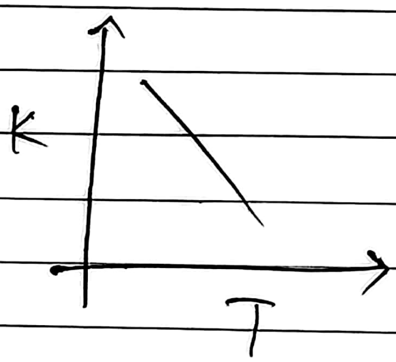
$T_i = 45°C$

$T_i \rightarrow$ inversion Temperature

ii) explosion



iii)



Oxidation of NO

$2NO + O_2 \longrightarrow 2NO_2$

Temp coeffecient = -ve