

⇒ CHEMICAL
KINETICS

⇒ FORMULA
SHEET

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r_{av} : Average Rate of Reaction

r_{inst} : Instantaneous Rate of Reaction

(i) $r_{av} = \frac{\text{Total change in conc. of reactant or product}}{\text{Time Interval}}$

(ii) For a rxn: $R \rightarrow P$

Avg. rate / rate of disappearance of R $= -\frac{\Delta[R]}{\Delta t} = -\frac{[R_2] - [R_1]}{t_2 - t_1}$

Imp: $[R_2 - R_1]$ will be '-ve' but rate can't be -ve so we will multiply by '-1'.

Avg. rate / rate of appearance of P $= \frac{\Delta[P]}{\Delta t} = \frac{[P_2] - [P_1]}{t_2 - t_1}$

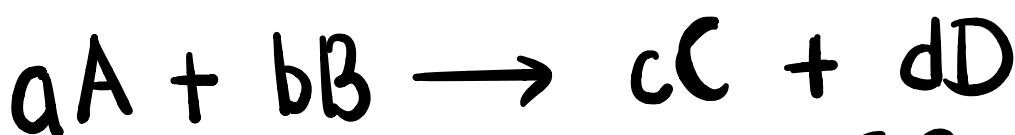
Instantaneous rate of disappearance of R $= -\frac{d[R]}{dt}$

Instantaneous rate of appearance of P = $+\frac{d[P]}{dt}$

(iii) Unit of rate of rxnⁿ:

- * If conc. $\rightarrow \text{mol} \cdot \text{L}^{-1}$ & t $\rightarrow \text{s}$ then $\text{mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}$
- * In gaseous reactions $\rightarrow \text{atm} \cdot \text{s}^{-1}$

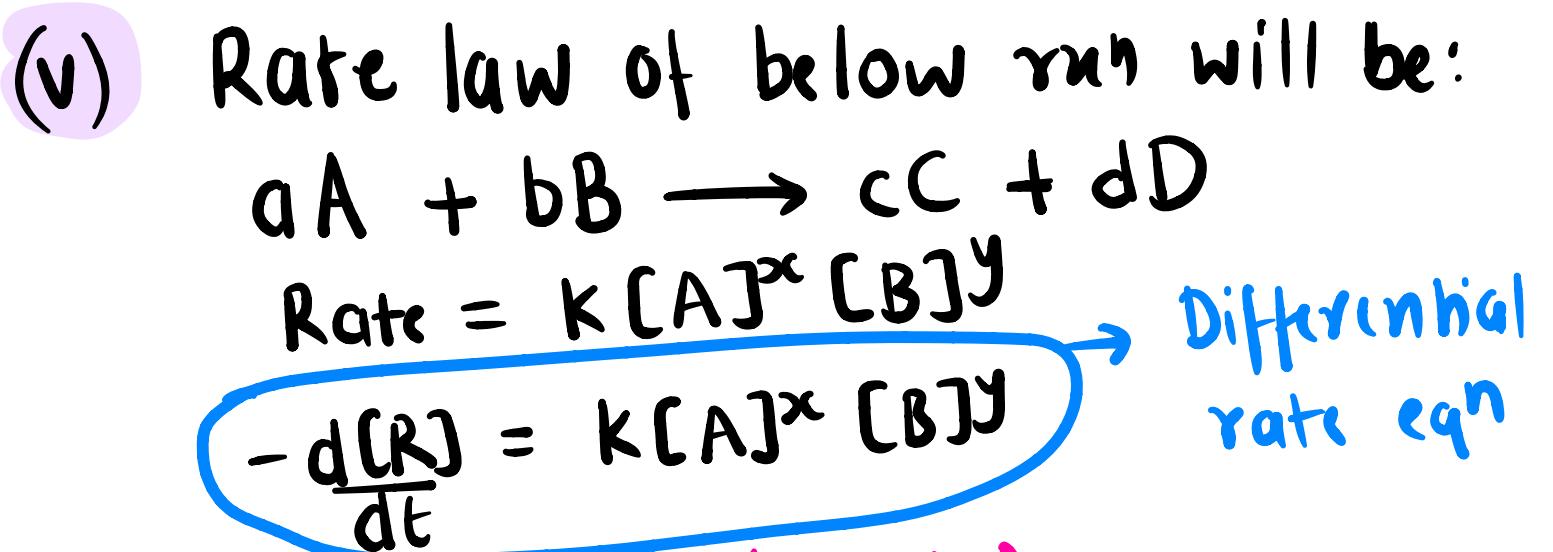
(iv) For a reaction



$$r_{\text{av}} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t} = \frac{1}{c} \frac{\Delta[C]}{\Delta t} = \frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

Imp: We divide by stoichiometric coefficients to make rate same nb matter which reactant | product we use in expression.

$$r_{\text{inst}} = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$



x : Order of run w.r.t A

y : Order of run w.r.t. B

n : Overall order of run

$$n = x + y$$

$$(mol \cdot L^{-1})^{1-n} \cdot s^{-1}$$

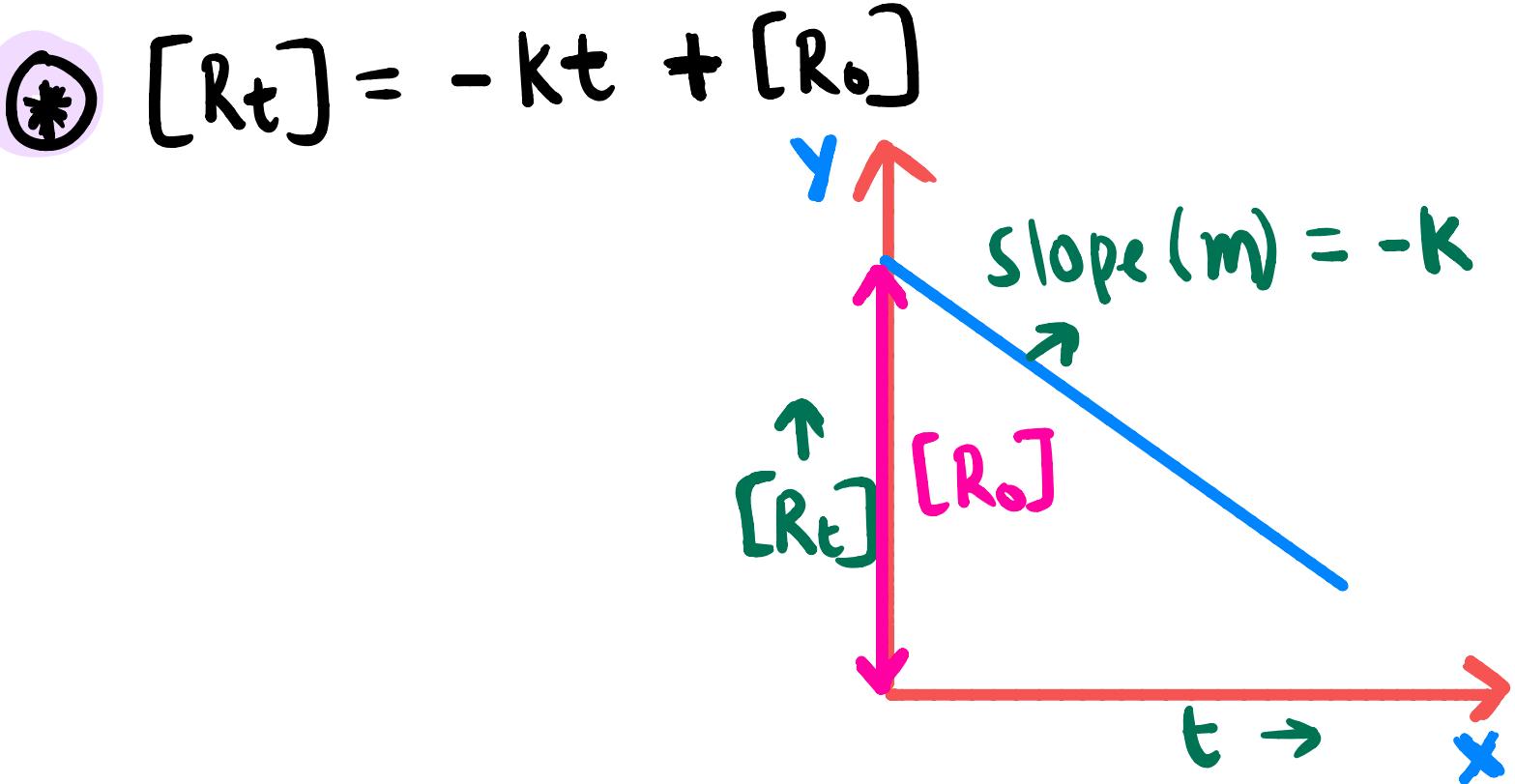
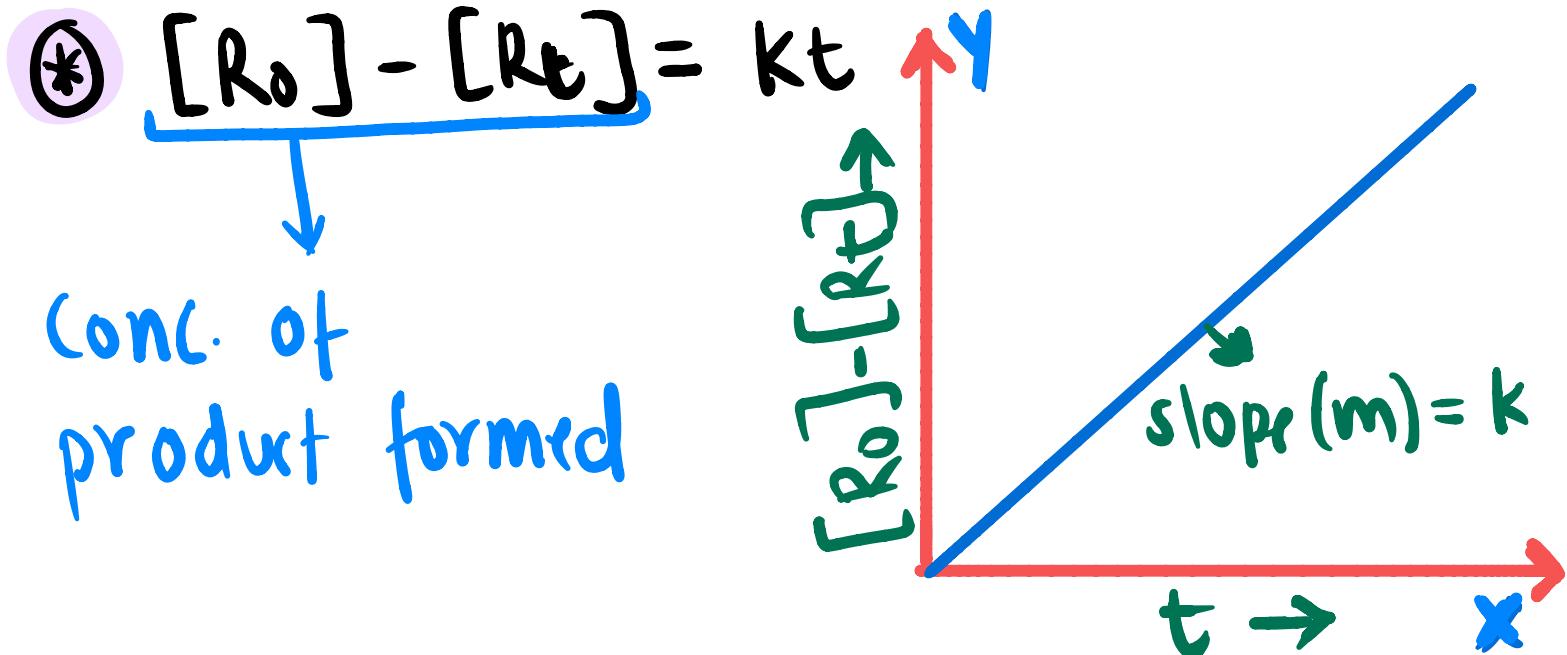
| Reaction | Order (n) | Units of rate constant |
|-----------------------|--------------|---|
| Zero order reaction | 0 | $(mol \cdot L^{-1})^{1-0} \cdot s^{-1} = mol \cdot L^{-1} \cdot s^{-1}$ (Unit of k = unit of rate of run) |
| First order reaction | 1 | $(mol \cdot L^{-1})^{1-1} \cdot s^{-1} = s^{-1}$ |
| Second order reaction | 2 | $(mol \cdot L^{-1})^{1-2} \cdot s^{-1} \Rightarrow (mol \cdot L^{-1})^{-1} \cdot s^{-1}$ $\Rightarrow mol^{-1} \cdot L \cdot s^{-1}$ |

(vi) Integrated Rate Eqn - ZERO ORDER

at time,

$t=0$, conc. of reactant is $[R_0]$

$t=t$, conc. of reactant is $[R_t]$



+ Half-life of a zero order n^n

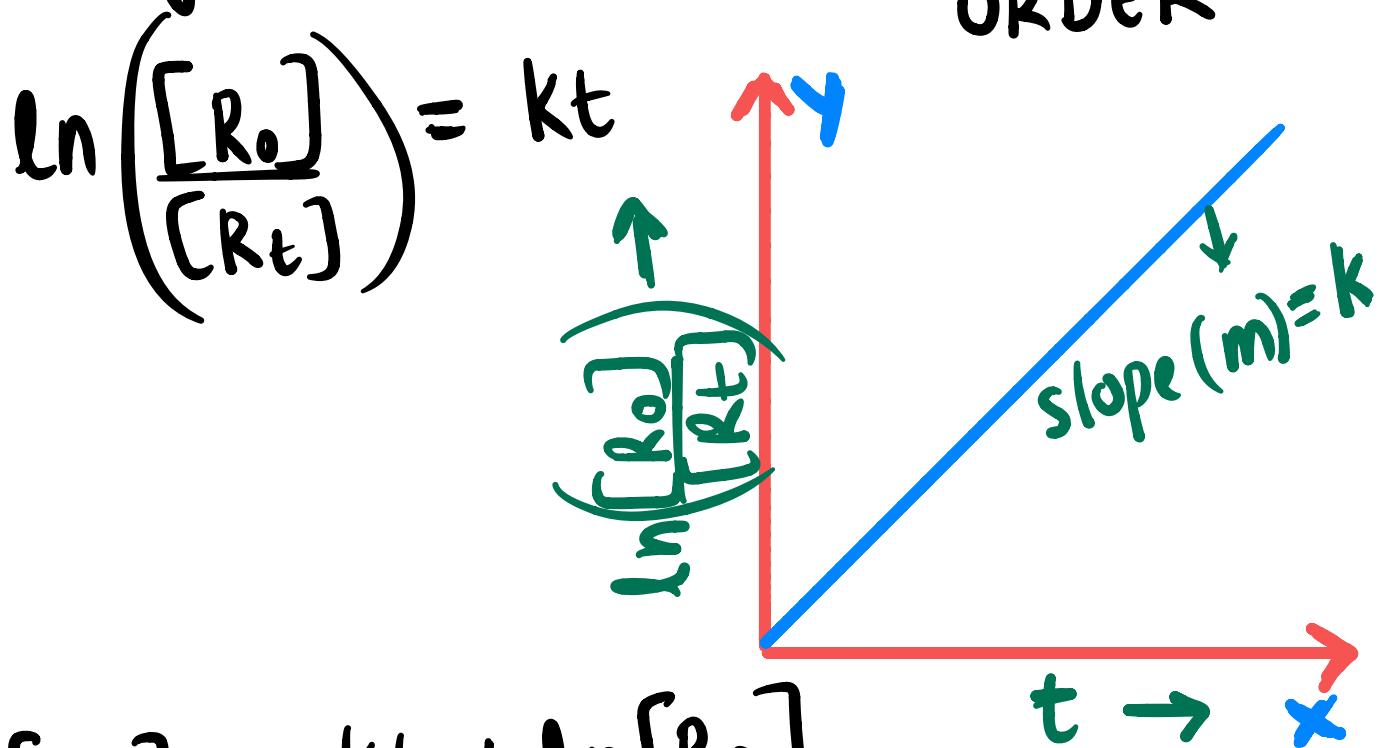
$$t_{50\%} \text{ or } t_{1/2} = \frac{[R_0]}{2k}$$

$$t_{100\%} = \frac{[R_0]}{k}, \quad t_{100\%} = 2 \times t_{50\%}$$

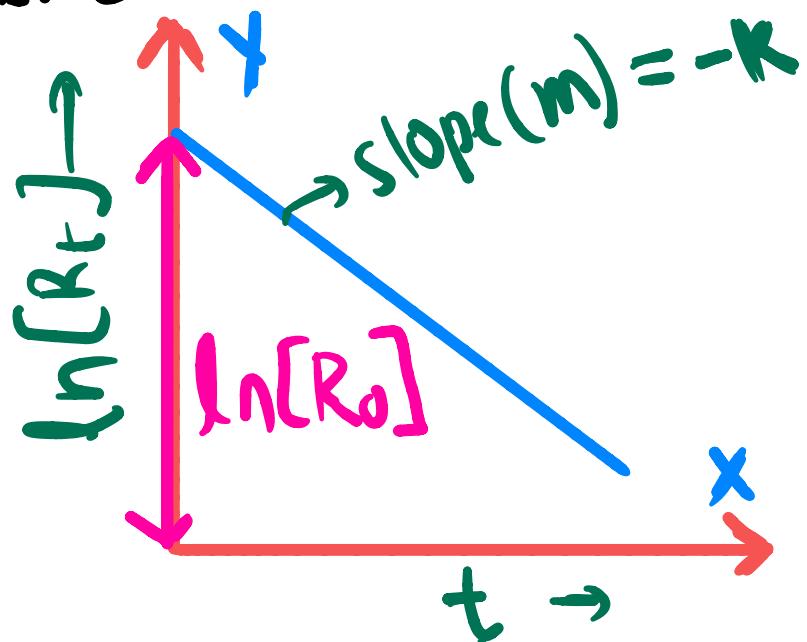
* $t_{75\%} = \frac{3}{4} \frac{[R_0]}{k}$, $t_{75\%} = \frac{3}{2} \times t_{50\%}$

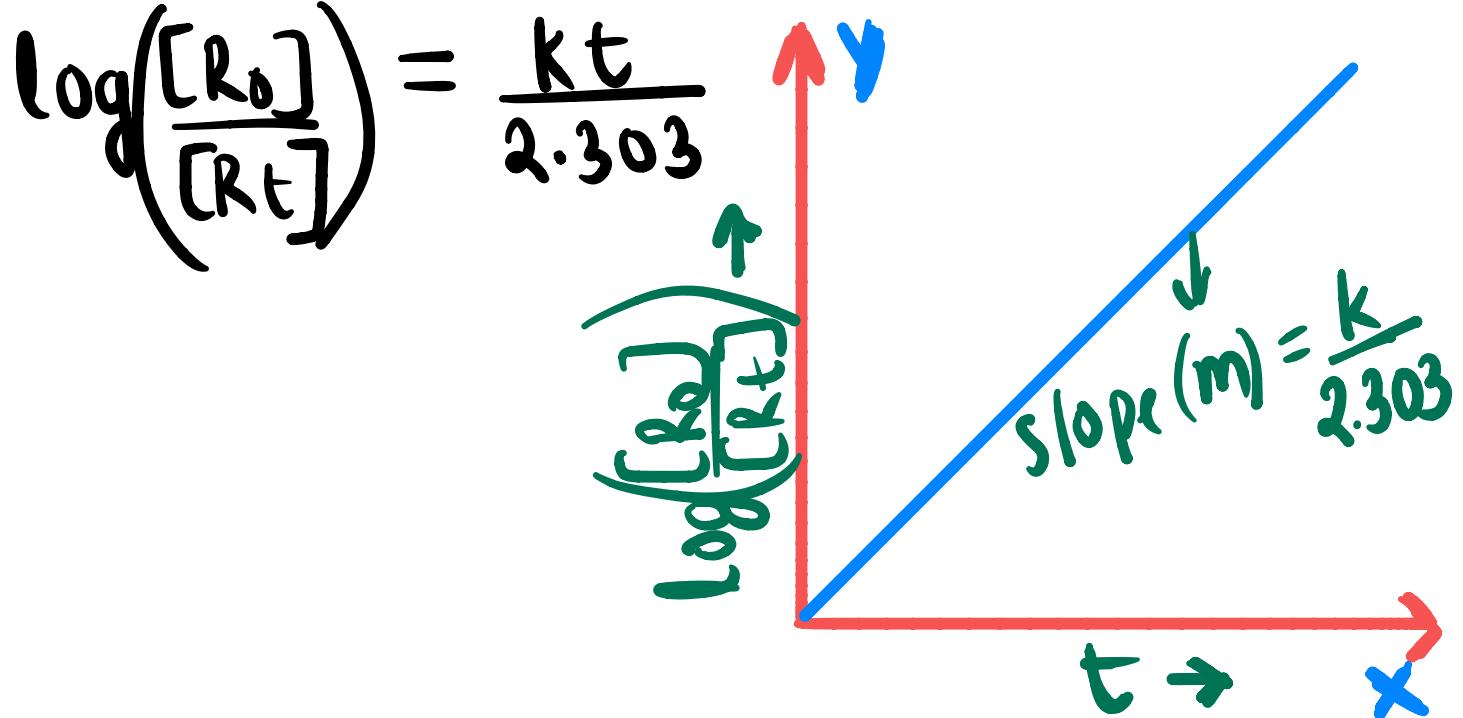
* $t_{25\%} = \frac{[R_0]}{4k}$, $t_{25\%} = \frac{1}{2} \times t_{50\%}$

(vii) Integrated Rate Eqn - FIRST ORDER



* $\ln[R_t] = -kt + \ln[R_0]$





* $[R_0] e^{-kt} = [R_t]$

* First Order - Gas Phase Rxn

| | A(g) | \rightarrow | B(g) | + | C(g) |
|-------------|-----------------|---------------|---------|---|---------|
| At $t = 0$ | p_i atm | | 0 atm | | 0 atm |
| At time t | $(p_i - x)$ atm | | x atm | | x atm |

where, p_i is the initial pressure at time $t = 0$.

$$\log \frac{(p_i)}{(2p_i - p_t)} = \frac{kt}{2.303}$$

Total pressure = $P_A + P_B + P_C$

Half life of a first order rxn

$$t_{50\%} = \frac{0.693}{k}$$

$$t_{99\%} = \frac{4.606}{k}$$

$$t_{99.9\%} = \frac{6.909}{k}$$

$$t_{99.9\%} = 10 \times t_{50\%}$$

(viii) Arrhenius Eqⁿ:

$$K = A e^{-E_a/RT}$$

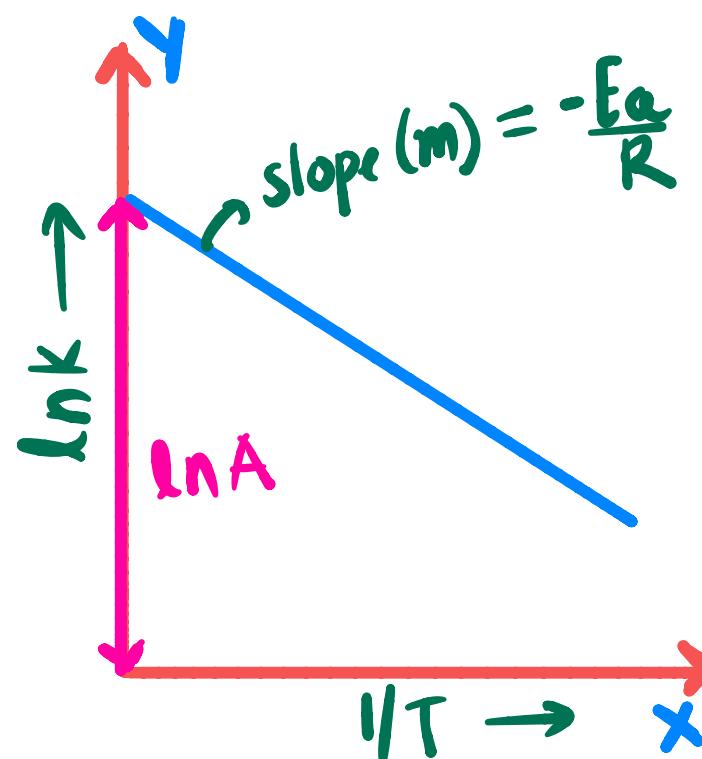
exponential factor

Frequency factor

$E_a \rightarrow$ Activation Energy
 $R \rightarrow$ Universal gas constant
 $T \rightarrow$ Temperature

* Arrhenius Eqⁿ - Natural log form

$$\ln K = -\frac{E_a}{RT} + \ln A$$



* Arrhenius Eqn - Common Log Form

$$\log K = \log A - \frac{E_a}{2.303 RT}$$

at K_1, T_1 \rightarrow eqn will be:
at K_2, T_2

$$\log \left(\frac{K_2}{K_1} \right) = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

(ix)

Collision Theory

→ For simple molecules / atomic species

$$\text{Rate} = Z e^{-E_a/RT}$$

↳ collision frequency

→ for complex molecules

$$\text{Rate} = PZ e^{-E_a/RT}$$

↳ orientation factor