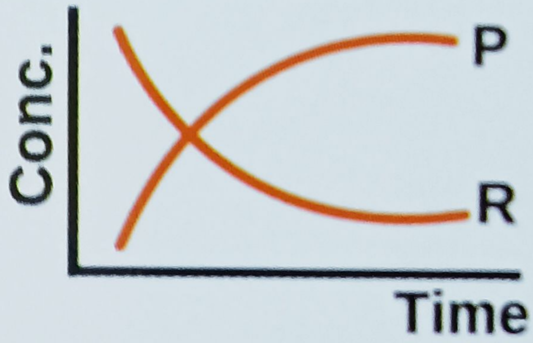
CHEMICAL KINETICS

Rates of a Reactions (mol L^{-1} s^{-1})

$$\text{Rate of a reaction} \propto \frac{\text{Change in concentration of species}}{\text{Time}}$$

For a reaction, $mA + nB \rightarrow pC + qD$

$$\frac{-1}{m}\frac{d[A]}{dt} = \frac{-1}{n}\frac{d[B]}{dt} = \frac{+1}{p}\frac{d[C]}{dt} = \frac{+1}{q}\frac{d[D]}{dt}$$

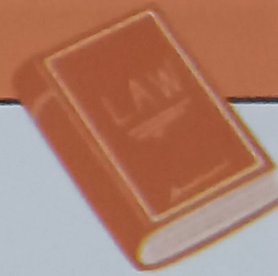


- Reactant R, Decreases with time
- Product P, Increases with time

Factors Influencing Rate of a Reaction

- Rate $\propto$ **Concentration** of the reacting species
- For every 10° rise in **Temperature**, rate becomes 2x
- **Catalyst** increases the rate without getting involved
- Greater **Surface Area** of reactant, faster the reaction
- **Light** (*hv*) increases the rate in some cases.

Rate Law and Rate Constant



For a reaction, $mA + nB \rightarrow pC + qD$

$$\text{Rate} \propto [A]^x[B]^y \Rightarrow \text{Rate} = k[A]^x[B]^y$$

k depends on Temperature	k in independent of $conc^n$

k defines speed of the reaction, Large k - fast reaction

Order of the reaction = x + y = m + n (for elementary rxn)

- It can be Zero, Positive or Fraction.
- For a multistep reaction, order is not equal to sum of stoichiometry, it is calculated using slowest step of reaction. **Order = x + y**

Molecularity = No. of Particles participating in reaction

- Molecularity ranges between 1 to 3. NEVER 0.
- For a single step reaction, Molecularity = Order.

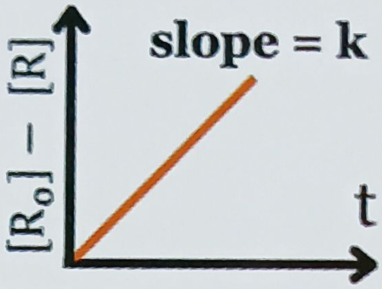
Integrated Rate laws & Graphs

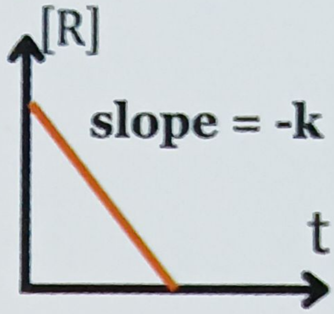
Zero Order Reaction, Units : mol L^{-1} s^{-1}

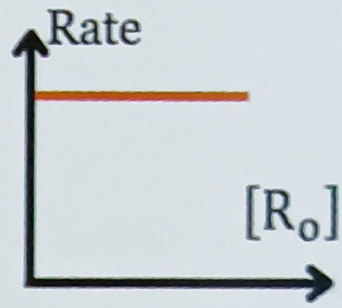
• **Differential Rate Law**	$-d[R]/dt = k$
• **Integrated Rate Law**	$kt = [R_o] - [R]$

Example : Adsorption of gases on metal surface at high P.

$[R_o]$ = a (initial conc.) ; **[R] = a-x** (Conc. after t)

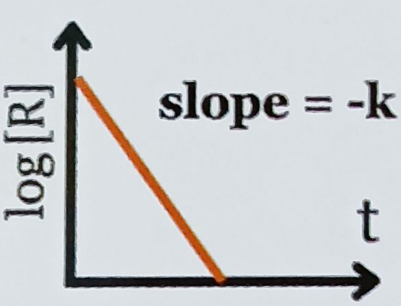


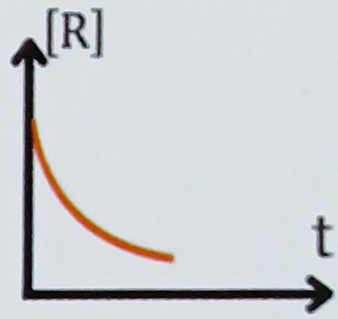


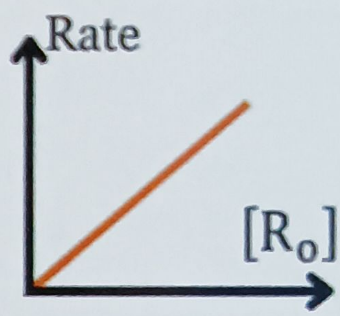


First Order Reaction, Units : s^{-1}

• **Differential Rate Law**	$-d[R]/dt = k[R]$
• **Integrated Rate Law**	$kt = 2.303 \log \left([R_o]/[R] \right)$





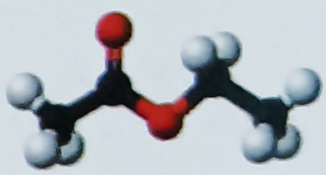


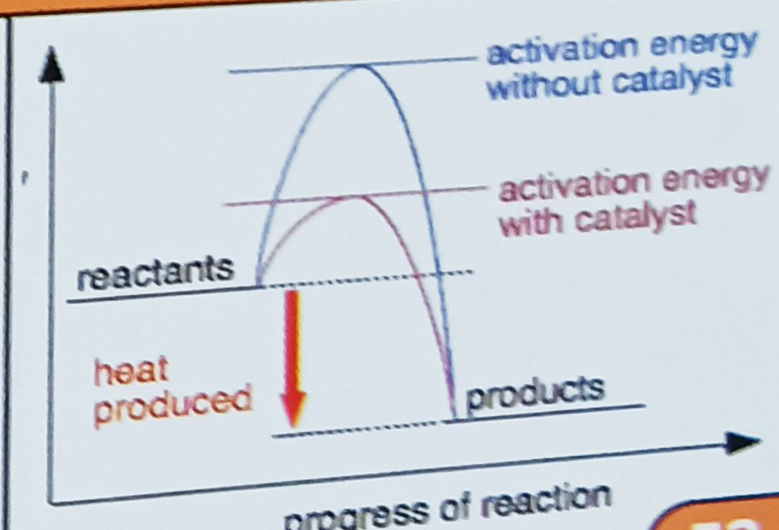
Pseudo First order reactions

Reactions which are second order but tend to behave as first order reactions. e.g. Hydrolysis of Ester in acid

$$CH_3COOC_2H_5(aq.) + H_2O(l) \xrightarrow{H^+} CH_3COOH\,(aq.) + C_2H_5OH\,(aq.)$$

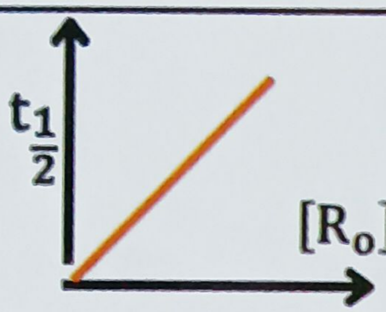
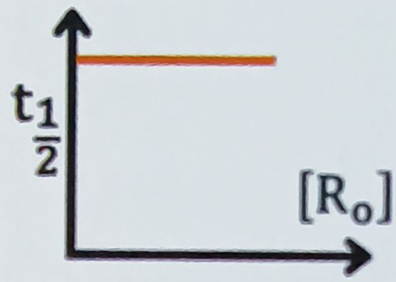
$$Rate = k[CH_3COOC_2H_5][H_2O]$$
$$Rate = k'[CH_3COOC_2H_5]$$



Some examples of first order rate constants	
Gas phase reactions A (g) → B(g) + C (g)	
Partial pressure of A given Initially, P_o and at t, P_t	$k = 2.303 \log \frac{P_o}{P_t}$
Total pressure given Initially, P_o and at t, P_t	$k = 2.303 \log \frac{P_o}{2P_o - P_t}$
General nth order terms	
• **Units**	$(\text{mol L}^{-1})^{1-n}(\text{time})^{-1}$
• **Integrated Rate Law (1st)**	$kt = \frac{1}{n-1}\left(\frac{1}{[R]^{n-1}} - \frac{1}{[R_o]^{n-1}}\right)$
• **Half Life**	$t_{1/2} = \frac{1}{k(n-1)}\left[\frac{2^{n-1} - 1}{a^{n-1}}\right]$
Effect of Catalyst on rate	
A catalyst provides an alternative route for a reaction with a lower activation energy. **Thus, Speeds up reaction**	

(initial conc.) ; [R] = a-x (Conc. after t)

Half life and relations

Zero Order	First Order	Second Order
$t_{\frac{1}{2}} = \frac{[R_o]}{2k}$	$t_{\frac{1}{2}} = \frac{0.693}{k}$	$t_{\frac{1}{2}} = \frac{1}{k[R_o]}$
		

Important Relations

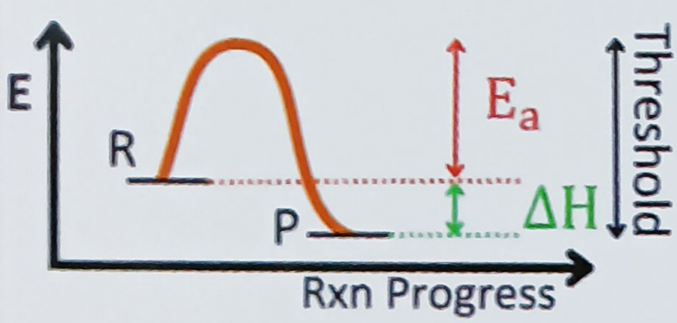
$t_{75\%} = 2\, t_{1/2}$	$t_{99.9\%} = 10\, t_{1/2}$
Substance left after n half lives	$[R_o]/2^n$

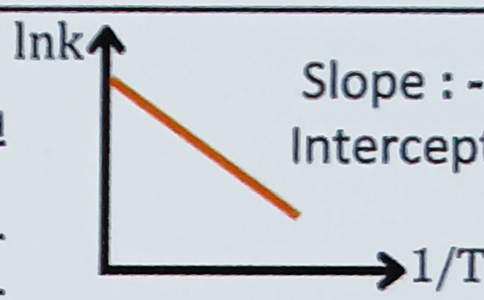
Temperature Dependence of rate of reaction

Arrhenius eqn : Relates Temperature with rate constant.

$$k = Ae^{-E_a/RT}$$

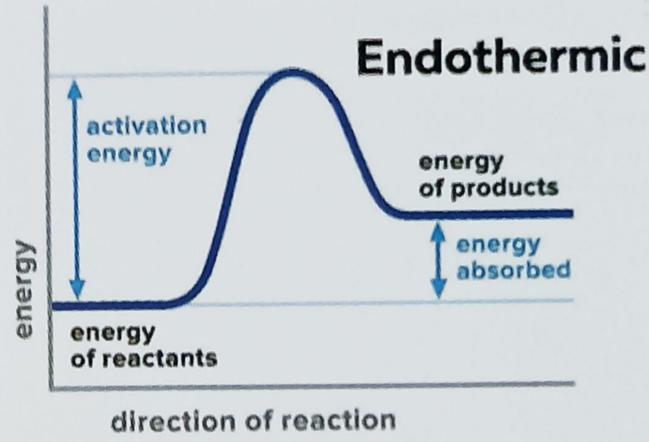
- E_a = Activation Energy
- A = Frequency factor

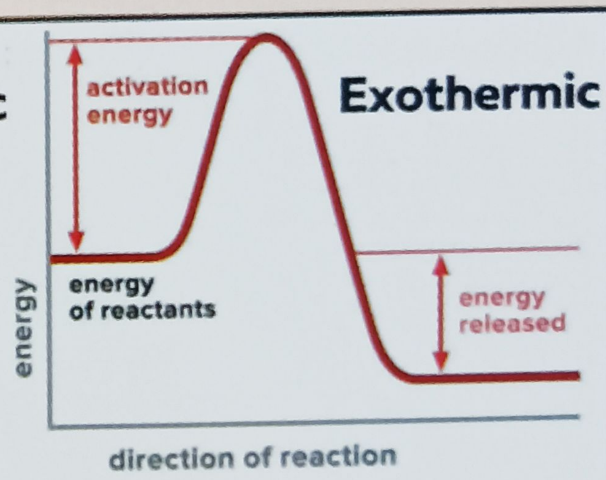




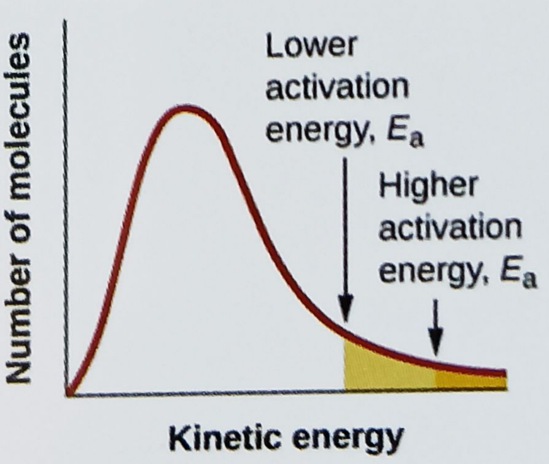
Slope : $-E_a/R$
Intercept : **lnA**

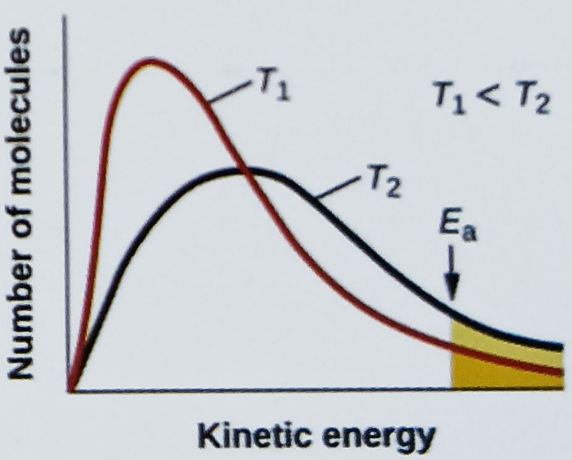
$$\ln k = \ln A - \frac{E_a}{RT}$$





For a a reaction at two different temperatures	$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
Temperature Coefficient Rate constant doubles or triples with every 10° rise in temperature	$\frac{k_t + 10}{k_t} \approx 2$





Collision theory

- The rate of a chemical reaction is proportional to the number of collisions between reactant molecules.
- Only Effective collision results in Products.