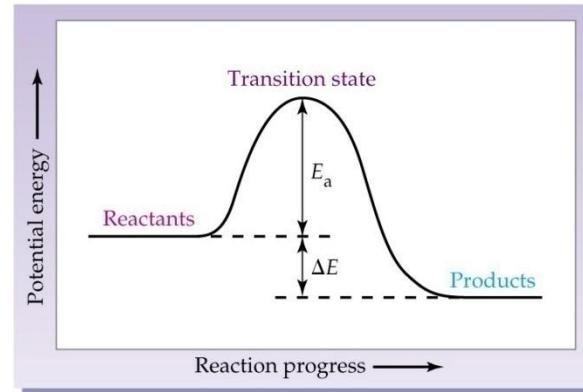


Thermodynamics & kinetics

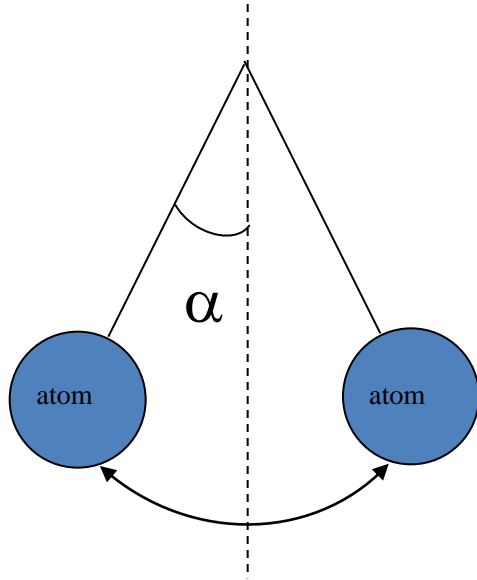


(a)

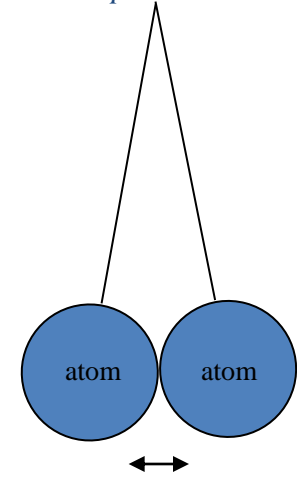


(b)

1

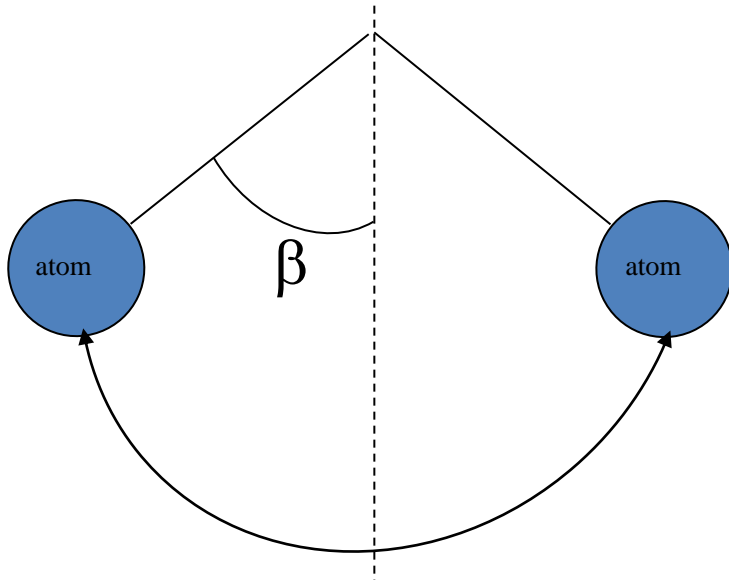


$$E_k = \frac{1}{2} mV^2 < E_a$$



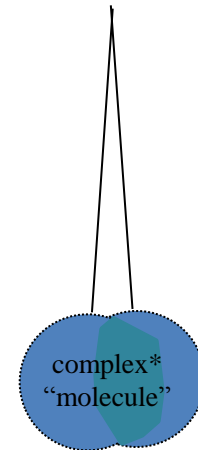
not reacted

2

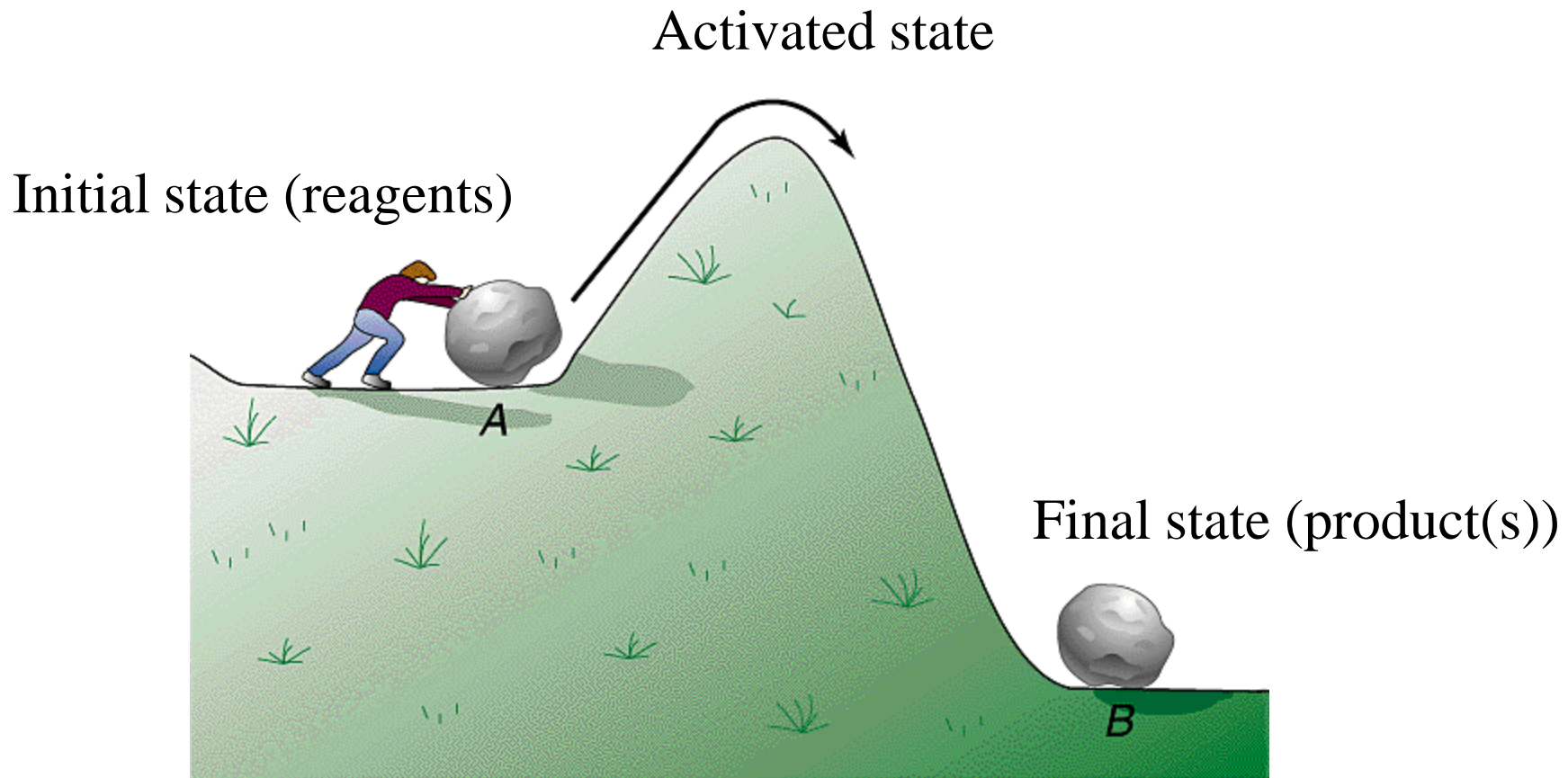


$$\beta > \alpha$$

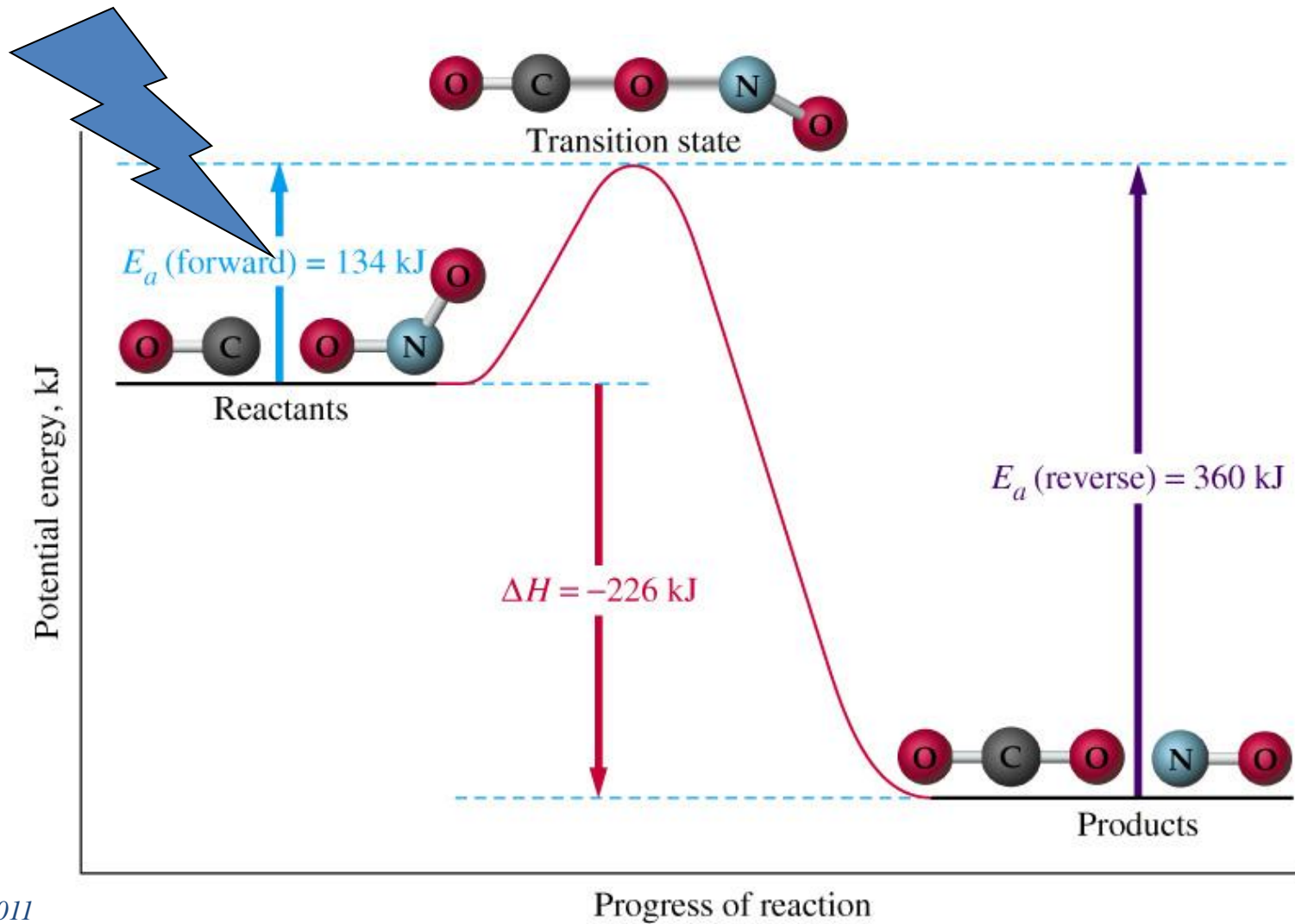
$$E_k = \frac{1}{2} mV^2 > E_a$$



reacted



E_k necessary to generate “useful collisions” $\geq E_a$



Kinetics

Provides info on:

- 1) Reaction mechanism
- 2) Reaction time course (time needed to reach equilibrium)

How do we make a kinetic measurement?
What do we measure?

In gaseous phase \rightarrow pp and volumes, $f(\text{time})$

In liquid phase (solution) \rightarrow concentrations, $f(\text{time})$

$$\underbrace{n^{\circ} \text{ moles} \times V^{-1}} \times \text{time}^{-1}$$

$$[\text{conc}] \times \text{time}^{-1} \rightarrow \text{Rate -Velocity!!}$$

Thermodynamic parameters

$$\Delta G = \Delta H - T \Delta S$$

$$\Delta G = - 57 \text{ Kcal/Mol}$$

$$\Delta H = - 68 \text{ Kcal/mol}$$

$$T = 298 \text{ K}$$

$$\Delta S = - 0.039 \text{ Kcal/mol}$$

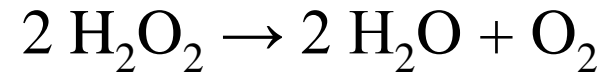
do they give any info
on rate...!?

No !

can we predict a rate
based on ΔG ?

No !

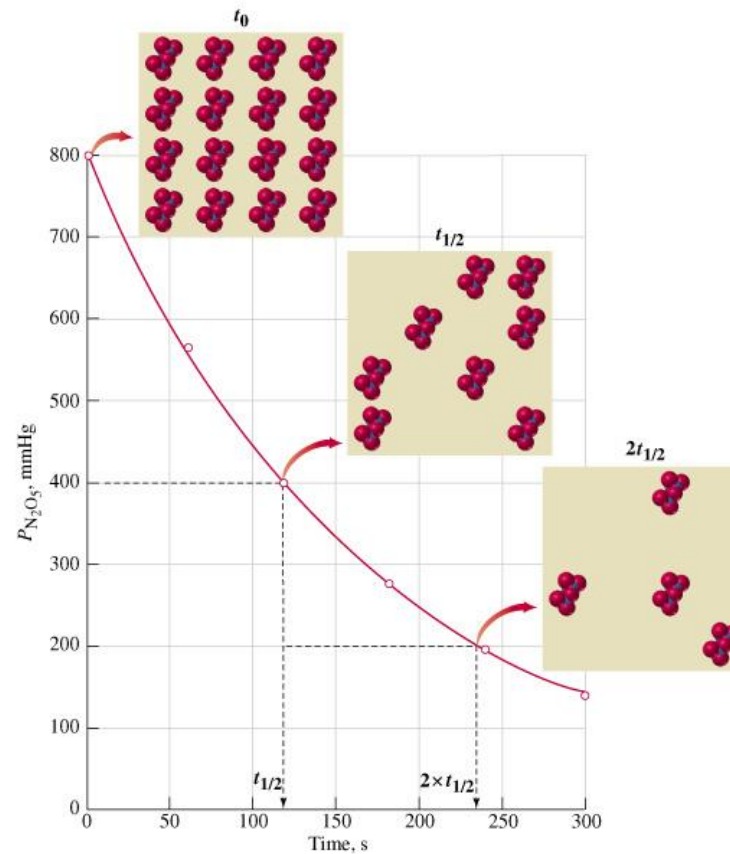
Es.



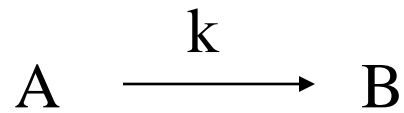
To measure kinetics
we need to know:

- reagents degradation $f(t)$
- products formation $f(t)$
- thus, rate at given time t

Example

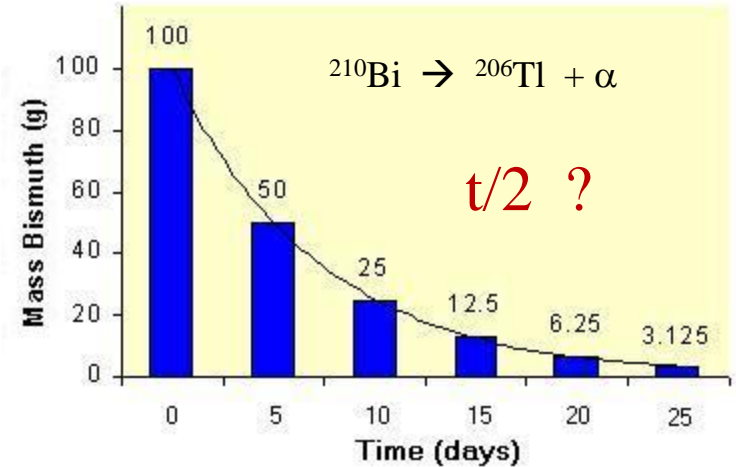
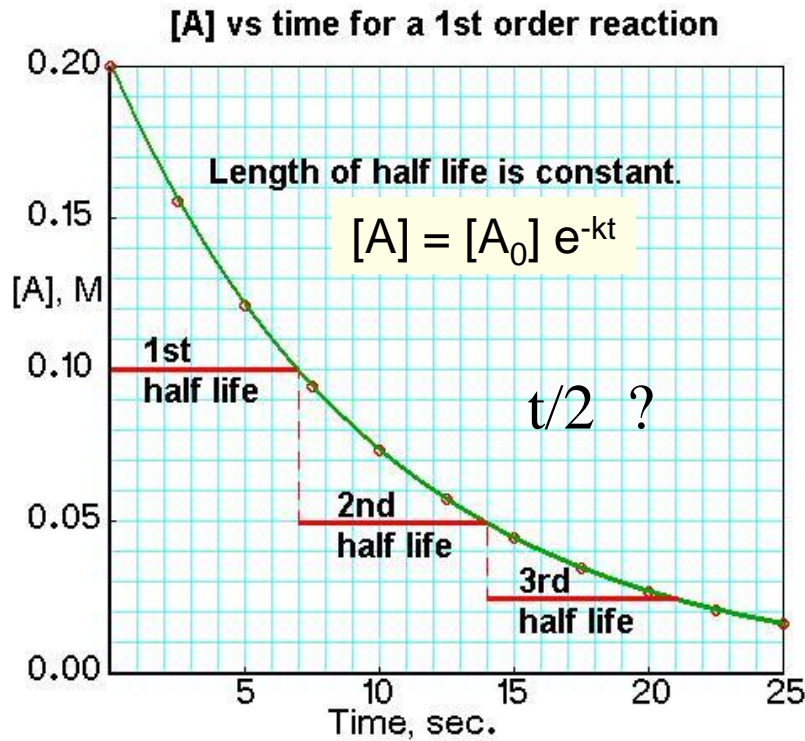


$$A = A_0 e^{-kt}$$

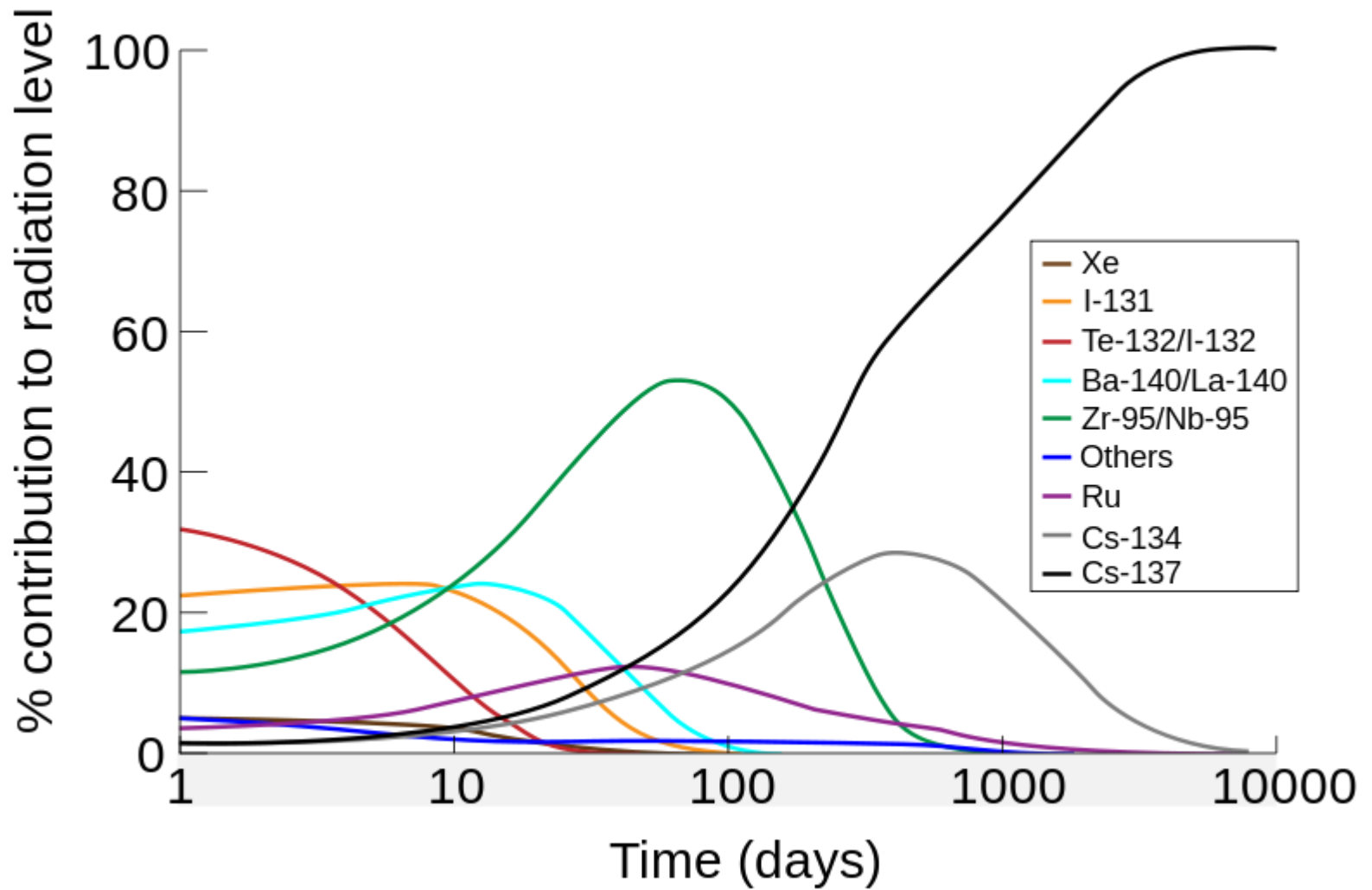


Iodine-131 $t/2 = 8$ days
 Iodine-125 $t/2 = 59$ days

$$V = k [A]^1$$



| $t/2$ | % residuo |
|-------|-----------|
| 1 | 50 |
| 2 | 25 |
| 3 | 12.5 |
| 4 | 6.25 |
| 5 | 3.125 |



Zr = zirconium
 Nb = niobium

$$[A] = [A_0] e^{-kt}$$

for $t = t/2$

$$A = A_0/2$$

$$\ln A / \ln A_0 = -kt$$

$$\ln A_0 - \ln 2 - \ln A_0 = -kt/2$$

$$\cancel{\ln A_0} - \ln 2 - \cancel{\ln A_0} = -kt/2$$

$$\ln 2 = k \times t/2$$

$$k = \ln 2 / t/2 = 0.693 / t/2$$

$$t/2 = \text{constant}$$

$$t/2 = 0.693 / k$$

Parameters affecting the rate of a reaction :

- 1) Reagents concentration**
- 2) Temperature**
- 3) Catalysts/enzymes**
- 4) Physico-chemical properties of reagents & products**

Velocity & concentration

It is intuitive 2 atoms/molecules needs to meet to react !

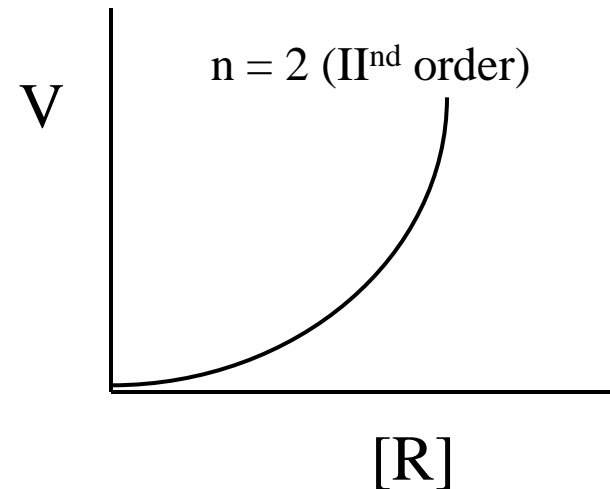
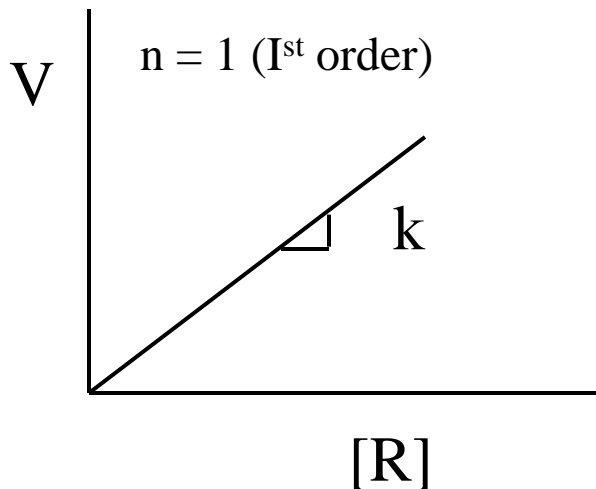
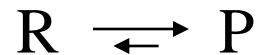
Consequently the reaction rate

$$V \uparrow, f [R]$$

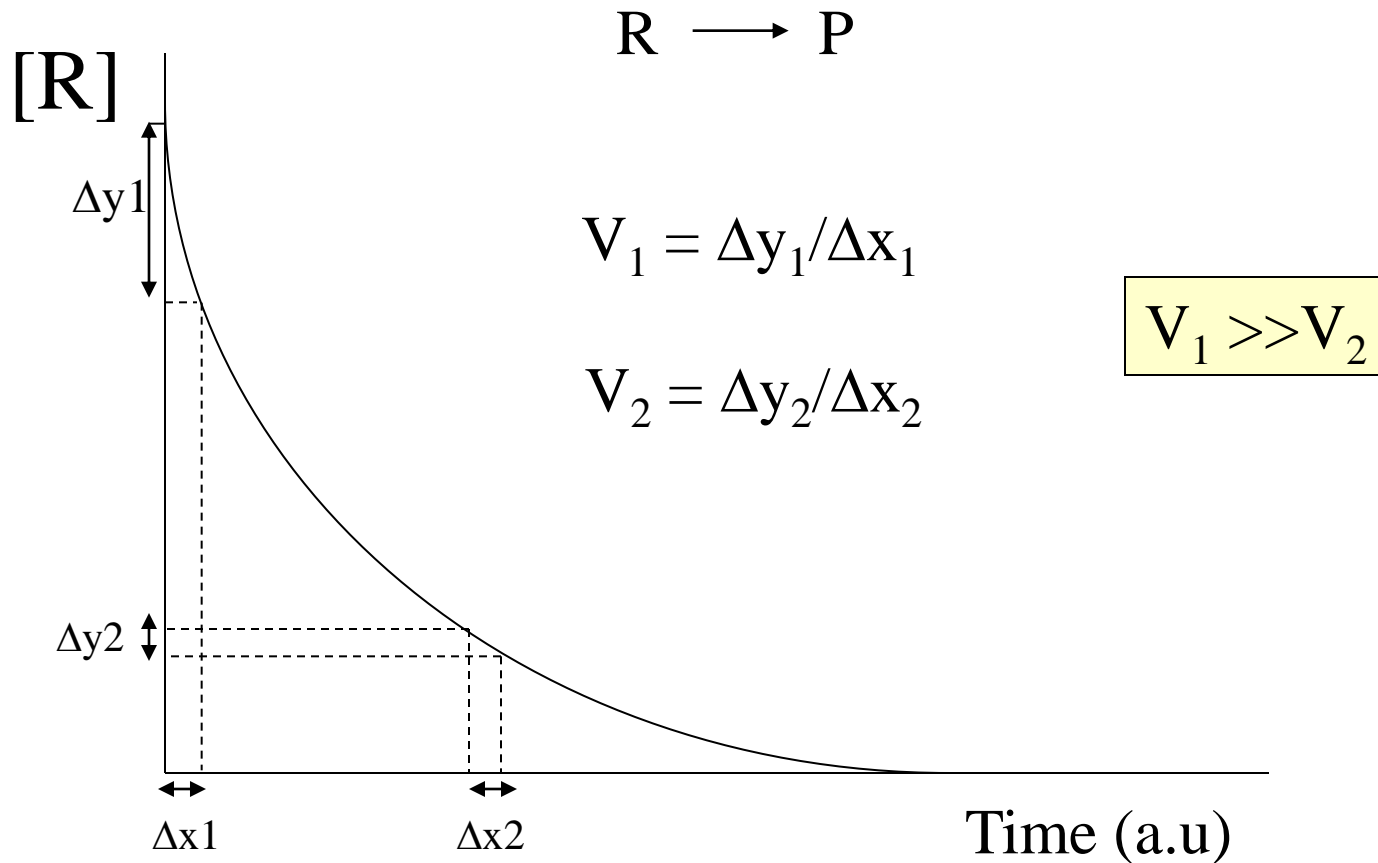
Kinetic equation

$$V = k [R]^n$$

(n = reaction order)

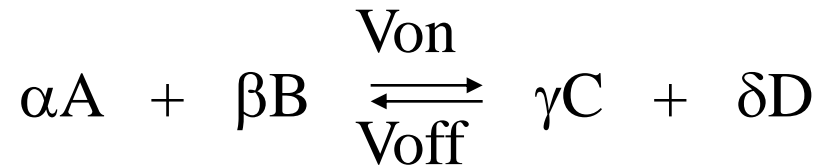


If the rate depends upon the reagents concentration
Then V has to decrease as a function of time!



and for an equilibrium ?

The kinetic of a reaction



$$V_{\text{on}} = k [A]^n * [B]^m \quad (n, m = \text{on-reaction orders, } \textit{partial})$$

$(n + m = \text{on-reaction order, } \textit{global})$

$$V_{\text{off}} = k [C]^{n'} * [D]^{m'} \quad (n', m' = \text{off-reaction orders, } \textit{partial})$$

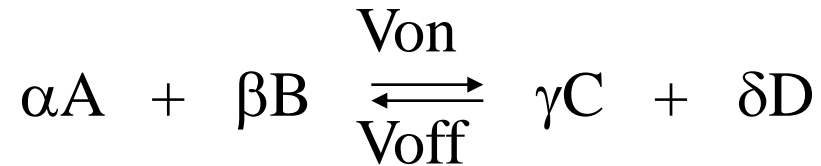
$(n' + m' = \text{off-reaction orders, } \textit{global})$

Reaction orders & stoichiometric coefficients

Do not make confusion !!! They are different parameters

Any coincidence is just fortuitous!!

K_{eq} and the reaction rates



$$V_{on} = k_{on} [A] [B]$$

$$V_{off} = k_{off} [C] [D]$$

At equilibrium

$$V_{on} = V_{off}$$

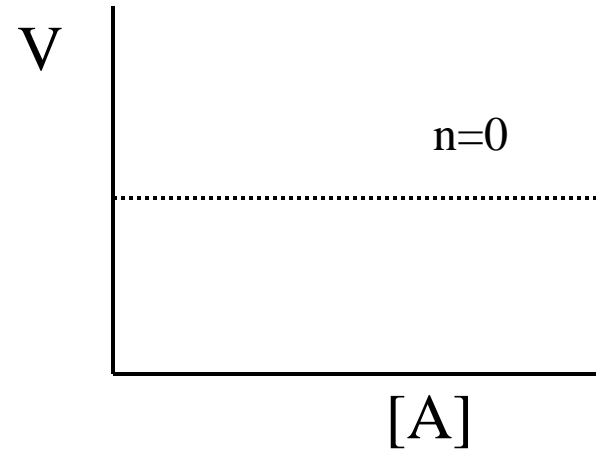
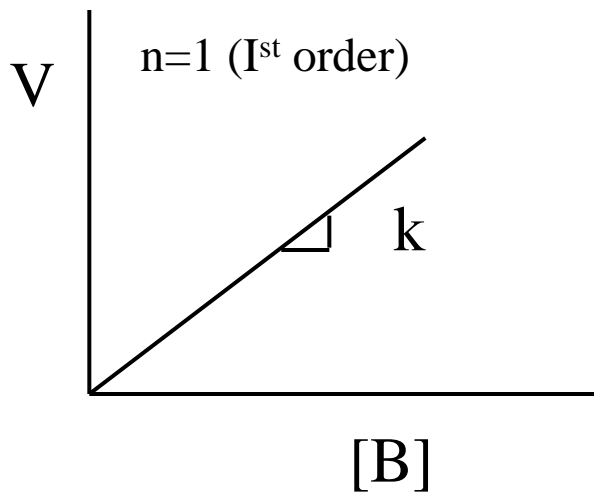
$$k_{on} [A] [B] = k_{off} [C] [D]$$

$$k_{on}/k_{off} = [C][D]/[A][B] = K_{eq}$$

This is interesting!!



$$V = k [A]^0 [B]^n \quad (n = 1, \text{ most commonly!})$$



Enzymatic catalysis

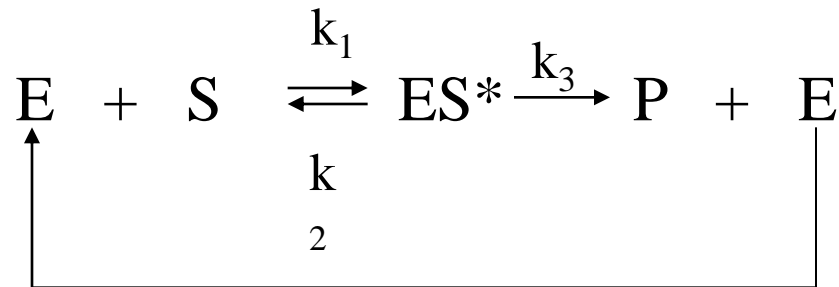
Michaelis-Menten model (1913)



$$V = k [A]^0 [B]^1$$

$$V = k [S]^0 [E]^1 \text{ (at steady state)}$$

Model :



Michaelis Menten constant K_M



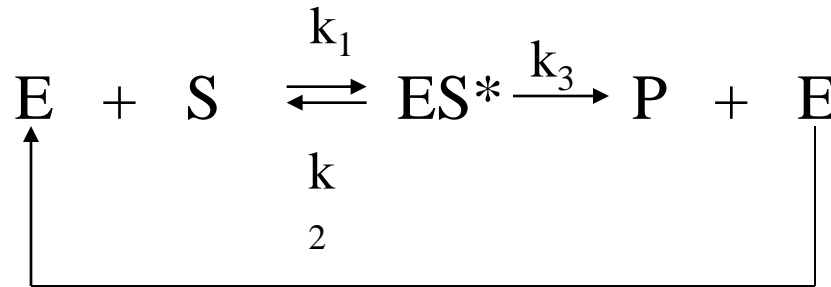
$$V = k [A]^0 [B]^1$$

$$V = k [S]^0 [E]^1$$

$$V_1 = k_1 [E][S]$$

$$V_2 = k_2 [ES]$$

$$V_3 = k_3 [ES]$$



when $t = t_{\text{steady state (st)}}$

$$V_1 = V_2 + V_3$$

$$k_1 [E] [S] = (k_2 [ES] + k_3 [ES])$$

$$k_1 [E] [S] = (k_2 + k_3) [ES]$$

$$\frac{(k_2 + k_3)}{k_1} = \frac{[E] [S]}{[ES]} = K_M$$

Equilibrium & steady state (are they the same...!?)

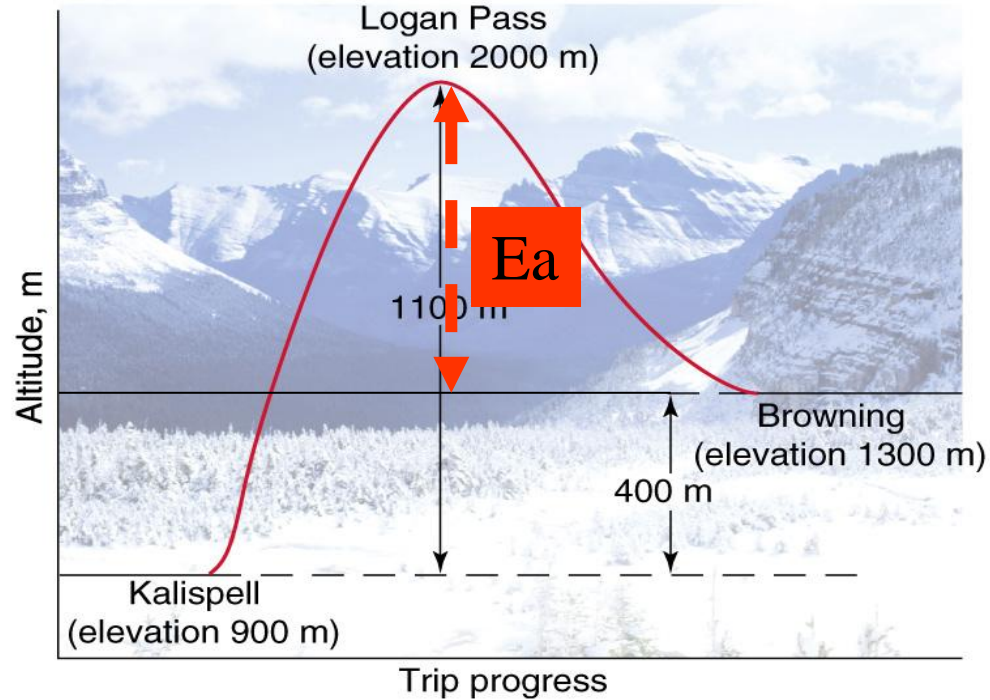
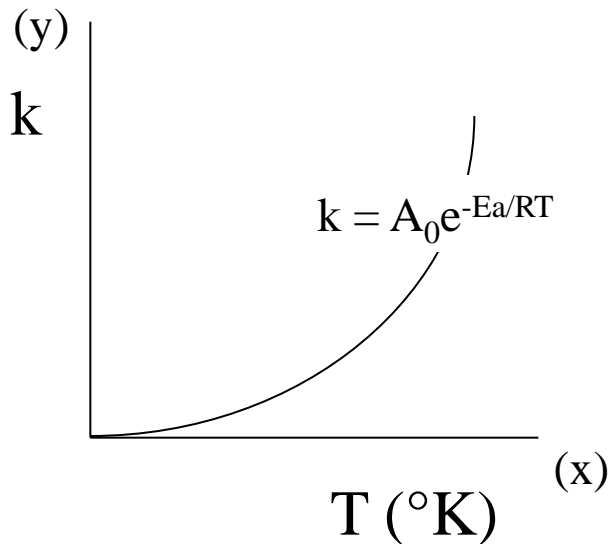
The rate of a reaction and T (Arrhenius)

Useful collision $\approx E_a$ se $T \uparrow E_K \uparrow$ & $V \uparrow$

Useful collisions \uparrow with $V \uparrow$

$V \propto$ fraction (f) of molecules with $E_K \geq E_a$
 $f \propto (T)$; $f \propto (1/E_a)$

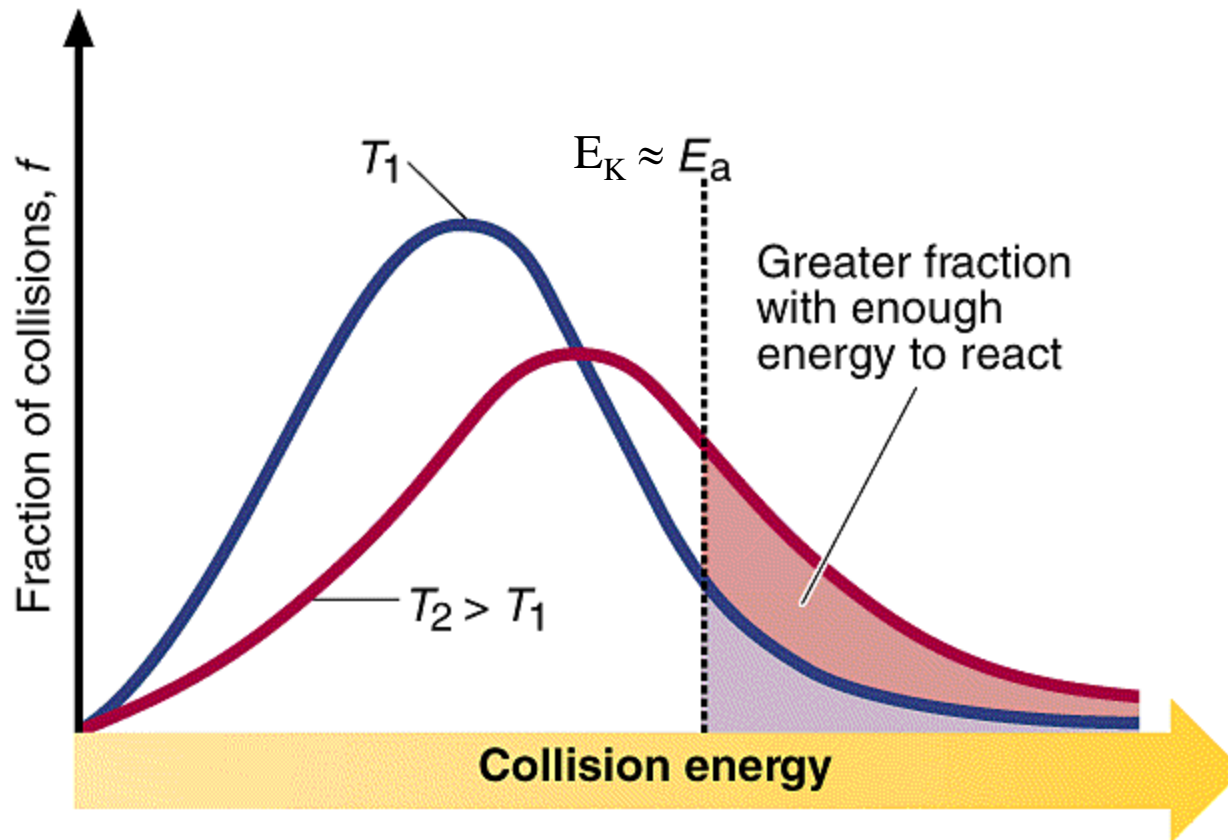
$$k, f \propto e^{-E_a/RT}$$



$$\lim_{x \rightarrow -\infty} e^x = 0$$

if $T \rightarrow 0$, $e^{-\infty} = 0 \rightarrow V = 0$

if $T \rightarrow \infty$, $e^{-0} = 1 \rightarrow V = V_{\max}$



“the energy that must be overcome in order for a chemical reaction to occur (E_a)”

S. Arrhenius (1859-1927)

