

## < Chemical Kinetics >

- \* rate of chemical reactions.
- ⇒ Influence of ① temperature, ② pressure and ③ composition on rxn rates.
- ⇒ Energy barriers separating reactants and products.
- \* Sequence of individual reactions: mechanism.
- ⇒ detonation/explosion limits, flammability limits, flame speed & production of pollutants.

Collision rate  $Z_{A,BC}$ .

$$= n_A n_{BC} \sigma_{A,BC} \left( \frac{8k_B T}{\pi \mu_{A,BC}} \right)^{1/2}$$

$k_B$ : Boltzmann const. =  $1.38054 \times 10^{-23}$  J/K.

$\sigma_{A,BC}$ : collision cross-section =  $\pi (d_A + d_{BC})^2 / 4$  for hard sphere

$\mu_{A,BC}$ : reduced mass =  $\frac{m_A m_{BC}}{m_A + m_{BC}}$

$n_A, n_{BC}$ : number density of A and BC.

ex)  $Z_{N_2, N_2}$  @ 5800 K, 1 bar assuming a hard-sphere collision diameter for  $N_2 = 3.7 \text{ \AA}$ ,  $m_{N_2} = 4.65 \times 10^{-26}$  kg.

$$Z_{N_2, N_2} = \frac{n_{N_2}^2}{2} d_{N_2, N_2}^2 \sqrt{\frac{8\pi k_B T}{m_{N_2, N_2}}}$$

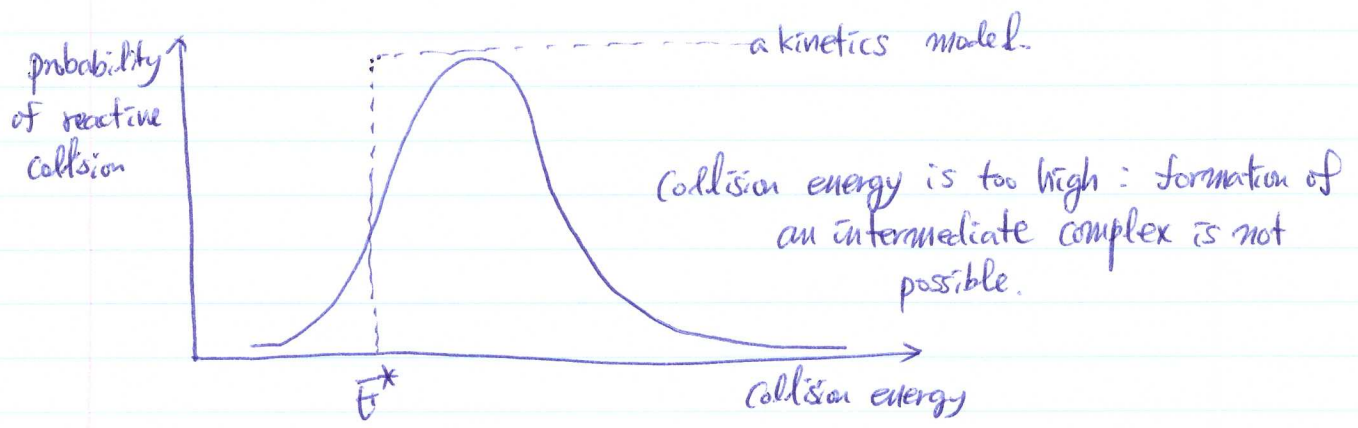
↓  
to avoid double counting

$$Z_{N_2, N_2} = 1.0 \times 10^{33} \text{ m}^{-3} \text{ s}^{-1} \propto \sqrt{T}$$

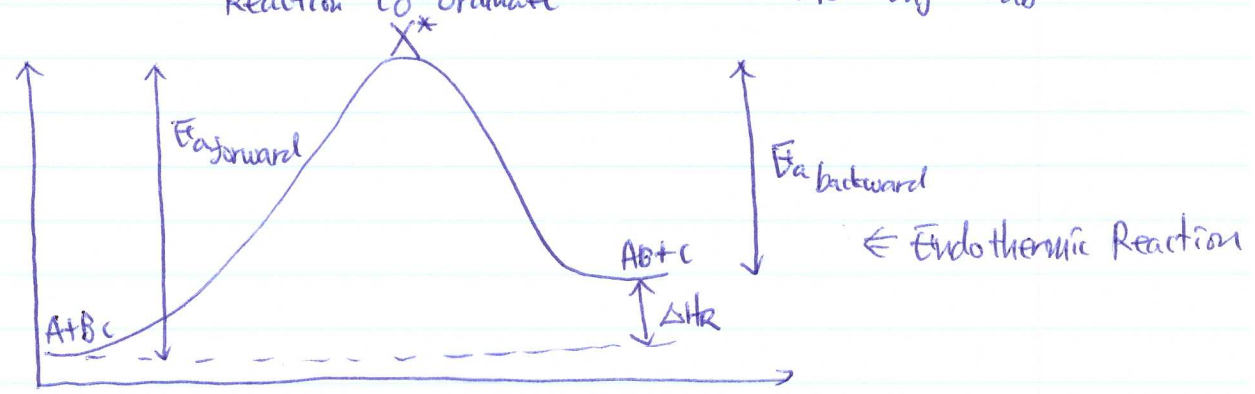
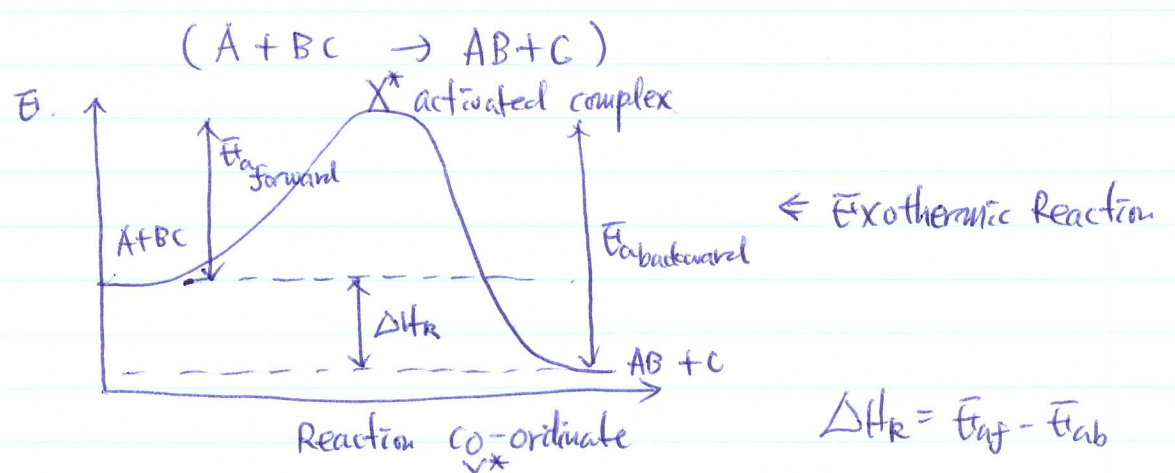
- non-reactive collisions: no chemical bonds are broken or made
- reactive collisions: one or more chemical bonds are broken or made

⇒ upper limit of reactive collisions =  $Z_{A,B}$

⊙ a certain amount of energy (kinetic + internal) is required to break a bond.



\* Energy barrier to chemical reaction



→ Among all collisions, only those which form the activated complex,  $X^*$  can result in a chemical transformation, but not all activated complexes form products.

◦ Boltzmann distribution

⇒ the fraction of collisions with an energy greater than  $E_a$  is proportional to  $\exp(-\frac{E_a}{RT})$

∴ Reaction rate  $\propto Z_{A,BC} \cdot \exp(-E_a/\hat{R}T)$

⇒ Reaction rate =  $k(T) [A][BC]$   
from Boltzmann &  $Z_{A,BC}$   $\uparrow$  from  $Z_{A,BC}$   
a temperature dependent factor  $\uparrow$  moles per volume

$[A] = n_A / N_A$   
Avogadro's # =  $6.02214 \times 10^{23}$  /mole

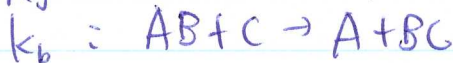
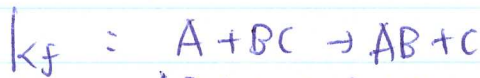
$k(T) \propto T^{1/2} \exp(-\frac{E_a}{RT})$

Arrhenius form.

Van't Hoff eqn.

$\frac{d \ln K_c}{dT} = \frac{\Delta H_R}{\hat{R}T^2}$

$K_c = k_f / k_b$ ,  $\Delta H_R = E_{af} - E_{ab}$ .



∴  $\frac{d(\ln k_f - \ln k_b)}{dT} = \frac{(E_{af} - E_{ab})}{\hat{R}T^2}$

⇒  $\frac{d \ln k_f}{dT} = \frac{E_{af}}{\hat{R}T^2}$  &  $\frac{d \ln k_b}{dT} = \frac{E_{ab}}{\hat{R}T^2}$

$k(T) = P \left( \frac{\delta k_B T}{\pi \mu_{A,BC}} \right)^{1/2} \sigma_{A,BC} \exp(-\frac{E_a}{\hat{R}T})$

$P$  an empirical steric factor, independent of T.

$$p: 10^{-5} \sim 1$$

A is a pre-exponential factor, independent of T.

$$k(T) = A T^{1/2} \exp\left(-\frac{\bar{E}_a}{RT}\right)$$

\* Definition of Reaction Rate ( $\widehat{RR}_i'''$ ,  $\widehat{RR}''$ )



$$dN_i = (\nu_i' - \nu_i) d\xi \quad \text{extent of reaction}$$

↓  
change in # of moles of species i ( $A_i$ )

$\frac{dN_i}{dt}$ : rate of change of the moles of  $A_i$

⇒ reaction rates customarily are expressed in terms of the molar concentrations of the participating species,  $[A_i]$

$$\widehat{RR}_i''' \equiv \frac{1}{V} \frac{dN_i}{dt}$$

$$[A_i] = \frac{N_i}{V} \quad \text{volume.} \quad \frac{d[A_i]}{dt} = \frac{1}{V} \left( \frac{dN_i}{dt} \right) - \frac{N_i}{V^2} \left( \frac{dV}{dt} \right)$$

$= \widehat{RR}_i''' \quad \quad \quad = 0 \text{ when Constant } V.$

change of concentration due to system volume change.

∴ in constant volume

$$\frac{d[A_i]}{dt} = \widehat{RR}_i''' = \frac{1}{V} (\nu_i' - \nu_i) \frac{d\xi}{dt}$$

$$\widehat{RR}''' \equiv \frac{d\xi}{dt} \cdot \frac{1}{V} \quad \therefore \widehat{RR}''' = \frac{\widehat{RR}_i'''}{(\nu_i' - \nu_i)}$$

\* law of mass action

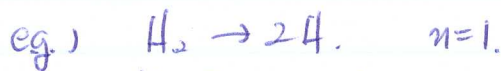
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⇒ the reaction rate of an elementary reaction is proportional to the product of the concentrations of the reactants, each raised to a power equal to its stoichiometric coefficient.

$$\widehat{RR}_i^{\text{net}} = (\nu_i' - \nu_i) k(T) \prod_{i=1}^N [A_i]^{\nu_i}$$

↑  
nominally independent of concentration

$$\text{order of reaction, } n \equiv \sum_{i=1}^N \nu_i$$



◦ Elementary reaction: a chemical reaction in which one or more of the chemical species react directly to form products in a single reaction step and with a single transition state.

→ unimolecular elementary rxn.



$$\frac{d[\text{A}]}{dt} = \ominus k[\text{A}]$$

$(0 - 1) = \nu_i' - \nu_i$

Reverse rxn must be as plausible as the forward one

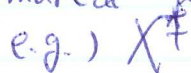
→ bimolecular elementary rxn.



$$\frac{d[\text{A}]}{dt} = \frac{d[\text{B}]}{dt} = -k[\text{A}][\text{B}]$$

◦ Transition state

The state corresponding to the highest energy along a reaction coordinate.  
Often marked with double dagger ‡



- Global reactions represent only the stoichiometric relations among major species, usually include the fuel, oxidizer and the most stable combustion products.
  - No realistic pathway is implied.
  - fractional stoichiometric coefficients, only molecular species (no radicals or atoms)
  - Unrealistic number of reactants
  - Implausible reverse reaction. e.g.) products → reactants
  - The law of mass action is not applicable to global reactions
  - Global exns are defined as the sum of the exponents assigned from experimental data.

