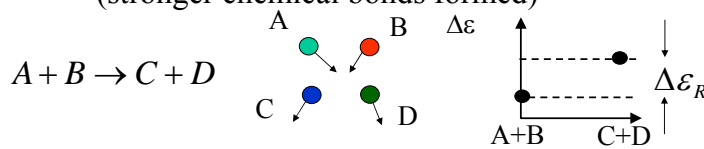


## Inelastic Collisions

- Chemical reactions involve collisions with change in kinetic (thermal) energy
  - *endothermic*: KE  $\rightarrow$  chemical energy (breaking strong chemical bonds)
  - *exothermic*: chemical energy  $\rightarrow$  (in part) to KE (stronger chemical bonds formed)



- How to adjust bimolecular collision rate model
 
$$z_{AB} = \frac{n_A n_B}{\delta_{AB}} \int_0^{\infty} \left( \frac{m_{AB}^*}{2\pi kT} \right)^{3/2} e^{-\frac{m_{AB}^* g^2}{2kT}} \sigma_{AB}^T(g) 4\pi g^3 dg$$

Inelastic Collisions and Chemical Kinetics-1

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## Conservation Laws

- Review conservation laws in CM coordinates
- Momentum conservation
  - inelastic collision does not change momentum requirements
  - CM speed still conserved ( $w_i = w_i'$ )
- Energy conservation
  - must include internal energy change

$$\frac{1}{2}(m_A + m_B)w^2 + \frac{1}{2}m_{AB}^*g^2 = \frac{1}{2}(m_A + m_B)w'^2 + \frac{1}{2}m_{AB}^*g'^2 + \Delta\epsilon_R$$

$$\frac{1}{2}m_{AB}^*g^2 = \frac{1}{2}m_{AB}^*g'^2 + \Delta\epsilon_R$$

Inelastic Collisions and Chemical Kinetics-2

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## Energy Barrier

- Limit on relative speed after collision

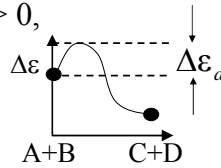
$$- g_i' \geq 0$$

$$\Rightarrow \frac{1}{2} m_{AB}^* g^2 \geq \Delta \epsilon_R$$

- Energy barrier (**activation energy**)

- limits on which collisions have sufficient relative kinetic energy to cause reaction to occur

- while only endothermic reactions  $\Delta \epsilon_R > 0$ , more complex analysis shows even exothermic reactions have energy barrier,  $\Delta \epsilon_a$



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## Bimolecular Collision Rate - Energy

- Rewrite  $z_{AB}$  in terms of relative translational kinetic energy is  $\epsilon_{rt}$

$$\begin{aligned} z_{AB} &= \frac{n_A n_B}{\delta} \int_0^{\infty} \left( \frac{m_{AB}^*}{2\pi kT} \right)^{3/2} e^{-\frac{m_{AB}^* g^2}{2kT}} \sigma_{AB}^T 4\pi g^3 dg & \epsilon_{rt} &= \frac{1}{2} m_{AB}^* g^2 \\ &= \frac{n_A n_B}{\delta} \left( \frac{1}{\pi kT} \right) \left( \frac{m_{AB}^*}{2\pi kT} \right)^{1/2} \int_0^{\infty} e^{-\frac{\epsilon_{rt}}{kT}} \sigma_{AB}^T 4\pi \epsilon_{rt} \frac{d\epsilon_{rt}}{m_{AB}^*} & d\epsilon_{rt} &= m_{AB}^* g dg \\ &= \frac{n_A n_B}{\delta} \left( \frac{8kT}{\pi m_{AB}^*} \right)^{1/2} \left( \frac{1}{kT} \right)^2 \int_0^{\infty} e^{-\frac{\epsilon_{rt}}{kT}} \sigma_{AB}^T(\epsilon_{rt}) \epsilon_{rt} d\epsilon_{rt} \\ z_{AB} &= \frac{n_A n_B}{\delta} \bar{g} \left( \frac{1}{kT} \right)^2 \int_0^{\infty} e^{-\frac{\epsilon_{rt}}{kT}} \sigma_{AB}^T(\epsilon_{rt}) \epsilon_{rt} d\epsilon_{rt} \end{aligned}$$

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## Inelastic Collision Rate

- Now consider collision process that results in specific inelastic change, e.g., chemical reaction (drop *rt* subscripts)

$$z_{AB}^{process} = \frac{n_A n_B}{\delta} \bar{g} \left( \frac{1}{kT} \right)^2 \int_0^{\infty} e^{-\frac{\varepsilon}{kT}} \sigma_{AB}^{process}(\varepsilon) \varepsilon d\varepsilon$$

$$\sigma_{AB}^{process}(\varepsilon) = \begin{cases} 0 & \varepsilon \leq \varepsilon_a \\ \sigma_{in}(\varepsilon) & \varepsilon > \varepsilon_a \end{cases}$$

$$z_{AB}^{process} = \frac{n_A n_B}{\delta} \bar{g} \frac{1}{(kT)^2} \int_{\varepsilon_a}^{\infty} e^{-\frac{\varepsilon}{kT}} \sigma_{in}(\varepsilon) \varepsilon d\varepsilon$$

## Inelastic Bimolecular Rate - Example

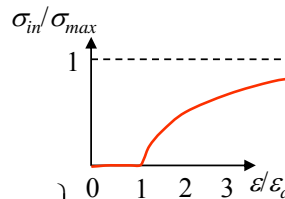
- Assume  $\sigma_{in}(\varepsilon) = \sigma_{max} \left( 1 - \frac{\varepsilon_a}{\varepsilon} \right)$

$$z_{AB}^{process} = \frac{n_A n_B \bar{g}}{\delta (kT)^2} \int_{\varepsilon_a}^{\infty} e^{-\frac{\varepsilon}{kT}} \sigma_{max} \left( 1 - \frac{\varepsilon_a}{\varepsilon} \right) \varepsilon d\varepsilon$$

$$= \frac{n_A n_B \bar{g} \sigma_{max}}{\delta (kT)^2} \left\{ \int_{\varepsilon_a}^{\infty} e^{-\frac{\varepsilon}{kT}} \varepsilon d\varepsilon - \int_{\varepsilon_a}^{\infty} e^{-\frac{\varepsilon}{kT}} \varepsilon_a d\varepsilon \right\}$$

$$z_{AB}^{process} = \frac{n_A n_B}{\delta} \bar{g} \sigma_{max} e^{-\frac{\varepsilon_a}{kT}}$$

*fraction of high energy collision  
∝ exp(-ε<sub>a</sub>/kT)*



$$-kT \varepsilon e^{-\frac{\varepsilon}{kT}} \Big|_{\varepsilon_a}^{\infty} = kT \varepsilon_a e^{-\frac{\varepsilon_a}{kT}}$$

$$-(kT)^2 e^{-\frac{\varepsilon}{kT}} \left( 1 + \frac{\varepsilon}{kT} \right) \Big|_{\varepsilon_a}^{\infty} = (kT)^2 e^{-\frac{\varepsilon_a}{kT}} \left( 1 + \frac{\varepsilon_a}{kT} \right)$$

## Chemical Kinetics

- Reaction  $A + B \xrightarrow{k_f} C + D$
- **Reaction rate constant,  $k_f$**   $\frac{dn_C}{dt} \equiv k_f n_A n_B$
- Compare to example inelastic bimolec. collision rate  

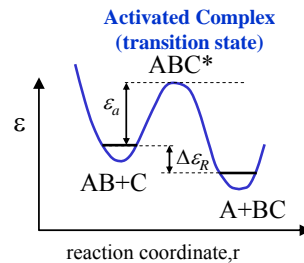
$$z_{AB}^{process} = n_A n_B \bar{g} \sigma_{max} e^{-\epsilon_a/kT}$$

$$\Rightarrow k_f = \sigma_{max} \bar{g} e^{-\frac{\epsilon_a}{kT}} \quad \text{Collision model for reaction rate constant}$$
- Examine temperature dependence **More general T dependence**  

$$\bar{g} \propto \sqrt{T} \quad \boxed{k_f = AT^{1/2} e^{-\epsilon_a/kT}} \quad \text{Arrhenius Rate} \quad k_f(T) = AT^n e^{-\epsilon_a/kT}$$

## Collision Complex Model

- Why is there activation energy in most reactions (including exothermic reactions)
- **Activated Collision Complex**
  - based on assumption that for the reaction (inelastic energy transfer) to take place, molecules temporarily form unstable collision complex
- activation energy required to form complex

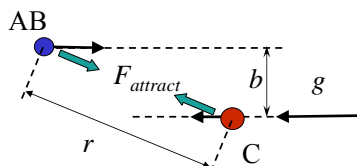


## Impact Parameter Interpretation

- To form collision complex, molecules must be able to get “close” enough to exchange nuclei (i.e., react)
  - complex must exist for some time for molecular rearrangement to occur – molecules must “orbit”
  - attractive forces will keep complex together

neutral species

$$V_{attr}(r) = \sum \frac{a}{r^\alpha}$$



- if attractive forces larger than “centrifugal barrier” (will momentum cause molec. to pass by)

$$V_{cb}(r) \equiv \frac{L^2}{2m^* r^2} = \frac{(m^* g b)^2}{2m^* r^2} = \frac{m^* g^2 b^2}{2r^2} = \frac{\epsilon_{tr} b^2}{r^2}$$

## Activate Complex Reaction Rate

- So collision only occurs if

$$V_{attr}(r) \geq V_{cb}(r, b, \epsilon_{tr}) \propto \epsilon_{tr} b^2$$

- or given some  $\epsilon_{tr}$ , formation of activated complex requires

$$b \leq b_o$$

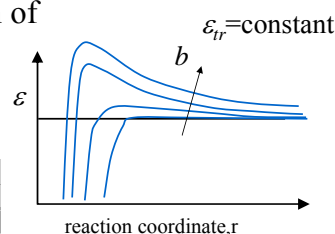
- Example – Lennard-Jones potential

$$V(r) = 4\beta \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]$$

solve for  $V_{attr} = V_{cb}$

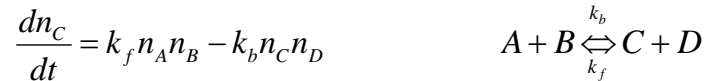
dipole-induced dipole

$$b_o = \frac{3^{1/2}}{2^{1/3}} \left( \frac{\sigma}{\epsilon_{tr}} \right)^{1/6} \Rightarrow k(T) = \bar{g} \frac{1}{(kT)^2} \int_{\epsilon_a}^{\infty} e^{-\epsilon/kT} \pi b_o^2(\epsilon) \epsilon d\epsilon$$



## Forward and Backward Reaction Rates

- How will concentrations change in time?
- Consider forward and backward reactions



- At equilibrium  $\frac{dn_C}{dt} = 0 \Rightarrow k_f n_A^* n_B^* = k_b n_C^* n_D^* \leftarrow \text{equil.}$

**Law of Mass Action (again!)**

$$K_c(T) \equiv \frac{k_f(T)}{k_b(T)} = \frac{n_C^* n_D^*}{n_A^* n_B^*}$$

## Equilibrium Constant

- Examine equilibrium constant based on simple collision rate model

$$\frac{k_f}{k_b} \sim \frac{\sigma_f(T) \bar{g} e^{-\varepsilon_{af}/kT}}{\sigma_b(T) \bar{g} e^{-\varepsilon_{ab}/kT}} \quad A + B \xrightleftharpoons[k_f]{k_b} C + D$$

$$\sim \frac{\sigma_f(T)}{\sigma_b(T)} e^{-(\varepsilon_{af} - \varepsilon_{ab})/kT}$$

$$K_c = \frac{\sigma_f(T)}{\sigma_b(T)} e^{-\Delta\varepsilon_r/kT}$$

*Q ratio in Stat. Mech.*

