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Inelastic Collisions

- So far we have examined elastic collisions
  - defined as no (net) change in total translational kinetic energy of colliders
    - so $g' = g$
  - usually this means no (net) change in internal energies of colliders
- **Inelastic collisions** involve changes in internal energies of collider(s)
  - can be rotational, vibrational, electronic and/or chemical (internuclear bond) energies
- **Any *net* change in internal energy must be balanced by change in translational kinetic energy**
  - note: it is possible to have exchange between internal energies of colliders *without* change in translational energy
    - but not typically an important process

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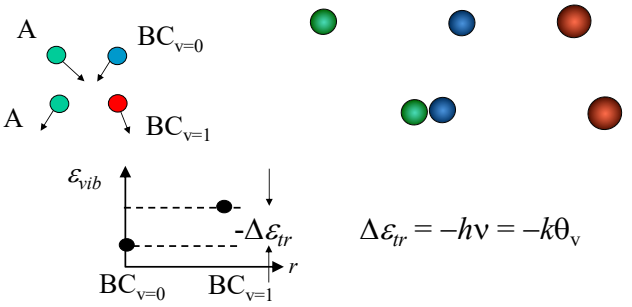
Inelastic Coll.: Vibrational Excitation

- Let's look at one example: a collision that increases the vibrational energy of one of the colliders
  - without changing any other internal energy mode

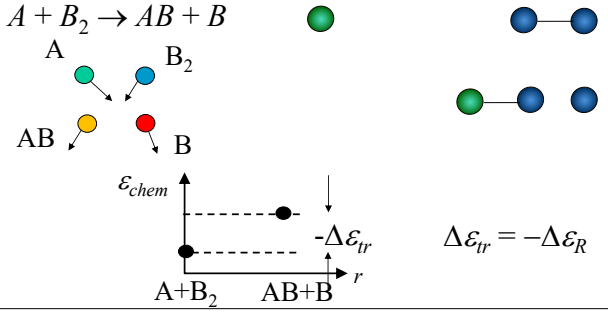
$$A + BC(\text{v=0}) \rightarrow A + BC(\text{v=1})$$



$$\Delta\varepsilon_{tr} = -h\nu = -k\theta_v$$

Inelastic Coll.: Chemical Reaction

- Another example: endothermic chemical reaction
  - that does not change other internal energy modes
- Recall *endothermic*: increases chemical energy
  - *exothermic*: decreases chemical energy



Inelastic Collisions: Rate Expression

- We already have a rate expression for bimolecular elastic collisions

$$z_{AB} = \frac{n_A n_B}{\delta_{AB}} \int_0^\infty \left(\frac{m^*_{AB}}{2\pi kT} \right)^{3/2} e^{-\frac{m^*_{AB}}{2kT} g^2} \sigma^T_{AB}(g) 4\pi g^3 dg$$

- How can we adjust this to account for inelastic collisions?
- What are the differences between elastic and inelastic collisions?

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Conservation Laws

- Begin by reviewing conservation laws in CM coordinates
- **Momentum conservation**
  - momentum equation does not change for inelastic collisions
  - center-of-mass speed still conserved (w_i=w_i') (before, after)
- **Energy conservation**
  - must include internal energy change, $\Delta\varepsilon_{int}$

$$\frac{1}{2}\cancel{(m_A+m_B)w^2}+\frac{1}{2}m^*_{AB}g^2=\frac{1}{2}\cancel{(m_A+m_B)w'^2}+\frac{1}{2}m^*_{AB}g'^2+\Delta\varepsilon_{int}$$

$$\frac{1}{2}m^*_{AB}g^2=\frac{1}{2}m^*_{AB}g'^2+\Delta\varepsilon_{int}$$

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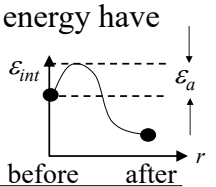
Activation Energy

- However, there is a limit on the relative speed after a collision

$$\frac{1}{2}m^*_{AB}g^2=\frac{1}{2}m^*_{AB}g'^2+\Delta\varepsilon_{int}$$

  - $g_i' \geq 0 \quad \Rightarrow \tfrac{1}{2}\, m^*_{AB}\, g^2 \geq \Delta\varepsilon_{int}$
- So inelastic collisions can have a translational "energy barrier", often denoted as the **activation energy, ε_a**
  - limits which collisions have enough relative translational kinetic energy to cause the inelastic process to occur
  - while only collisions that raise internal energy have $\Delta\varepsilon_{int} > 0$, more complex analysis shows that even $\Delta\varepsilon_{int} < 0$ collisions can have an activation energy, i.e., $\varepsilon_a > \Delta\varepsilon_{int}$



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Bimolecular Collision Rate - Energy

- First let's rewrite the (elastic) z_{AB} in terms of relative translational kinetic energy, ε_{rt}

$$z_{AB} = \frac{n_A n_B}{\delta}\int_0^\infty \left(\frac{m_{AB}^*}{2\pi kT}\right)^{3/2} e^{\frac{-m_{AB}^* g^2}{2kT}} \sigma_{AB}^T 4\pi g^3 dg$$

$$\varepsilon_{rt} = \frac{1}{2} m_{AB}^* g^2$$

$$d\varepsilon_{rt} = m_{AB}^* g\, dg$$

$$\varepsilon_{rt} d\varepsilon_{rt} = \frac{1}{2}\left(m_{AB}^*\right)^2 g^3 dg$$

$$= \frac{n_A n_B}{\delta}\left(\frac{m_{AB}^*}{2\pi kT}\right)^{3/2}\int_0^\infty e^{\frac{-\varepsilon_{rt}}{kT}} \sigma_{AB}^T 8\pi \frac{\varepsilon_{rt} d\varepsilon_{rt}}{\left(m_{AB}^*\right)^2}$$

$$= \frac{n_A n_B}{\delta}\left(\frac{8kT}{\pi m_{AB}^*}\right)^{1/2}\left(\frac{1}{kT}\right)^2\int_0^\infty e^{\frac{-\varepsilon_{rt}}{kT}} \sigma_{AB}^T(\varepsilon_{rt})\varepsilon_{rt} d\varepsilon_{rt}$$

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

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Inelastic Collision Rate

- We can write the bimolecular collision rate for a process that results in a specific *inelastic* energy change (and dropping the *rt* subscripts)

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

  - where we have defined a cross-section for the process that has the following behavior

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

the inelastic collision process does not occur for relative translational energies below the activation energy

- Can then rewrite the integral limits since integrand is zero for $\varepsilon < \varepsilon_a$

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

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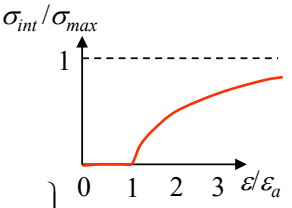
Inelastic Collision Rate: Example

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

illustrative example, leads to simple result



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

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

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

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

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

fraction of high energy collisions ∝ exp(-ε_a/kT)

$$\boxed{z_{AB}^{process} = \frac{n_A n_B}{\delta} \bar{g} \sigma_{avg}(T) e^{-\varepsilon_a/kT}}$$

more general expression

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Chemical Reaction Rates: Comparison

- For a chemical reaction, it is common to define a (forward) **reaction rate constant, k_f** such that

$$A + B \rightarrow C + D$$

molar volumetric production rate of species C

$$\frac{dn_C}{dt} \equiv k_f n_A n_B$$

molar concentrations of reactants

- Compare this to our simple inelastic bimolecular collision rate
  - and using $\bar{g} \propto \sqrt{T}$

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

simple collision model for reaction rate constant

$$\Rightarrow k_f = \sigma_{\max} \bar{g} e^{-\varepsilon_a/kT}$$

$$\boxed{k_f = AT^{1/2} e^{-\varepsilon_a/kT}}$$

- Compare this to a standard empirical model for k, (modified) **Arrhenius Rate**

$$k_f(T) = AT^n e^{-\varepsilon_a/kT}$$

collision (kinetic) theory properly captures the underlying physics of reactions

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Forward, Backward Chem. Reaction Rates

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

$$\frac{dn_C}{dt} = k_f n_A n_B - k_b n_C n_D \qquad A + B \underset{k_f}{\overset{k_b}{\Leftrightarrow}} C + D$$

- At equilibrium $\frac{dn_C}{dt} = 0$

$$\Rightarrow k_f n_A^* n_B^* = k_b n_C^* n_D^* \quad \leftarrow \text{equil.}$$

Law of Mass Action *(again!)*

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

Note: even if not in chemical equilibrium, $k_f/k_b = K_c$!

- collision properties (σ, $\bar{g}$) for given collision don't depend on chemical composition

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Equilibrium Constant

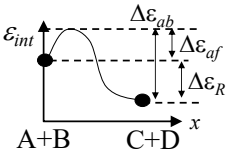
- Examine equilibrium constant based on the more general collision rate model with $\sigma_{avg} = \sigma(T)$

$$\frac{k_f}{k_b} = \frac{\sigma_f(T)\bar{g}_{AB} e^{-\varepsilon_{af}/kT}}{\sigma_b(T)\bar{g}_{CD} e^{-\varepsilon_{ab}/kT}} \qquad A + B \underset{k_f}{\overset{k_b}{\Leftrightarrow}} C + D$$

from reduced mass terms with $m_A+m_B=m_C+m_D$

$$= \sqrt{\frac{m_C m_D}{m_A m_B}} \frac{\sigma_f(T)}{\sigma_b(T)} e^{-(\varepsilon_{af} - \varepsilon_{ab})/kT}$$

$$K_c = \underbrace{C \frac{\sigma_f(T)}{\sigma_b(T)}}_{\text{related to Q ratio from Statistical Mechanics}} e^{-\Delta\varepsilon_R/kT}$$



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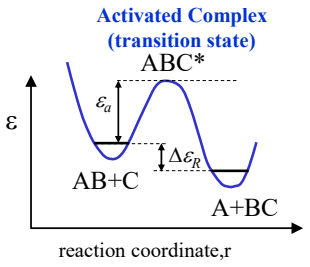
Collision Complex Model

- Why is there an activation energy in many inelastic collisions?
- **Activated Collision Complex**
  - based on assumption that for the inelastic energy transfer process to take place, molecules temporarily form unstable collision complex that has high energy
  - so activation energy required to form the complex
  - example: chemical reaction



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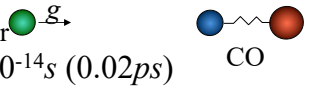
Interaction Time Constraints

- Another energy barrier source occurs in vibrational and translational energy exchanges (collisions)
  - even when the vibrational energy is decreasing
- Consider vibrationally excited CO colliding with Ar
  - to remove a quanta of vibr. energy, Ar must "hit" C or O nucleus when it is moving quickly



- $\nu_{vib,CO} \sim 6\times10^{13}\ Hz$, so period $\tau_{vib} \sim 2\times10^{-14} s$ $(0.02 ps)$
- Ar is in vicinity of CO for time $\tau_{coll} \sim d_{CO}/g \sim 0.4 nm/g$
  - for g=400 m/s, $\tau_{coll} \sim 10^{-11} s$ $(10 ps)$, so $\tau_{vib}/\tau_{coll} \sim 0.002$
    - Ar will most likely impact when CO is at maximum extension (when KE is small)

$\Rightarrow$ highly unlikely it can de-excite CO vibration

- Requiring $\tau_{vib}/\tau_{coll} \geq 0.01$ (for example) $\Rightarrow g_{min} = 2\ km/s \Rightarrow \varepsilon_a$

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Inelastic Collisions w/o Energy Barrier

- A number of important inelastic collisions do not require an activation energy, for example
  - radical-radical exchange
    e.g., $OH+HO_2 \rightarrow O_2+H_2O$
  - 3-body association reactions
    e.g., $O+O+Ar \rightarrow O_2+Ar$
  - de-excitation (quenching) of electronically excited states
    e.g., $NO(A)+N_2 \rightarrow NO(X)+N_2$
- These collisions depend on long-range attractive potentials to form the collision complex that allows the inelastic process to occur
  - is their cross-section energy dependent?

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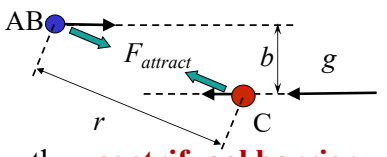
Centrifugal Barrier Model

- Simple model for complex formation w/o activation energy, assumes
  - molecules must be able to get "close" enough to change internal energy; complex must exist for some minimal time for process to occur – molecules must "orbit"
  - then process will happen
- Attractive forces will keep complex together



for neutral species $\alpha \geq 3$ $V_{attr}(r) = \sum \frac{a}{r^{\alpha}}$

  - **only if** attractive force larger than **centrifugal barrier** (or momentum will cause molecules to just "pass by")

angular momentum, moment of inertia

$$E_{angular} = \frac{1}{2}\frac{L^2}{I} \Rightarrow V_{cb}(r) \equiv \frac{L^2}{2m^* r^2} = \frac{(m^* g b)^2}{2m^* r^2} = \frac{m^* g^2 b^2}{2r^2} = \frac{\varepsilon b^2}{r^2} \qquad \varepsilon = \tfrac{1}{2} m^* g^2$$

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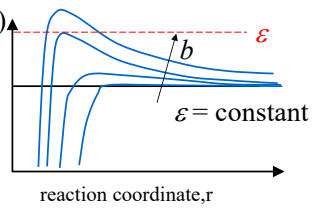
Centrifugal Barrier: Cross-Section

- So can write long-range potential including effective repulsive centrifugal barrier
  $$V(r) = \varepsilon b^2 / r^2 - \Sigma a/r^{\alpha}$$
- For fixed ε, looks like →
  - for each b, there is maximum in $V(r)$
  - if $\varepsilon \geq V_{max}(b,\varepsilon)$, the collision complex can form



- So for a given relative KE, formation of the complex requires a limit on the impact parameter
  $b \leq b_o$ (the impact parameter for $V_{max} = \varepsilon$)
- Can model cross-section as $\sigma_{cb} = \pi b_o^2(\varepsilon)$, $z_{AB}^{cb} = n_A n_B \bar{g} \frac{1}{(kT)^2} \int_0^{\infty} e^{\frac{-\varepsilon}{kT}} \pi b_o^2(\varepsilon) \varepsilon d\varepsilon = n_A n_B \bar{g} \sigma(T)$

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Centrifugal Barrier: Example

- For simple dipole-induced dipole attraction model
  $$V(r) = \varepsilon b^2 / r^2 - a/r^6$$
  - e.g., LJ-like $a/r^6 = \varepsilon_{well} (d/r)^6$
- Then get peak from $dV(r)/dr = 0$ $\quad r_o = \left(\frac{3a}{\varepsilon b^2}\right)^{1/4} \Rightarrow V(r_o) = 2\varepsilon^{3/2} \frac{b^3}{3^{3/2} a^{1/2}}$
  - and for $V(r_o) = \varepsilon$ $\quad b_o^2 = \frac{3}{2^{2/3}} \left(\frac{a}{\varepsilon}\right)^{1/3}$
- So "averaged" cross-section

$$\int_0^{\infty} e^{-\alpha x} x^{\beta} dx = \frac{\Gamma(1+\beta)}{\alpha^{1+\beta}}$$

$$\sigma_{avg}(T) = \frac{1}{(kT)^2} \int_0^{\infty} e^{\frac{-\varepsilon}{kT}} \pi \frac{3a^{1/3}}{2^{2/3}} \frac{\varepsilon}{\varepsilon^{1/3}} d\varepsilon = \frac{3\pi a^{1/3}}{2^{2/3}} \frac{1}{(kT)^2} \int_0^{\infty} e^{\frac{-\varepsilon}{kT}} \varepsilon^{2/3} d\varepsilon$$

decreases with T

$$= \frac{3\pi a^{1/3}}{2^{2/3}} \frac{1}{(kT)^2} \frac{\Gamma(5/3)}{(kT)^{-5/3}} \cong 0.903 \frac{3\pi a^{1/3}}{2^{2/3}} \frac{1}{(kT)^{1/3}}$$

Rate constant $k(T) = \sigma_{avg}(T)\, \bar{g}$; increases with $T \propto T^{1/6}$

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Inelastic Collisions: Summary

- For bimolecular collision that involves defined inelastic change, simple kinetic theory result is

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

  - neglects orientation of molecules in the collision
  - in general, inelastic process cross-section will depend on ε_{rt} and thus contribute additional T dependence to collision rate
- Activation energy ε_a = minimum relative translational kinetic energy (ε_{rt}) required for collision to succeed
  - can exist even for inelastic process that reduces internal energy of the molecules, for example due to activated complex intermediate
  - for $\varepsilon_a > 0$ $\quad z_{AB}^{inelastic} = n_A n_B F(T) e^{-\varepsilon_a / kT}$ ***dominates T dep. for $T \ll \varepsilon_a/k$***
- Rate constants or averaged cross-sections for forward and backward processes related by equilibrium considerations
  - if, for example, translational mode remains in equilibrium