Kinetics & Dynamics of Chemical Reactions

Course CH-310

Prof. Sascha Feldmann

Recap from last session

2-body classical scattering

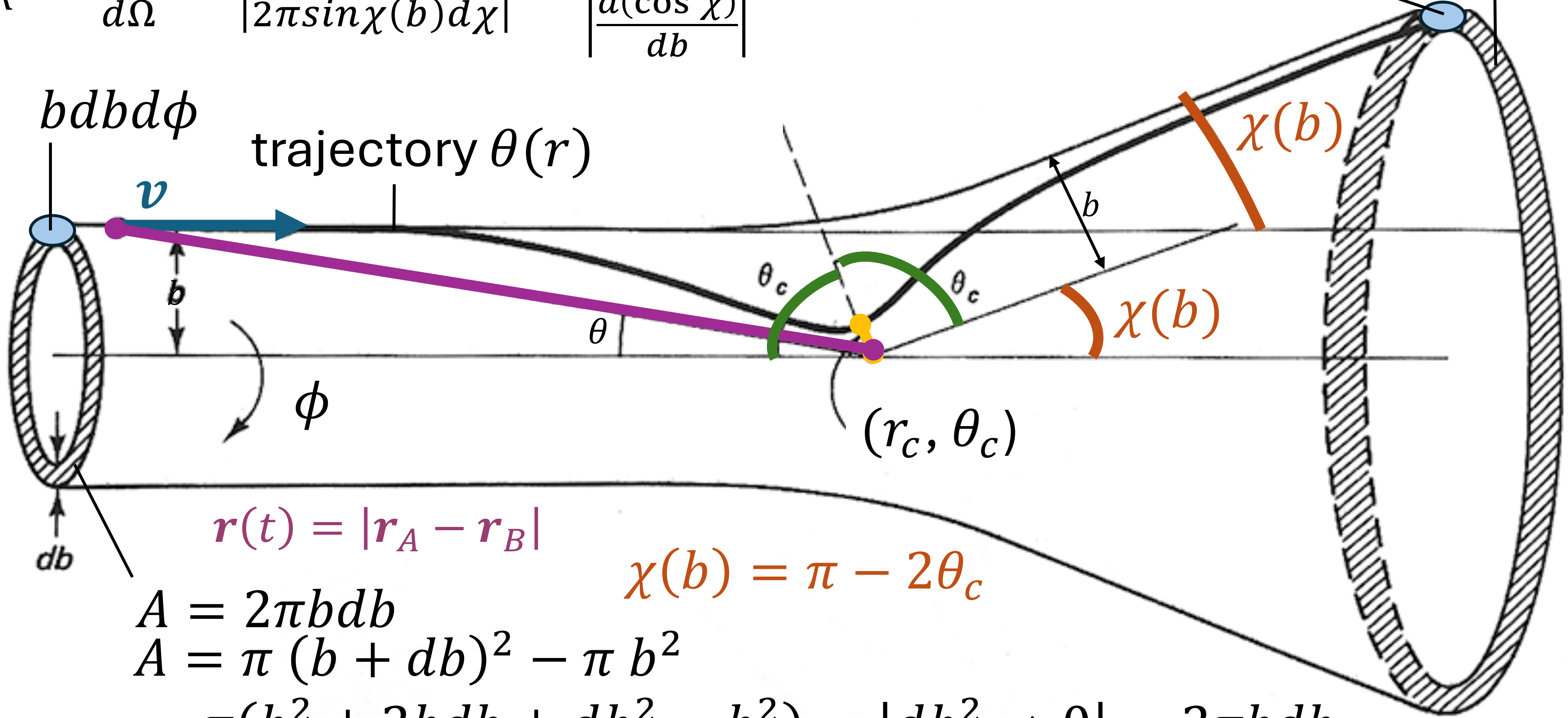
$$I_R = \frac{d\sigma_R}{d\Omega} = \frac{2\pi b db}{|2\pi sin\chi(b) d\chi|} = \frac{b}{\left|\frac{d(\cos\chi)}{db}\right|}$$

$A' = 2\pi sin\chi d\chi$

$d\Omega = sin\chi d\chi d\phi$

$bdbd\phi$

trajectory $\theta(r)$



$\boldsymbol{r}(t) = |\boldsymbol{r}_A - \boldsymbol{r}_B|$

$\chi(b) = \pi - 2\theta_c$

$A = 2\pi b db$

$A = \pi\,(b + db)^2 - \pi\, b^2$

$= \pi(b^2 + 2bdb + db^2 - b^2) = |db^2 \to 0| = 2\pi b db$

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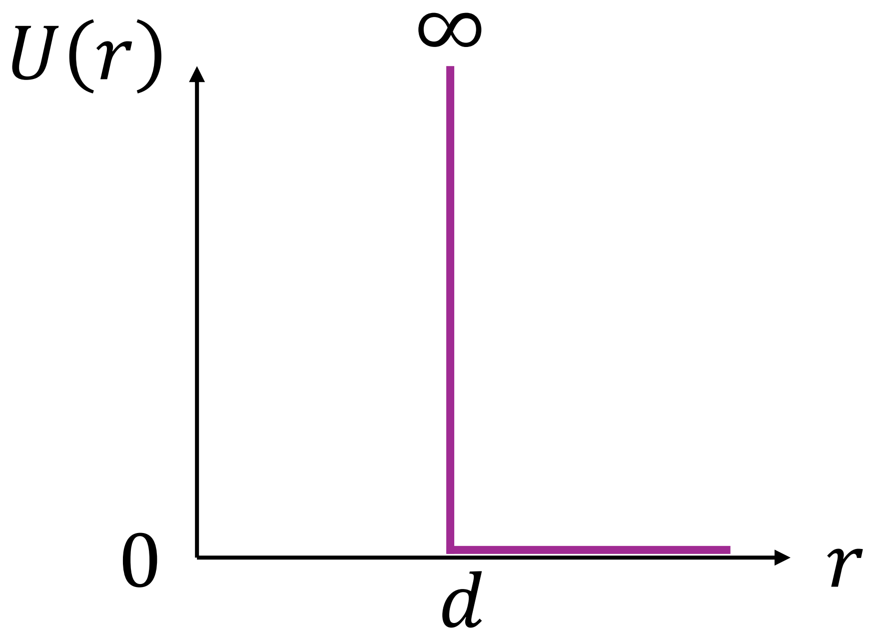
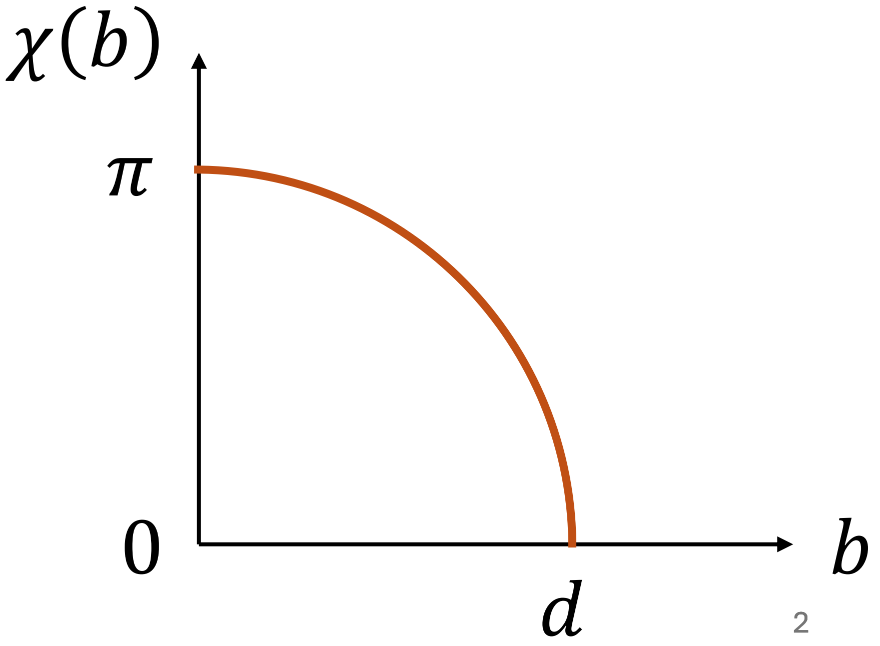


- for hard spheres: $U(r) = \begin{cases} 0 & (r > d) \\ \infty & (r \leq d) \end{cases}$
  - $\chi(E,b) = 2\arccos\frac{b}{d}$
  - $I_R(E,\chi) = \frac{d^2}{4}$



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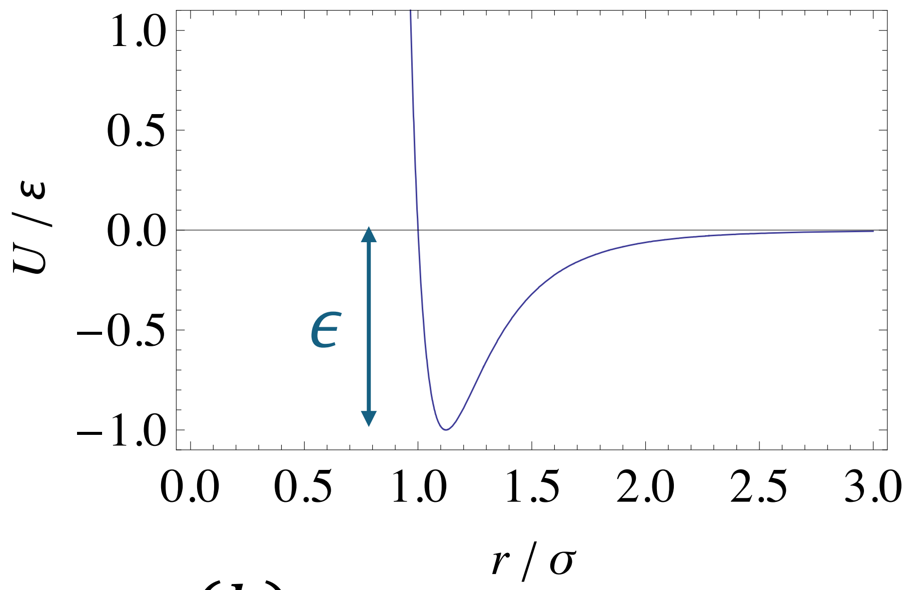
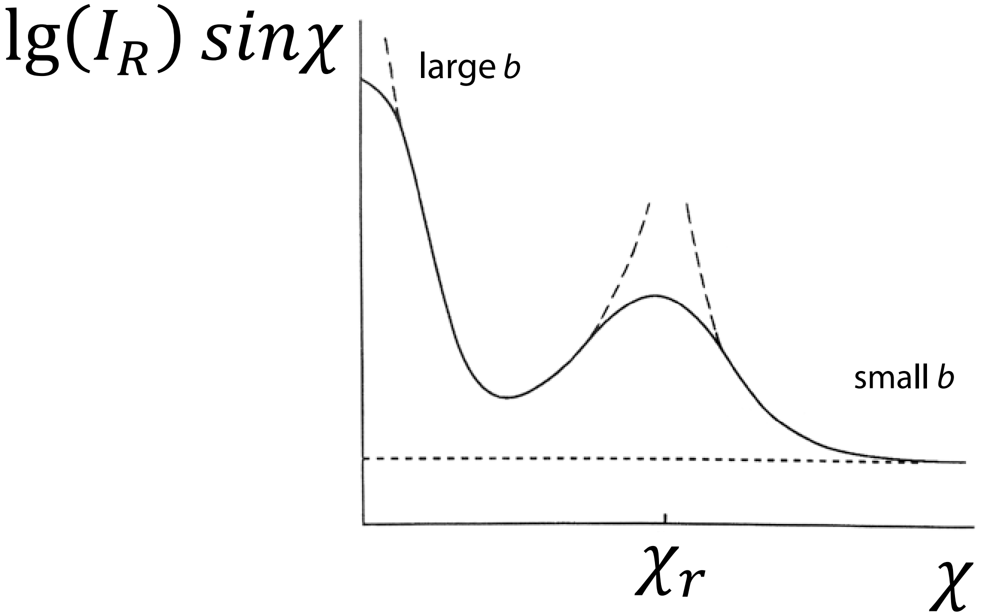
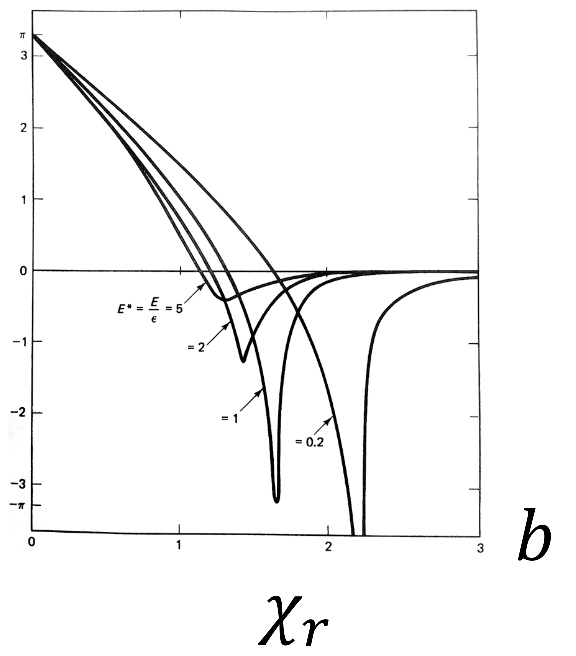


- for Lennard-Jones: $U(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]$
  - χ_r rainbow angle





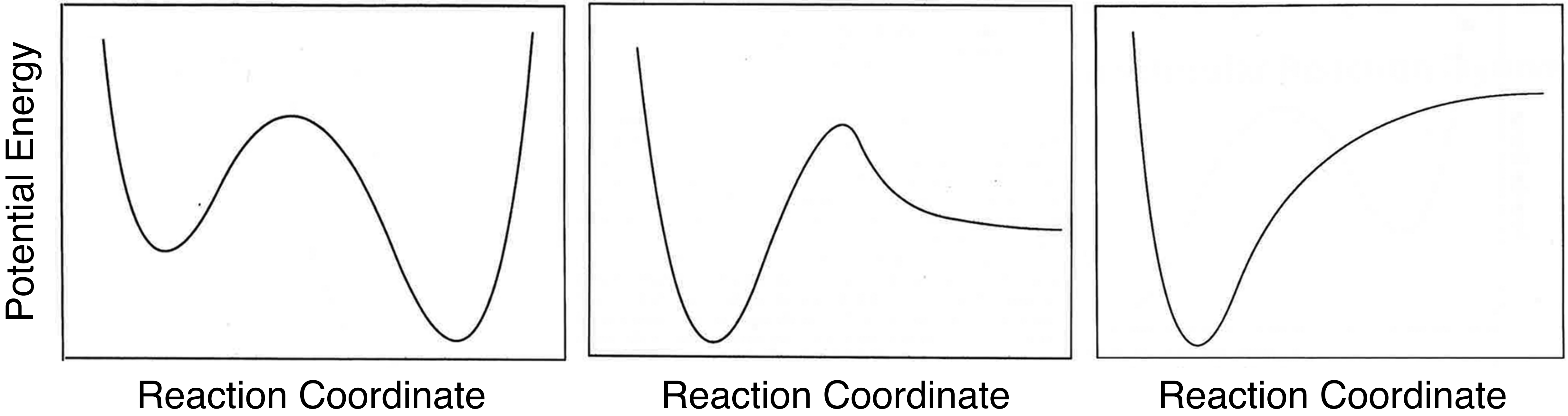
Chapter 6

Unimolecular Reaction Dynamics

- Unimolecular reaction: $\mathrm{A}^* \rightarrow \mathrm{products}$

- Why would we want to understand such a boring case?
- because it is simple enough to understand the mechanism on a deeper level!
- Asterisk $*$: particle needs to be in an excited state ($e.g.$, sufficiently high vibrational energy) to react – a reactive/activated state
- We can distinguish 3 different types of unimolecular reactions based on features of the respective potential energy surface

Unimolecular reaction: $A^* \rightarrow \text{products}$



a) Isomerization

b) Dissociation with barrier for recombination

c) Dissociation without barrier for recombination

$CH_3NC \longrightarrow CH_3CN$

$C_2H_5Cl \longrightarrow HCl + C_2H_4$

$C_2H_6 \longrightarrow 2\ CH_3$

Unimolecular reaction: $\mathrm{A}^* \rightarrow \text{products}$

- How does a molecule acquire enough energy to overcome the barrier to react?
- Absorption of radiation from walls of reaction vessel (1919, Perrin)?
- … only found to be dominant mechanism for gas molecules at very low pressures, in absence of collisions:
- Then, predominant dissociation mechanism is indeed absorption of a large number of IR photons originating from black-body radiation of walls of container
- But what about at moderate pressures?
- *Dependence* of reaction rate on pressure found (contradicts Perrin!)
- also, *no dependence* found on surface-to-volume-ration of container or presence of absorbers (contradicts Perrin!)

→ instead this suggests that molecules are activated by *collisions*

6.1 Lindemann-Hinshelwood Theory of unimolecular reactions

Lindemann proposed 1922 we need a collision partner M to activate/deactivate A :

$$\mathrm{A} + \mathrm{M} \overset{k_1}{\rightarrow} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* + \mathrm{M} \overset{k_{-1}}{\rightarrow} \mathrm{A} + \mathrm{M}$$

$$\mathrm{A}^* \overset{k_2}{\rightarrow} \text{products}$$

- What does this scheme remind you of?

$$\mathrm{A} + \mathrm{M} \overset{k_1}{\rightarrow} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* + \mathrm{M} \overset{k_{-1}}{\rightarrow} \mathrm{A} + \mathrm{M}$$

$$\mathrm{A}^* \overset{k_2}{\rightarrow} \text{products}$$

- Let's apply the steady-state approximation to A^*
- We make an additional approx. here:
  - we assume every collision of $\mathrm{A}^* + \mathrm{M}$ *fully* deactivates A^* to A
  - so called: ***strong collision assumption***
- How to calculate k_{-1} for deactivation rate?
- could use gas-kinetic collision rate z_{AM} we derived before

$$z_{\mathrm{AM}} = \sigma_{\mathrm{AM}} \langle u_{\mathrm{AM}} \rangle \rho_{\mathrm{A}} \rho_{\mathrm{M}} = k_{-1} [\mathrm{A}][\mathrm{M}]$$

- Now we just need to find also k_1 and k_2, let's do it!

$$\mathrm{A} + \mathrm{M} \xrightarrow{k_1} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M}$$

$$\mathrm{A}^* \xrightarrow{k_2} \text{products}$$

- Let’s apply the steady-state approximation to A^*
- We get for the overall rate R of the reaction:

$$R = k_{uni}[\mathrm{A}] = k_2[\mathrm{A}^*] = \frac{k_1 k_2[\mathrm{A}][\mathrm{M}]}{k_{-1}[\mathrm{M}]+k_2}$$

<u>Limiting cases:</u>

A) *Low* pressure limit:

- at low pressure: $[\mathrm{M}] \rightarrow 0$ and

$$k_{uni} = k_0 = k_1[\mathrm{M}]$$

- here, collision activation is rate-limiting step
- k_{uni} grows linearly with pressure

$$\mathrm{A} + \mathrm{M} \xrightarrow{k_1} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M}$$

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Limiting cases:

B) *High* pressure limit:

- at high pressure: $[\mathrm{M}] \rightarrow \infty$ and

$$k_{uni} = k_\infty = \frac{k_1 k_2}{k_{-1}}$$

- now k_{uni} becomes independent of pressure
- reversible first step, so here we have a pre-equilibrium $\frac{[\mathrm{A}^*]}{[\mathrm{A}]} = \frac{k_1}{k_{-1}}$

$$\mathrm{A} + \mathrm{M} \overset{k_1}{\rightarrow} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* + \mathrm{M} \overset{k_{-1}}{\rightarrow} \mathrm{A} + \mathrm{M}$$

$$\mathrm{A}^* \overset{k_2}{\rightarrow} \text{products}$$

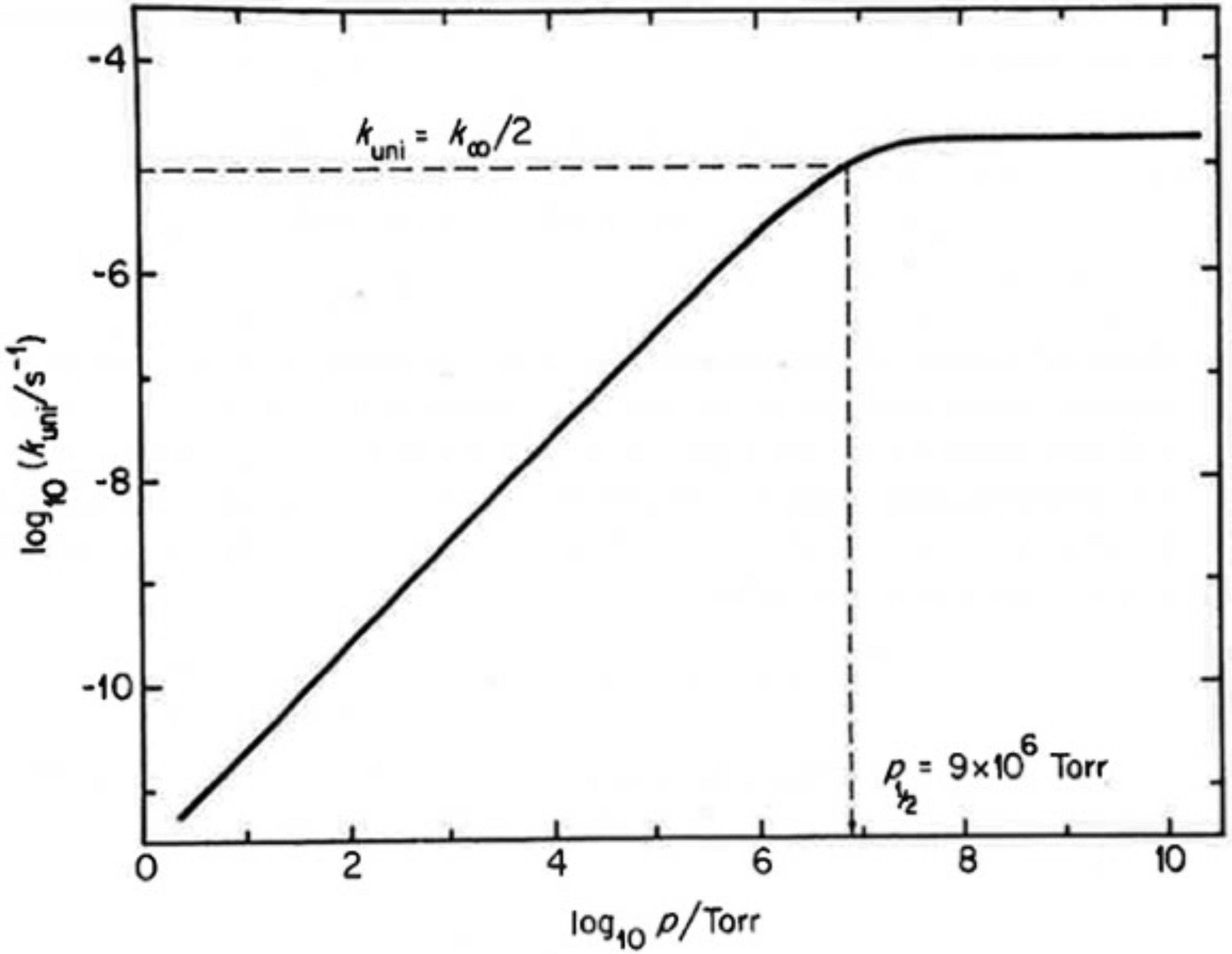
- A useful way of plotting is the log-log ***Lindemann plot***

using $k_{uni} = \dfrac{k_\infty}{1+\dfrac{k_\infty}{k_1[\mathrm{M}]}}$

- $p_{\frac{1}{2}} \propto [\mathrm{M}]_{\frac{1}{2}} = \dfrac{k_\infty}{k_1}$

  with $\dfrac{k_{uni}}{k_\infty} = \dfrac{1}{2}$

cis/*trans* isomerization of 2-butene at 496 °C



$$\mathrm{A} + \mathrm{M} \xrightarrow{k_1} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M}$$

$$\mathrm{A}^* \xrightarrow{k_2} \text{products}$$

- What's the best model we got so far to calculate rate constants like k_1 and k_2?

- Reactive-hard-spheres model:

$$k_1 = k(T) = \sigma_{\mathrm{AM}} \langle u_{\mathrm{AM}} \rangle \, p \; e^{-\frac{E^*}{k_B T}}$$

from gas-kinetic collision rate we got $\sigma_{\mathrm{AM}} \langle u_{\mathrm{AM}} \rangle = \mathrm{k}_{-1}$

so with $p = 1$ follows $k_1 = k_{-1} \, e^{-\frac{E^*}{k_B T}}$

- But experimentally we find this *underestimates* the rates measured!!! *Why*?

→molecules also have internal energy stored, *e.g.*, vibrational, that can be used to drive the reaction, not just E_{kin}

Hinshelwood Theory

- accounts for internal energy that is stored in vibrational degrees of freedom, which should lead to a higher activation rate k_1
- he derived in 1926: $k_1 = \frac{k_{-1}}{(s-1)!}\left(\frac{E_0}{k_B T}\right)^{s-1} e^{-\frac{E_0}{k_B T}}$

- s : number of vibrational degrees of freedom
- How many are there for a given molecule?
- $3N - 6$ (or $3N - 5$, if molecule linear)
- What happens if s is increased ($e.g.$, bigger molecule, rest same)?
- More energy stored, so *rate goes up*
- but only holds under assumption of $\frac{E_0}{k_B T} \gg s$ (uses an approximation)

To get an idea of the activation energy and limit for which the approximation holds:
To break C-C bond in ethane: $E_0 \approx$ *400 kJ/mol and* $k_B T$ *at r.t.* $\approx$ *2.5 kJ/mol*
→ $s \ll 160$ *here for the above Eq. to work*

Hinshelwood Theory

- Ratio $\frac{k_1}{k_{-1}} = \frac{[\mathrm{A}^*]}{[\mathrm{A}]}$ is fraction of molecules exceeding activation energy E_0 in thermal equilibrium
- Good approximation at *high* pressure $[\mathrm{M}] \to \infty$ where energized molecules in pre-equilibrium with ground-state ones
- We also assume it holds at *low* pressures for now, by making again a *strong collision assumption* (this time for energizing collisions)
- assumes no step-wise activation, but that one collision instantly excites/de-excited fully (drastic assumption at low pressure)

- Then we can say: $\frac{k_1}{k_{-1}} = \frac{[\mathrm{A}^*]}{[\mathrm{A}]} \approx \frac{[\mathrm{A}(E>E_0)]}{[\mathrm{A}_{total}]}$

How to calculate this fraction?

- We assume everything is in equilibrium and therefore can use statistical thermodynamics (quasi-equilibrium, but close enough, at least for high pressures)
- Remember: we are right now historically *before* quantum-mechanics, so continuous rather than discrete energy levels (and not the QM partition function, but classical oscillator one needed)
- So now we look at classical analogues for what you learned before in QM for discrete energy states

- Sum of states $G(E)$: # of levels with energies smaller than or equal to E

- How did this look for the quantum-mechanical oscillator?

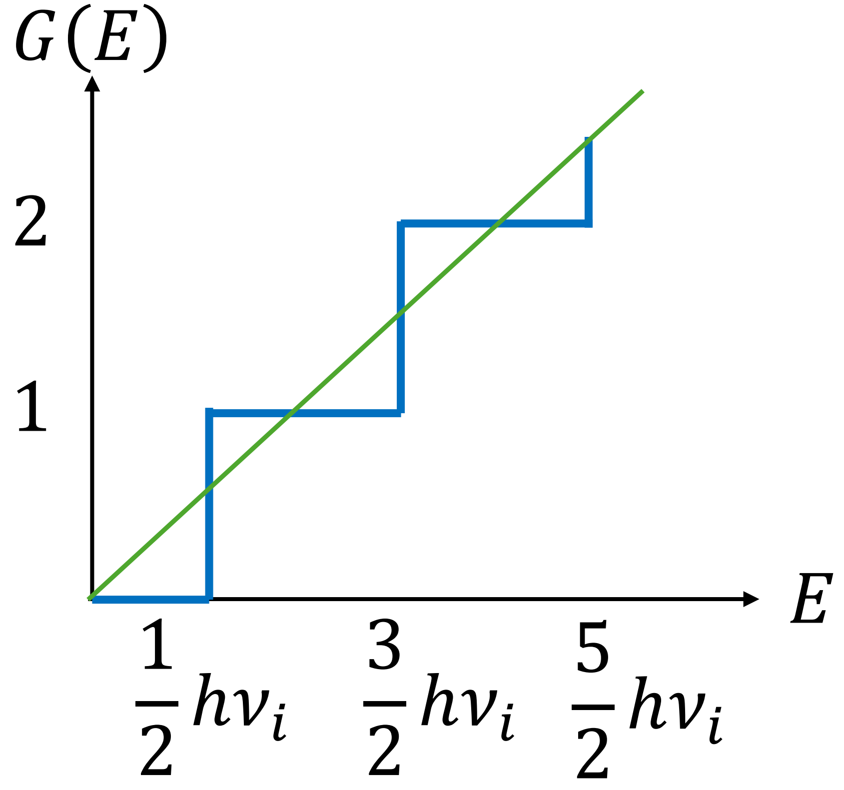
Sum of states $G(E)$: # of levels with energies smaller than or equal to E

- How did this look for the quantum-mechanical oscillator?
- discrete energy levels $E = \left(v + \frac{1}{2}\right) h\nu_i$
- ν_i : eigenfrequency of oscillator
- Sum of states *classically*: $G(E) = \frac{E}{h\nu_i}$
- Density of states (DoS) $N(E)$ is number of levels per unit energy:

$$N(E) = \frac{dG(E)}{dE}$$

which is simply

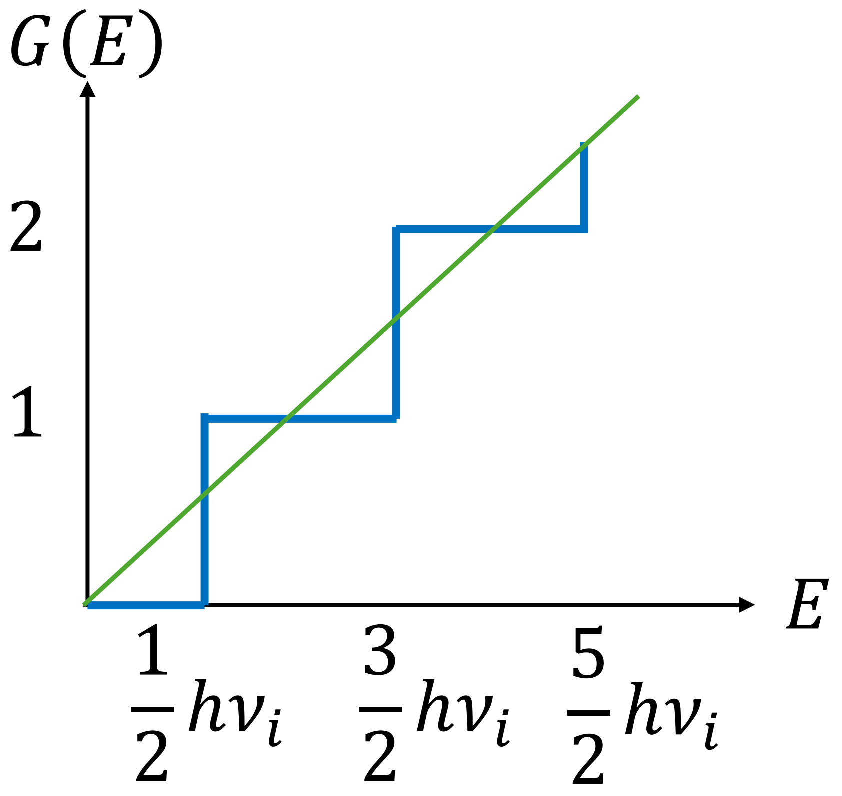
$$N(E) = \frac{1}{h\nu_i}$$



- Probability for such an oscillator to have energy between E and $E + dE$?

Probability for such an oscillator to have energy between E and $E + dE$ follows Boltzmann statistics and is thus:

- $P(E)dE = \dfrac{N(E)e^{-\frac{E}{k_BT}}dE}{\underbrace{\int_0^\infty N(E)e^{-\frac{E}{k_BT}}dE}_{\text{partition function for one classical oscillator}}} = e^{-\frac{E}{k_BT}}dE$



- Now need to generalize to $3N - 6$ (or s) oscillators, that have a total energy E
- For 1 oscillator, we had found $N(E) = \frac{1}{h\nu_1}$

  and for the sum of states $G(E) = \frac{E_1}{h\nu_1}$ (*i.e.*, the integral $\int_0^E \frac{dE_1}{h\nu_1}$)
- What is the sum of states for s oscillators then?

- For s oscillators of energies E_i with $\sum_{i=1}^{s} E_i = E$ we then find for the sum of states:
- $G(E) = \int_0^E \frac{dE_1}{h\nu_1} \int_0^{E-E_1} \frac{dE_2}{h\nu_2} \; \dots \int_0^{E-E_1-\dots-E_{s-1}} \frac{dE_s}{h\nu_s}$
- as for more than one oscillator, those oscillators share the energy between them
- So, if the first oscillator has already energy E_1, then the second one can only have at most $E - E_1$, and so on
- We can rewrite this to
- $G(E) = \frac{1}{\prod_{i=1}^{s} h\nu_i} \int_0^E dE_1 \int_0^{E-E_1} dE_2 \dots \int_0^{E-E_1-\dots-E_{s-1}} dE_s$
- which after some further steps becomes

$$G(E) = \frac{E^s}{s! \prod_{i=1}^{s} h\nu_i}$$

- For s oscillators of energies E_i with $\sum_{i=1}^{s} E_i = E$ we then find for the sum of states:

$$G(E) = \frac{E^s}{s! \prod_{i=1}^{s} h\nu_i}$$

- and for the DoS we then find:

$$N(E) = \frac{E^{s-1}}{(s-1)! \prod_{i=1}^{s} h\nu_i}$$ (which is just the derivative)

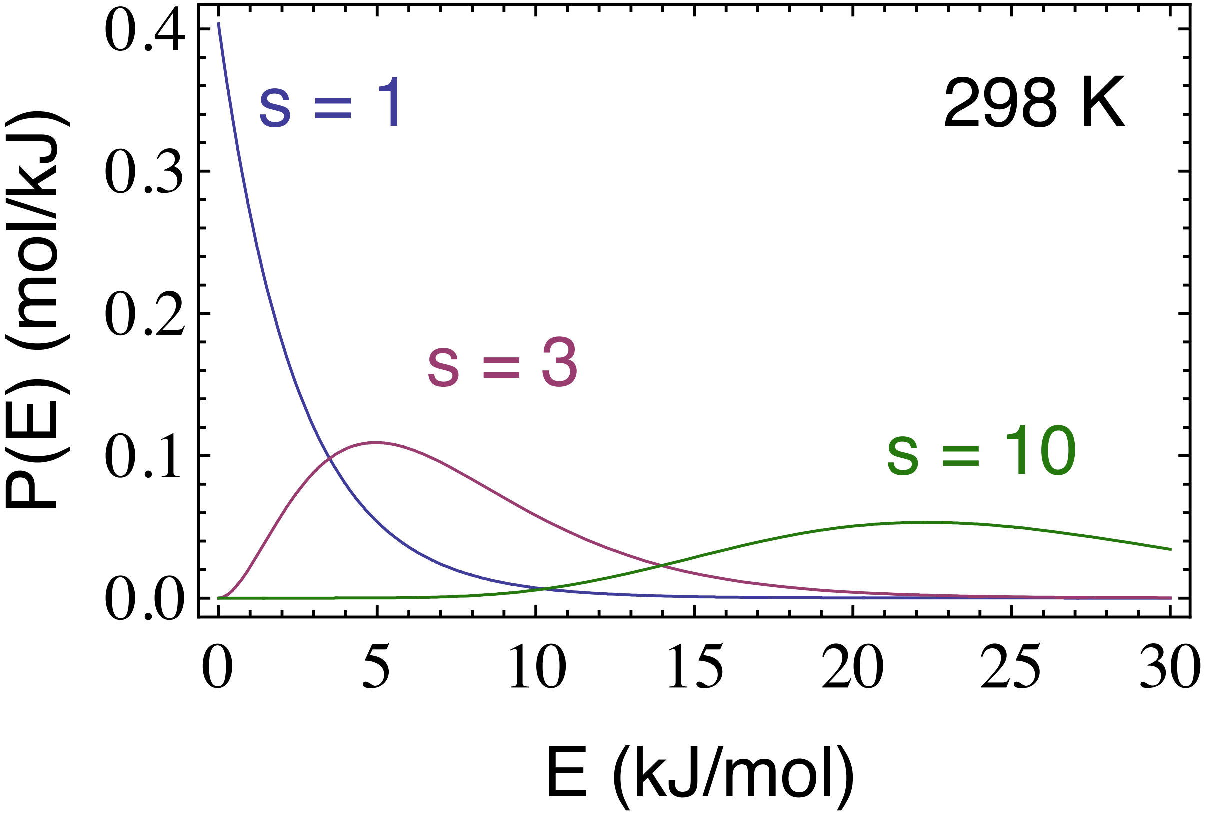
- With this we can now calculate our probability following Boltzmann statistics, inserting our solution for $N(E)$:

$$P(E)dE = \frac{N(E)e^{-\frac{E}{k_BT}}dE}{\int_0^\infty N(E)e^{-\frac{E}{k_BT}}dE} = \frac{E^{s-1}e^{-\frac{E}{k_BT}}dE}{\underbrace{\int_0^\infty E^{s-1}e^{-\frac{E}{k_BT}}dE}_{\int_0^\infty x^{s-1}e^{-x}dx = \Gamma(s) = (s-1)!}} = \frac{1}{(s-1)!}\left(\frac{E}{k_BT}\right)^{s-1} e^{-\frac{E}{k_BT}}\left(\frac{dE}{k_BT}\right)$$

Now we know the probability for a molecule with s classical harmonic oscillations having a certain energy E:

$$P(E)dE = \frac{1}{(s-1)!}\left(\frac{E}{k_BT}\right)^{s-1} e^{-\frac{E}{k_BT}}\left(\frac{dE}{k_BT}\right)$$

- Let’s plot this for different s at room temperature ($s = 1$ case is easy):



Probability for a molecule with s classical harmonic oscillations having a certain energy E:

$$P(E)dE = \frac{1}{(s-1)!}\left(\frac{E}{k_B T}\right)^{s-1} e^{-\frac{E}{k_B T}}\left(\frac{dE}{k_B T}\right)$$

- back to deriving k_1 according to Hinshelwood:
- We derive k_1 from fraction of molecules with energy exceeding activation energy E_0 through integration:

$$\frac{k_1}{k_{-1}} = \int_{E_0}^{\infty} P(E)dE = \int_{E_0}^{\infty} \frac{1}{(s-1)!}\left(\frac{E}{k_B T}\right)^{s-1} e^{-\frac{E}{k_B T}}\left(\frac{dE}{k_B T}\right)$$

- How can we solve this integral?
- by transforming and substituting $x = \frac{E}{k_B T}$

$$\frac{k_1}{k_{-1}} = \int_{E_0}^{\infty} P(E)dE = \int_{E_0}^{\infty} \frac{1}{(s-1)!}\left(\frac{E}{k_B T}\right)^{s-1} e^{-\frac{E}{k_B T}}\left(\frac{dE}{k_B T}\right)$$

- How can we solve this integral?
- by transforming and substituting $x = \frac{E}{k_B T}$ we get

$$\frac{k_1}{k_{-1}} = \frac{1}{(s-1)!} \int_{x_0=\frac{E_0}{k_B T}}^{\infty} (x)^{s-1} e^{-x} dx$$

- What does this function remind us of?
- a Γ-function, except for wrong integral boundary at bottom!
- So let’s further substitute $y = x - x_0$ and $dx = dy$

$$\frac{k_1}{k_{-1}} = \frac{1}{(s-1)!} \int_{x_0=\frac{E_0}{k_B T}}^{\infty} (x)^{s-1} e^{-x} dx$$

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- So let's further substitute $y = x - x_0$ and $dx = dy$ to get

$$\frac{k_1}{k_{-1}} = \frac{e^{-x_0}}{(s-1)!} \int_{0}^{\infty} \underbrace{(y + x_0)^{s-1}}_{} \, e^{-y} dy$$

- What now?
- We can develop our integral as a binomial series!
- each term will then contain a Γ-function that we know how to solve

$$\frac{k_1}{k_{-1}} = \frac{e^{-x_0}}{(s-1)!} \int_0^\infty \underbrace{(y+x_0)^{s-1}} \, e^{-y} dy$$

- We can develop our integral as a binomial series!
- each term will then contain a Γ-function that we know how to solve
- Binomial expansion of term $(y+x_0)^{s-1}$ yields

$$\frac{k_1}{k_{-1}} = \frac{e^{-x_0}}{(s-1)!} \sum_{j=0}^{s-1} \binom{s-1}{j} x_0^{s-1-j} \underbrace{\int_0^\infty y^j e^{-y} dy}$$

- and we know that $= \Gamma(j+1) = j!$
- k_{-1} we know from gas-kinetic collision theory

and rest we get from here, so mission accomplished for getting k_1 !☺

$$\frac{k_1}{k_{-1}} = \frac{e^{-x_0}}{(s-1)!}\sum_{j=0}^{s-1}\binom{s-1}{j}x_0^{s-1-j}\int_0^{\infty} y^j e^{-y}dy$$

- For $j = 0$ we get: $\binom{s-1}{0} = 1$ $\quad \left(\frac{E_0}{k_BT}\right)^{s-1}$ $\quad 0! = 1$

- For $j = 1$ we get: $\binom{s-1}{1} = s-1$ $\quad \left(\frac{E_0}{k_BT}\right)^{s-2}$ $\quad 1! = 1$

- What is the condition for the 2nd term and following terms to be much smaller than the 1st term?
- If $x_0 = \frac{E_0}{k_BT} \gg s-1$, then we can neglect all the terms except for the 1st

$$\frac{k_1}{k_{-1}} = \frac{e^{-x_0}}{(s-1)!} \sum_{j=0}^{s-1} \binom{s-1}{j} x_0^{s-1-j} \int_0^{\infty} y^j e^{-y} dy$$

- What is the condition for the 2nd term and following terms to be much smaller than the 1st term?
- If $x_0 = \frac{E_0}{k_B T} \gg s - 1$, then we can neglect all the terms except for the 1st

- *I.e.*, the activation energy E_0 must be large compared to the thermal energy $k_B T$ multiplied with number of oscillations s
- Meaning large E_0 or small number of oscillators, i.e., small molecules, are well suited to to justify our approximation from the start
- Then can neglect all subsequent terms of $j \geq 1$
- and are only left with the $j = 0$ term overall

$$\frac{k_1}{k_{-1}} = \frac{e^{-x_0}}{(s-1)!} \sum_{j=0}^{s-1} \binom{s-1}{j} x_0^{s-1-j} \int_0^{\infty} y^j e^{-y} dy$$

- Within approximation, we are only left with the $j = 0$ term of the binomial expansion to be relevant, and get:

$$\frac{k_1}{k_{-1}} = \frac{e^{-x_0}}{(s-1)!} x_0^{s-1} = \frac{1}{(s-1)!} \left(\frac{E_0}{k_B T}\right)^{s-1} e^{-\frac{E_0}{k_B T}}$$

- for comparison, in the beginning we wrote

$$\boxed{k_1 = \frac{k_{-1}}{(s-1)!} \left(\frac{E_0}{k_B T}\right)^{s-1} e^{-\frac{E_0}{k_B T}}}$$

- Good approximation for small molecules, medium to large activation energies, and high pressures