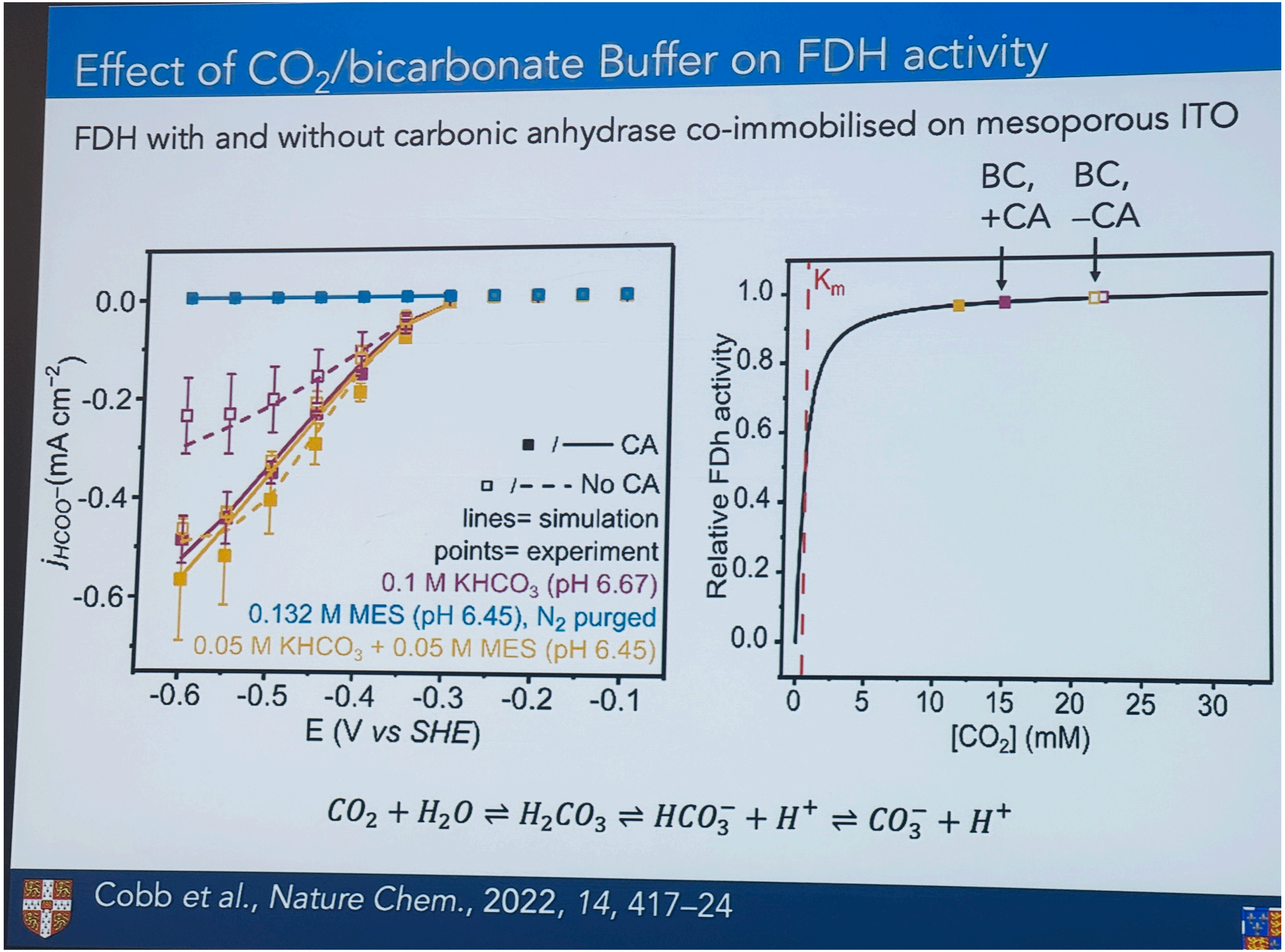
Kinetics & Dynamics of Chemical Reactions

Course CH-310

Prof. Sascha Feldmann

Kinetics in everyday science life:

An example from a conference last year



Effect of CO_2/bicarbonate Buffer on FDH activity

FDH with and without carbonic anhydrase co-immobilised on mesoporous ITO

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \rightleftharpoons CO_3^- + H^+$$

Cobb *et al.*, *Nature Chem.*, 2022, *14*, 417–24

Recap from last session

Unimolecular Reaction Dynamics

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

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

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

- Lindemann theory of collision-activated unimolecular reactions
  - *strong-collision assumption* for activation/deactivation

    →gas-kinetic collision rate z_{AM} for deactivation const. k_{-1}:

    $$z_{\mathrm{AM}} = \sigma_{\mathrm{AM}} \langle u_{\mathrm{AM}} \rangle \rho_{\mathrm{A}} \rho_{\mathrm{M}} = k_{-1} [\mathrm{A}][\mathrm{M}]$$
  - applied steady-state approximation for A^*
  - overall rate: $R = k_{uni}[\mathrm{A}] = k_2[\mathrm{A}^*] = \frac{k_1 k_2 [\mathrm{A}][\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2}$
  - considered high- & low-pressure limits

$$\boxed{\begin{gathered} k_{-1} = \sigma_{\mathrm{AM}} \langle u_{\mathrm{AM}} \rangle \\ k_{uni} = \frac{k_1 k_2 [\mathrm{M}]}{k_{-1}[\mathrm{M}] + k_2} \end{gathered}}$$

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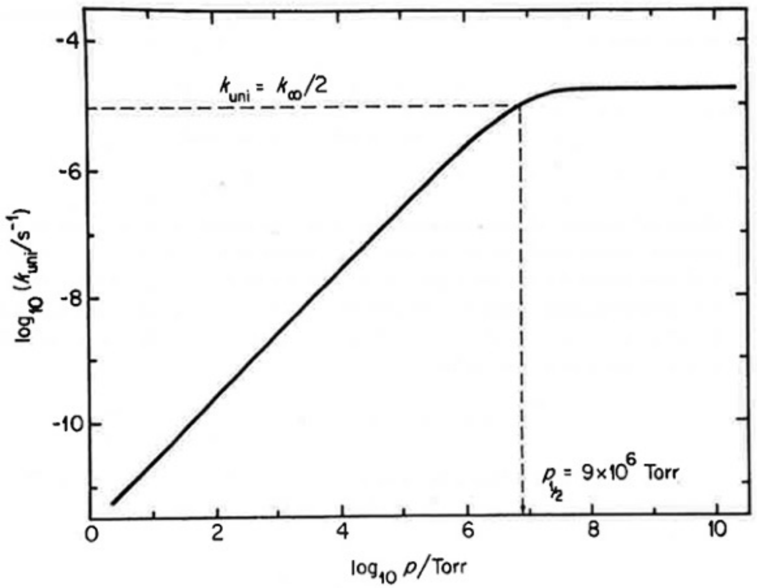
- Lindemann theory of collision-activated unimolecular reactions
  - at low pressure becomes 1st order in collision partner, linear increase of k_{uni} with pressure (activation step is rate-liming)
  - at high pressure becomes effectively 0th order, constant with pressure (pre-equilibrium, reaction rate-limiting)
  - $k_{uni} = \frac{k_\infty}{1+\frac{k_\infty}{k_1[\mathrm{M}]}}$
- realized that using k_1 from simply reactive-hard-spheres model *underestimated* experimental results…

$$k_{-1} = \sigma_{\mathrm{AM}} \langle u_{\mathrm{AM}} \rangle$$

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



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

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

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

Recap from last session

Unimolecular Reaction Dynamics

- Lindemann-Hinshelwood theory, to account for *internal* energy stored in vibrations that can drive reaction as well, to increase k_1 for better agreement with experiment
  - approximated the ratio

$$\frac{k_1}{k_{-1}} \approx \frac{[A_{E>E_0}]}{[A_{total}]}$$

  - only justified for pre-equilibrium approximation, *i.e*., at *high* pressures (drastic approximation for low ones!)
  - allowed us to apply statistical thermodynamics to calculate assuming a thermal distribution

Recap from last session

Unimolecular Reaction Dynamics

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

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

- Lindemann-Hinshelwood theory, to account for *internal* energy stored in vibrations that can drive reaction as well, to increase k_1 for better agreement with experiment
  - derived from first principles: $k_1 = \frac{k_{-1}}{(s-1)!}\left(\frac{E_0}{k_B T}\right)^{s-1} e^{-\frac{E_0}{k_B T}}$
  - assuming s *classical* harmonic oscillators, using stat. TD and DoS
  - approximate solution, only valid for rel. small molecules: s small if overall atom number N small, as $s = 3N - 6$ (or -5)
  - and for activation energy E_0 being relatively large (typical)
  - and assuming quasi-equilibrium, *i.e.* high-pressure limit
  - then, we could drop all terms in binomial expansion for $j > 0$

Recap from last session

Unimolecular Reaction Dynamics

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

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  - derived from first principles: $k_1 = \frac{k_{-1}}{(s-1)!}\left(\frac{E_0}{k_B T}\right)^{s-1} e^{-\frac{E_0}{k_B T}}$

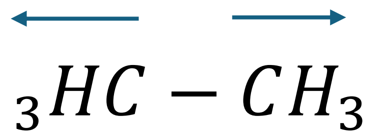
→ *compared to the reactive-hard-spheres model, we now know that the reaction rate depends on the internal energy as well, taking into account the vibrational energy stored, which can contribute to a successful activation and reaction, accounted for in the equation through* s

- What is left to do? Calculating k_2!
- How will reaction rate k_2 depend on the energy stored in activated molecule A^* ?
- it will *increase* with increasing energy stored in vibrations (oscillators have a total energy E)
- But how exactly? Consider *e.g.* a dissociation reaction: which vibration matters?
- specifically the energy stored in the vibrational mode along which the dissociation occurs will matter: the ***critical mode***
- need energy larger than threshold in exactly *this mode* for dissociation to occur!
- Morse Potential of oscillator

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

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

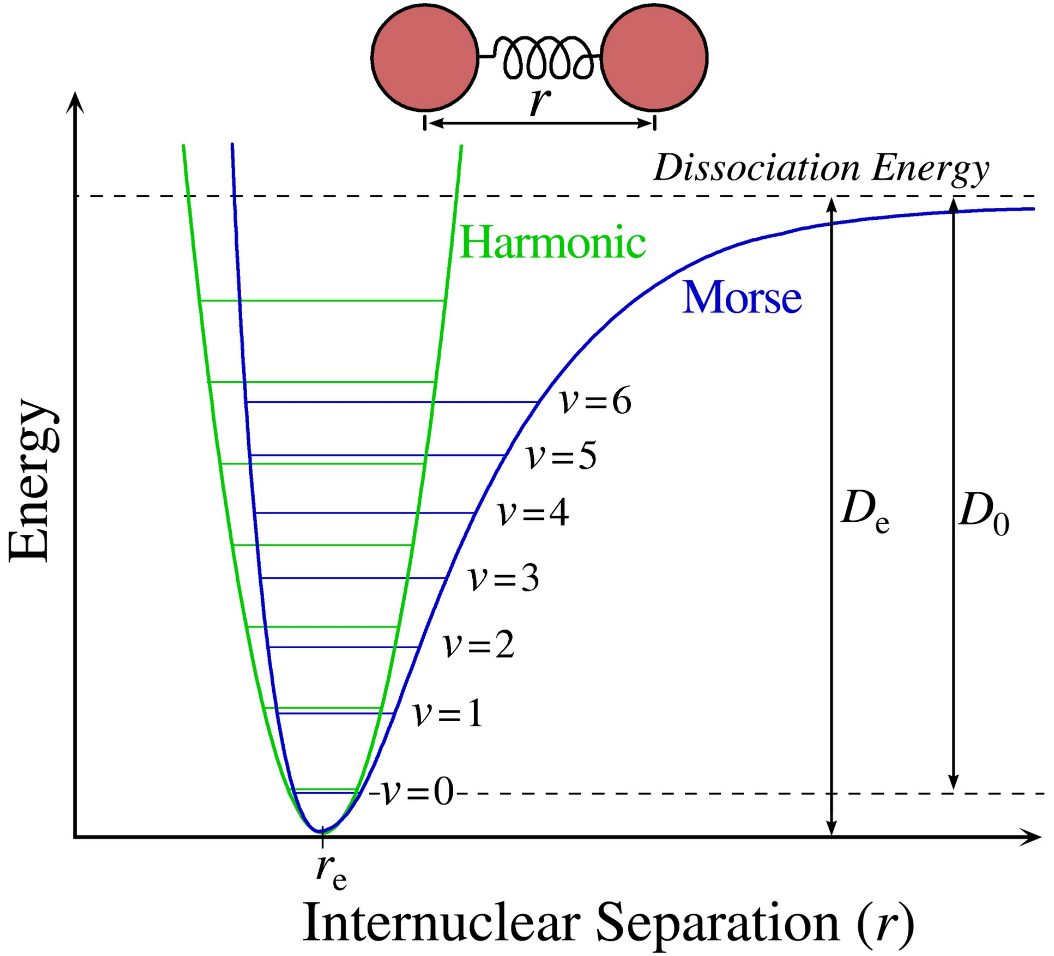
$$\mathrm{A}^* \xrightarrow{k_2} \mathrm{products}$$



$$_3HC - CH_3$$

- need energy larger than threshold in exactly this mode for dissociation to occur!
- ***Morse Potential***: need enough energy to dissociate

→ once I add more energy into <u>this</u> mode than the dissociation energy, this Morse oscillator will fall apart and dissociation occurs



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

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

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

$$\overleftarrow{{}_3HC} - \overrightarrow{CH_3}$$

- So, the more energy the system has overall, the higher the probability of having enough energy in the specific, ***critical* mode** for the reaction to take place
- therefore, we expect k_2 to *increase* with energy

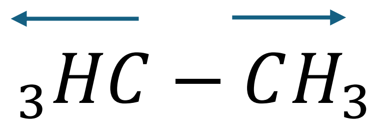
$$k_2 = k(E)$$

- But how will the reaction rate then depend on the *number* of oscillators s ?
- It will *decrease* with number of oscillators! Because the more there are, that I distribute my total energy E over, the *less likely* we are to exceed the threshold energy in the relevant critical mode for the reaction to occur

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

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

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



$$_3HC - CH_3$$

6.2 Rice-Ramsperger-Kassel (RRK) Theory

- statistical theory (1927-28) which considers that activation rate & reaction rate *both* depend on energy of activated molecule:

$$\mathrm{A} + \mathrm{M} \xrightarrow{k_1} \mathrm{A}^* + \mathrm{M} \qquad\qquad \mathrm{A} + \mathrm{M} \xrightarrow{dk_1} \mathrm{A}^*(E, E + dE) + \mathrm{M}$$

$$\mathrm{A}^* + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M} \qquad \Longrightarrow \qquad \mathrm{A}^*(E, E + dE) + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M}$$

$$\mathrm{A}^* \xrightarrow{k_2} \text{products} \qquad\qquad \mathrm{A}^*(E, E + dE) \xrightarrow{k(E)} \text{products}$$

reaction cannot be described fully by one k_1 anymore, but only by a fraction of that total rate, so a different dk_1 for each energy dE

- If activating into an infinitesimally small energy interval between E and $E + dE$, the rate will not anymore follow the total rate constant of this activation reaction (would be k_1), but only a small fraction of the total rate, characterized by dk_1
- with strong-collision assumption, we still keep k_{-1} unchanged

$$\begin{array}{lcl}
\mathrm{A} + \mathrm{M} \xrightarrow{k_1} \mathrm{A}^* + \mathrm{M} & & \mathrm{A} + \mathrm{M} \xrightarrow{dk_1} \mathrm{A}^*(E, E + dE) + \mathrm{M} \\
\mathrm{A}^* + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M} & \Longrightarrow & \mathrm{A}^*(E, E + dE) + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M} \\
\mathrm{A}^* \xrightarrow{k_2} \text{products} & & \mathrm{A}^*(E, E + dE) \xrightarrow{k(E)} \text{products}
\end{array}$$

- So now depending on the specific energy to activate towards, we will have a different rate constant for the first activation step, and thus for the final forward reaction step (k_2) as well
- How do those two rates depend on energy for a given temperature?

$$\mathrm{A} + \mathrm{M} \xrightarrow{k_1} \mathrm{A}^* + \mathrm{M} \qquad\qquad \mathrm{A} + \mathrm{M} \xrightarrow{dk_1} \mathrm{A}^*(E, E + dE) + \mathrm{M}$$

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$$\mathrm{A}^* \xrightarrow{k_2} \text{products} \qquad\qquad \mathrm{A}^*(E, E + dE) \xrightarrow{k(E)} \text{products}$$

- How do those two rates depend on energy for a given temperature?
- Rate of activation will *decrease* for higher energy values, as less and less likely to reach the very highest levels of energy of that activated molecule
- Reaction rate will *increase* with energy, as more and more likely to exceed activation energy in the critical mode to react

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

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

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

➡

$$\mathrm{A} + \mathrm{M} \xrightarrow{dk_1} \mathrm{A}^*(E, E + dE) + \mathrm{M}$$

$$\mathrm{A}^*(E, E + dE) + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M}$$

$$\mathrm{A}^*(E, E + dE) \xrightarrow{k(E)} \text{products}$$

- We thus arrive at a differential unimolecular rate constant:

$$dk_{uni} = \frac{k(E)\dfrac{dk_1}{k_{-1}}}{1 + \dfrac{k(E)}{k_{-1}[\mathrm{M}]}}$$

- just like Lindemann-Hinshelwood from before, except that we only consider a small fraction of the rate relevant to a given energy increment

$$\mathrm{A} + \mathrm{M} \xrightarrow{dk_1} \mathrm{A}^*(E, E + dE) + \mathrm{M}$$

$$\mathrm{A}^*(E, E + dE) + \mathrm{M} \xrightarrow{k_{-1}} \mathrm{A} + \mathrm{M}$$

$$\mathrm{A}^*(E, E + dE) \xrightarrow{k(E)} \text{products}$$

- We thus arrive at a *differential* unimolecular rate constant:

$$dk_{uni} = \frac{k(E)\,\dfrac{dk_1}{k_{-1}}}{1 + \dfrac{k(E)}{k_{-1}[\mathrm{M}]}}$$

- we call ω the *collision frequency* (a rate) of reactant: $\omega = k_{-1}[\mathrm{M}]$
- probability for a molecule to have a certain energy is: $\frac{dk_1}{k_{-1}} = P(E)dE$
- so we can rewrite:

$$dk_{uni} = \omega \frac{k(E)P(E)dE}{k(E) + \omega}$$

- Integration yields

$$k_{uni} = \omega \int_{E_0}^{\infty} \frac{k(E)P(E)dE}{k(E) + \omega}$$

So how can we get $k(E)$???

- RRK theory assumes **(1)** activated molecules of a specific energy $E > E_0$ form a ***microcanonical ensemble***, *i.e.*:
- all possible states of this energy are populated with equal probability
- A statistical thermodynamics assumption which is in reality not true, why not?
  - not enough time for energy to always flow from one collision-excited mode into all the others, before molecule reacts/collides again
  - not equally likely for energy to flow from one mode into any other, as not all modes will be coupled (equally strongly), so instead preferential flow from certain modes into others
- we still will make this drastic approximation here

- RRK theory also assumes **(2)** molecules with energy $E_0 + E'$ in the critical mode will **react** (dissociate/isomerize) **within one vibration**al period of duration $1/\nu$
- ν is eigenfrequency of that critical oscillator
- *i.e.*, these molecules will have a **dissociation (reaction) rate of $\boldsymbol{\nu}$**
- RRK theory also assumes **(3)** even after some molecules have dissociated, the rest will ***continue*** **to form a microcanonical** ensemble. This 3rd assumption relies on
- **(3a)** the ***ergodic hypothesis***, *i.e.*, we assume energy can freely redistribute between all vibrational degrees of freedom
- **(3b)** ***fast IVR*** (intramolecular vibrational energy redistribution), on timescales faster than that of the reaction, *i.e.*, fast energy exchange between all modes (strongly coupled)

- With all these assumptions we can then rather straightforwardly say:
- The classical RRK rate constant $k(E)$ is simply the dissociation rate of that critical mode (using assumption **(2)**) multiplied with the probability of having enough energy in that critical mode:

$$k(E) = \nu \ \cdot P(E, E_s \geq E_0)$$

- So let's calculate the probability for a molecule to have energy $E_s \geq E_0$ in the critical mode: $P(E, E_s \geq E_0)$
- we use our previously derived expressions for the DoS of a set of s classical oscillators
- Why can we just use the DoS of our levels for calculating the probability, and do *not* need to use a Boltzmann term here?
- Because it's a microcanonical ensemble: there is no temperature and thus spread of energies, but only one energy we consider here

- Why can we just use the DoS of our levels for calculating the probability, and do *not* need to use a Boltzmann term?
- Because it's a microcanonical ensemble: there is no temperature and thus spread of energies, but only one energy we consider here
- If I ask for one specific energy value "how probable is a given state?", I just have to know the degeneracy of this state and divide it by the total number of states
- So we can use the DoS here, which we derived before ☺
- The probability we look for is thus the DoS of a molecule with subset of states with sufficient energy in the critical mode divided by the total DoS:

$$k(E) = \nu \ \cdot P(E, E_s \geq E_0) = \nu \cdot \frac{N(E, E_s \geq E_0)}{N(E)}$$

- For the total DoS of s oscillators of total energy E we had derived:

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

- For the fraction of this total DoS with an energy in the critical mode of $E_s = E_0 + E'$, $N(E, E_s \geq E_0)$, we multiply the DoS of $s-1$ oscillators at a total energy of $E - E_0 - E'$ with the DoS of the critical oscillator at energy $E_s = E_0 + E'$ and then integrate over all energies E':

$$N(E, E_s \geq E_0) = \underbrace{\int_0^{E-E_0} N(remaining\ oscillators)\,dE'}_{\text{DoS of } s-1 \text{ oscillators with remaining energy of } E-E_s} \cdot \underbrace{N(critical\ oscillator)}_{\text{DoS of critical oscillator with energy } E_s = E_0 + E' \geq E_0}$$

$$N(E, E_s \geq E_0) = \int_0^{E-E_0} N(\text{remaining oscillators})dE' \cdot N(\text{critical oscillator})$$

$N(E)$ reduced by 1, which is reserved for critical oscillator

$$N(E, E_s \geq E_0) = \int_0^{E-E_0} \frac{\overbrace{(E - E_0 - E')}^{= E - E_s}{}^{s-2}}{(s-2)! \prod_{i=1}^{s-1} h\nu_i} dE' \cdot \frac{1}{h\nu_s}$$

- energy of at least E_0 is reserved for the critical oscillator for reaction
- So we need to integrate the DoS over all energies from 0 (*i.e.*, all energy is in the critical oscillator and nothing left for remaining ones) to $E - E_0$ (which would mean just the bare minimum amount of necessary energy, E_0, is in the critical oscillator, and all the rest is in the remaining ones)
- This way we get the DoS of the system having energy E, and of that, at least energy E_0 is in the critical oscillator

$$N(E, E_s \geq E_0) = \int_0^{E-E_0} \frac{(E - E_0 - E')^{s-2}}{(s-2)! \prod_{i=1}^{s-1} h\nu_i} \cdot \frac{1}{h\nu_s} dE'$$ which simplifies to

$$\boxed{N(E, E_s \geq E_0) = \frac{(E - E_0)^{s-1}}{(s-1)! \prod_{i=1}^{s} h\nu_i}}$$

- Now we can insert this result into our previous expression for the probability $P(E, E_s \geq E_0)$, and get for the fraction of molecules that have an energy of $E_s \geq E_0$ in the critical mode:

$$P(E, E_s \geq E_0) = \frac{N(E, E_s \geq E_0)}{N(E)} = \left(\frac{E - E_0}{E}\right)^{s-1}$$

- Now we can insert this result into our previous expression for the probability $P(E, E_s \geq E_0)$, and get for the fraction of molecules that have an energy of $E_s \geq E_0$ in the critical mode:

$$P(E, E_s \geq E_0) = \frac{N(E, E_S \geq E_0)}{N(E)} = \left(\frac{E - E_0}{E}\right)^{s-1}$$

- finally, we can insert this result into our desired expression for the

  RRK reaction rate constant:

$$k(E) = \nu \cdot P(E, E_s \geq E_0)$$

$$k(E) = \nu \cdot \left(\frac{E - E_0}{E}\right)^{s-1}$$

- ***RRK reaction rate constant***:

$$\boxed{k(E) = \nu \cdot \left(\frac{E-E_0}{E}\right)^{s-1}}$$

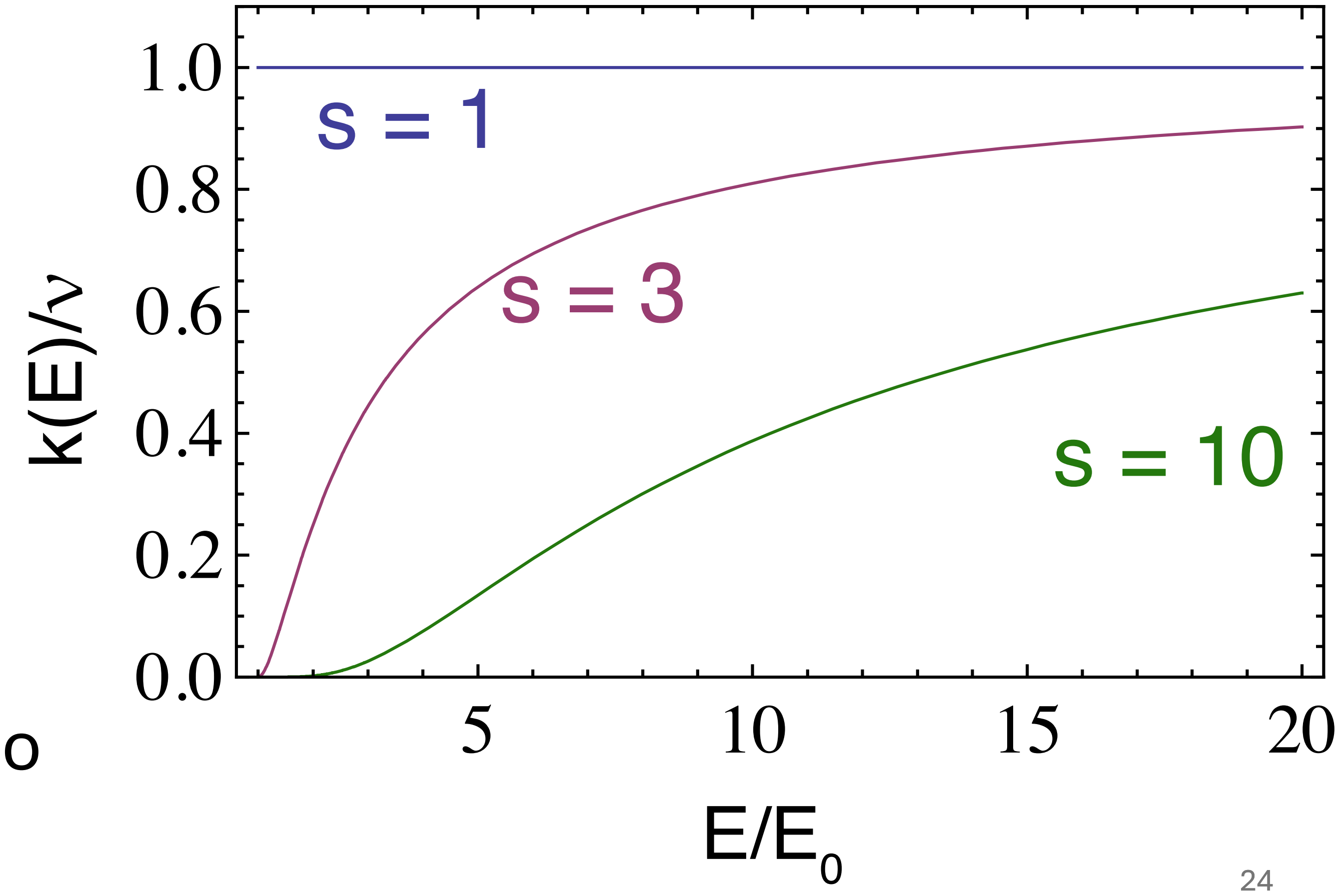
- How does it look plotted against energy?

- For diatomic molecule?

→ $k_{s=1}(E) = \nu$

→all energy in critical mode

→rate becomes as fast as possibly can be



- Quite nice that we only need to know ν, s and E_0 for this ☺

- ***RRK reaction rate constant***:

$$k(E) = \nu \cdot \left(\frac{E - E_0}{E}\right)^{s-1}$$

- ***Limitations*** of this RRK model arise from *classical* (as opposed to QM) treatment of vibrations:
- our pre-factor of the RRK model here (Arrhenius-like) is ν, so the eigenfrequency of the vibration of the critical molecular mode
- say such a vibration takes 10-100 fs (*i.e.* $1/\nu$) in reality
- in the experiment, the measured pre-factor is larger than just ν taken straight from the molecular vibration, *i.e.*, larger than 10^{14} s^{-1}
- other short-coming is that we treat all here statistical (due to pre-equilibrium assumption), which in reality it mostly is *not* (esp. not at lower pressures)
- RRK**M** theory improves this as a microcanonical transition-state theory

- RRK theory: developed by 1927 by **R**ice & **R**amsperger, and completed in 1928 by **K**assel
- RRK**M** theory improves this as a microcanonical transition-state theory:
- In 1952, Rudolph **M**arcus (Nobel Prize 1992) developed RRK theory further, by taking into account the *transition-state theory* (TST) developed by Eyring in 1935
- RRKM builds on TST using potential energy surfaces
- assumes potential energy surface does not have any "bottlenecks" for which certain vibrational modes may be trapped for longer than the average time of the reaction; also accounts for rotations

Rudi Marcus, Caltech

$$\mathrm{A}^* \xrightarrow{k(E)} \text{products} \quad \Longrightarrow \quad \mathrm{A}^* \xrightarrow{k(E)} \mathrm{A}^\ddagger \rightarrow \text{products}$$

Chapter 7

Basic Concepts of Statistical Thermodynamics

👉 has been covered already, but if you need a brief refresher, read Chapter 7 in the handout