

Virtual Kinetics Lab: Reaction Software

Online Workshop

Agenda

Intro

- Motivation
- Link

Reaction Mechanism

- Site vs State Model
- Site model: Manual
- Site model: Auto reaction mechanism generation
- State model: Manual

Agenda

Thermochemistry & Kinetics

- Statistical thermodynamics overview
- DFT to Macro Thermochemical Properties
- Transition state theory (TST)
 - Reaction barriers
 - Pre-exponential factors

- Misc
 - Re-referencing to standard state
 - Lateral Interactions
 - Empirical expressions

Python Multiscale Thermodynamic Toolbox (pMuTT)

- Overview
- Code demonstration



Agenda

Semi-Empirical Methods

- Group additivity
- Machine learning
- Bronsted-Evans-Polyani (BEP) Relationships
- Linear Scaling Relationships (LSR)

Python Group Additivity (pGrAdd)

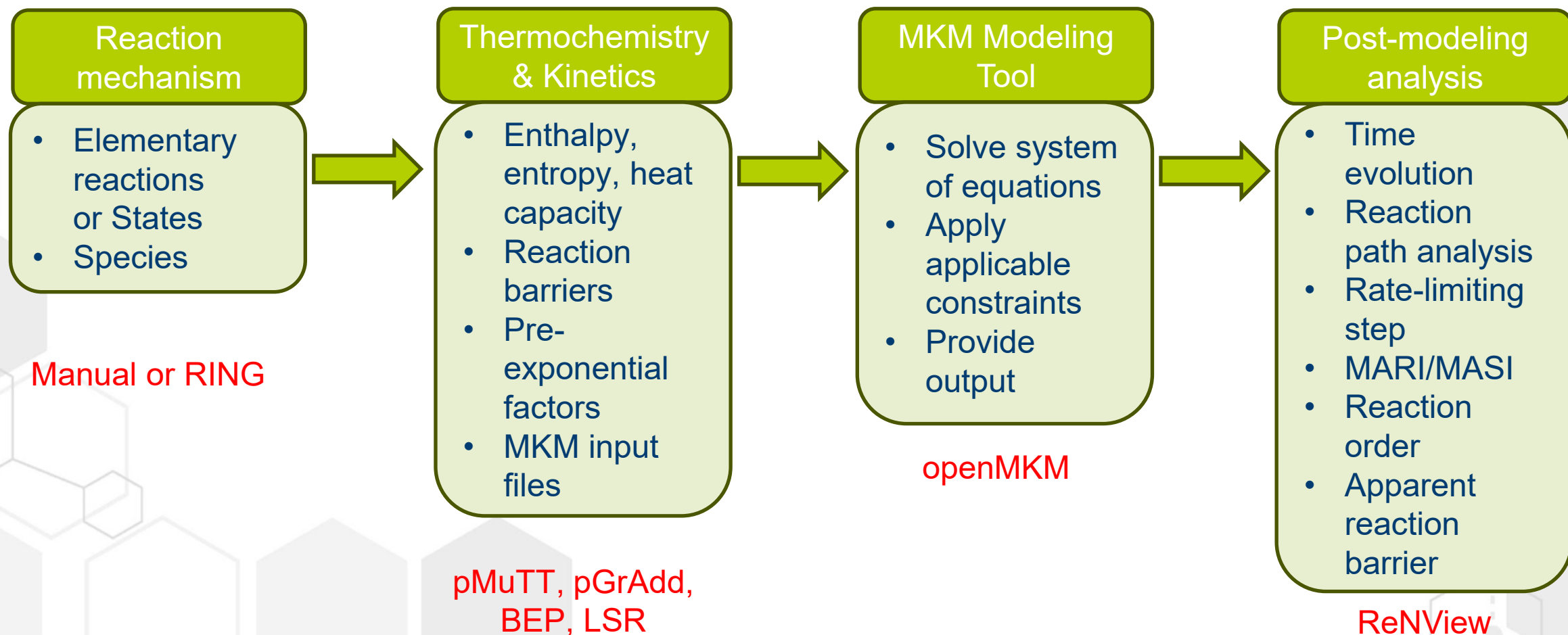
- Code demonstration



Python Code Examples

- DFT→pMuTT→openMKM
- Group additivity
- Interesting applications (Error propagation & Dynamic catalysis)

Introduction



Reaction Mechanism: Site vs State Model

Site model

- Active sites/Site density
- Exclusion principle
- Lateral interactions
- Exhaustive elementary reactions
- Mean-field
- Ideal for typical heterogeneous catalysis

State model

- Active sites/Site density
- States vs sites
- No interactions
- States defined manually
- Ideal for single atom and Zeolites

Reaction Mechanism: Site Model

Simple reaction
mechanism

- 1-2 Site types (Terrace vs step, Pt(111) & Pt(211))
- Small molecules (CH₄, NH₃)
- Manually generate all elementary reactions

Large reaction
mechanism

- >2 Site types
- Large molecules
- Automatic reaction mechanism generator (RING)

Reaction Mechanism: Simple Site Model

Ammonia: 2 Ru active sites (Terrace & Step)

Adsorption/Desorption	Surface Diffusion	Surface Reactions

Summary

19 Reactions
3 Gas species
10 Surface species

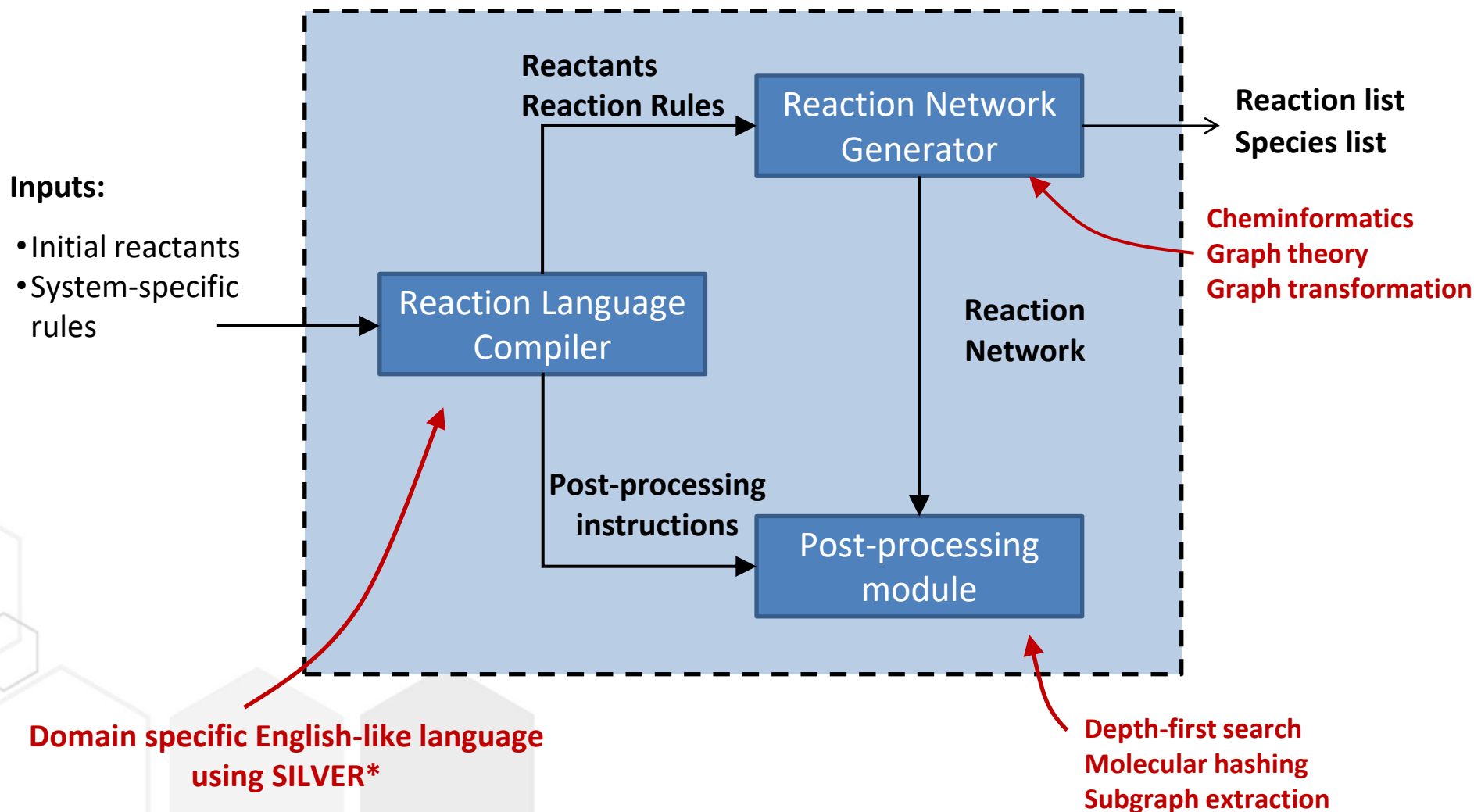
Reaction Mechanism: Large Site Model

Chemistry	System	Reactions (species)
Heterogeneous catalysis	Propane aromatization	19907 (5909)
Gas phase combustion	Hexadecane combustion ¹	8130 (2116)
Metabolism	E.coli genome ²	2077 (1039)
Metal chemistry	Glycerol decomposition ³	3313 (537)

- Manual construction generally impractical
- Automated network generators
 - Generate all possible reactions and species of the network
 - Use reaction rules as basis – **“rule-based”**

¹ Combustion and Flame 2009, 156 (1), 181; ² Mol Syst Biol. 2007, 3, 121; ³ Green Chem.,

Rule Input Network Generator (RING) for network generation



RING language: rule inputs

User-specification

input reactant "C=CC"
 input reactant "[{Zeo}H]"
 input reactant "N#N"

REACTANTS

rule OlefinAdsorption{
 gasPhase reactant r1{
 C labeled c1
 C labeled c2 double bond to c1}
 reactant r2{
 Zeo labeled z1 {! connected to >=1 C
 with any bond}
 H labeled h1 single bond to z1}

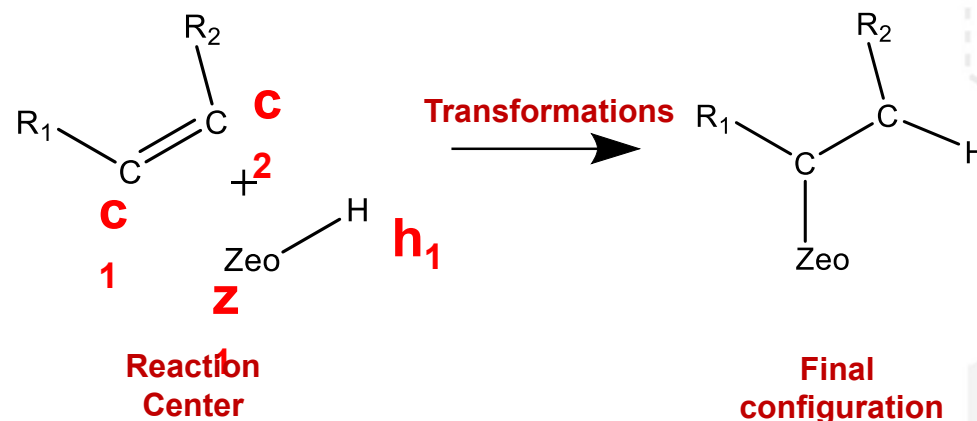
REACTION
 CENTER

constraints{! r1 is cyclic}

CONSTRAINTS

form bond (c1,z1)
 decrease bond order (c1,c2)
 form bond (c2,h1)
 break bond (z1,h1) }

TRANSFORMATIONS



RING Ruleset: Typical hydrocarbon

```
input reactant "CCC"
input reactant "{Pt}"
define composite atom Pt

global constraints on Molecule{
  fragment f1{
    C labeled c1
    C labeled c2 double bond to c1
    Pt labeled p1 single bond to c1
  }
  fragment f2{
    C labeled c1
    C labeled c2 triple bond to c1
    Pt labeled p1 single bond to c1
  }
  ! Molecule contains >=1 of f1
  ! Molecule contains >= 1 of f2
}
```

```
rule CCScission{
  reactant r1{
    C labeled c1
    C labeled c2 single bond to c1}
  reactant r2{
    Pt labeled m1{!connected to >0 $ with any bond}}
  reactant r3 duplicates r2 (m1=>m2)
  break single bond(c1, c2)
  form single bond(c1, m1)
  form single bond(c2, m2)}

rule CHScission{
  reactant r1{
    C labeled c1
    H labeled h1 single bond to c1}
  reactant r2{
    Pt labeled m1{!connected to >0 $ with any bond}}
  reactant r3 duplicates r2 (m1=>m2)
  break single bond(c1, h1)
  form single bond(c1, m1)
  form single bond(h1, m2)
}

rule OHScission{
  reactant r1{
    O labeled o1
    H labeled h1 single bond to o1}
  reactant r2{
    Pt labeled m1{!connected to >0 $ with any bond}}
  reactant r3 duplicates r2 (m1=>m2)
  break single bond(o1, h1)
  form single bond(o1, m1)
  form single bond(h1, m2)
}
```

RING Ruleset: Output for CCC

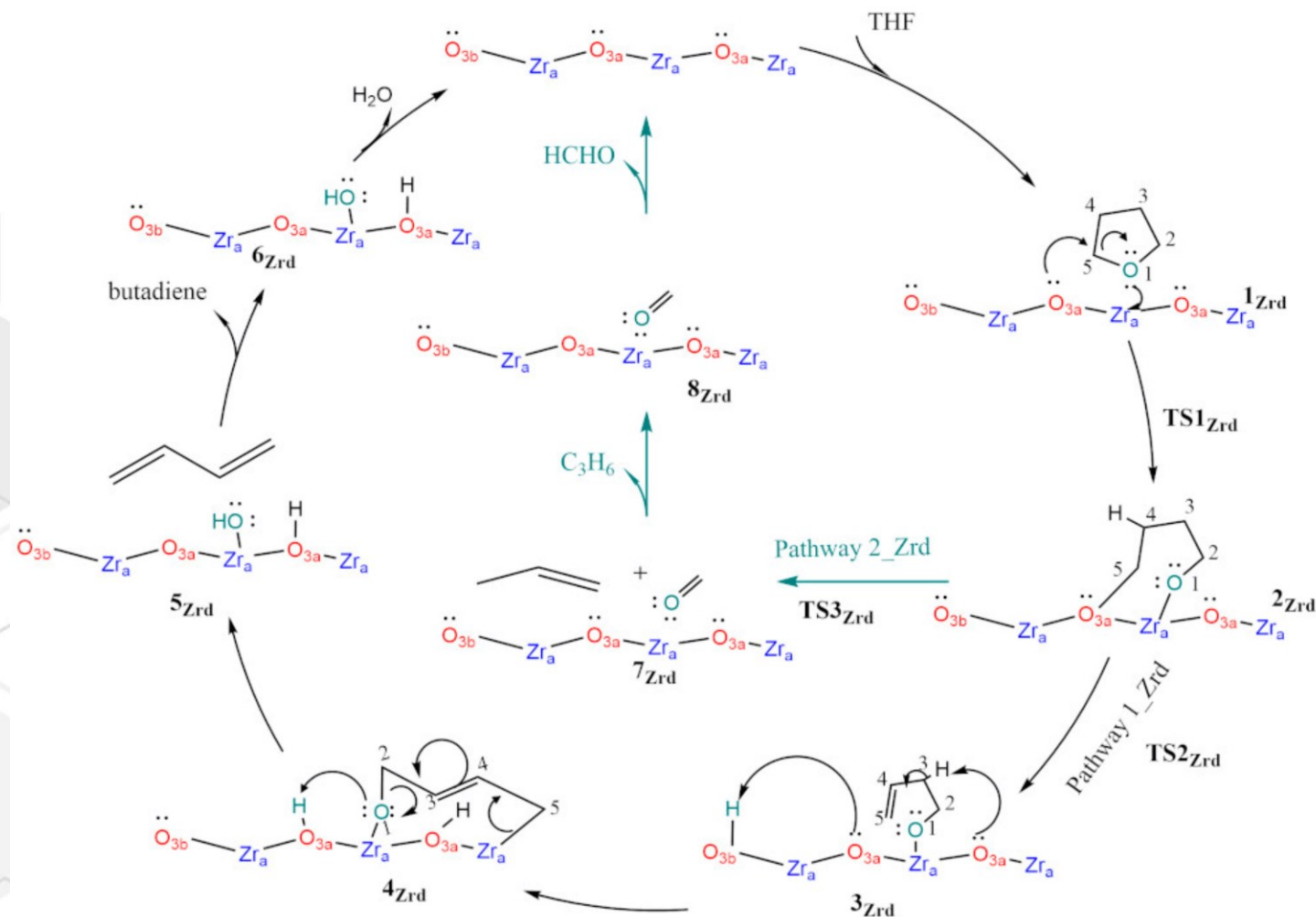
Reactions (144)

C(C)C.[Pt].[Pt]>>C([Pt])C.[Pt]C
C(C)C.[Pt].[Pt]>>C([Pt])(C)C.[Pt]H
C(C)C.[Pt].[Pt]>>C(C[Pt])C.[Pt]H
C([Pt])C.[Pt].[Pt]>>[Pt]C[Pt].[Pt]C
C([Pt])C.[Pt].[Pt]>>C([Pt])([Pt])C.[Pt]H
C([Pt])C.[Pt].[Pt]>>C(C[Pt])([Pt]).[Pt]H
[Pt]C.[Pt].[Pt]>>[Pt]C[Pt].[Pt]H
C([Pt])(C)C.[Pt].[Pt]>>C([Pt])([Pt])C.[Pt]C
C([Pt])(C)C.[Pt].[Pt]>>C([Pt])([Pt])(C)C.[Pt]H
C([Pt])(C)C.[Pt].[Pt]>>C(C[Pt])([Pt])C.[Pt]H
C(C[Pt])C.[Pt].[Pt]>>C([Pt])C.[Pt]C[Pt]
C(C[Pt])C.[Pt].[Pt]>>C(C[Pt])([Pt]).[Pt]C
C(C[Pt])C.[Pt].[Pt]>>C(C[Pt])([Pt])C.[Pt]H
Etc.

Species (55)

C(C)C 3 0
[Pt] 1 0
C([Pt])C 3 1
[Pt]C 2 1
C([Pt])(C)C 4 1
[Pt]H 1 1
C(C[Pt])C 4 1
[Pt]C[Pt] 3 2
C([Pt])([Pt])C 4 2
C(C[Pt])([Pt]) 4 2
C([Pt])([Pt])(C)C 5 2
C(C[Pt])([Pt])C 5 2
C(CC)([Pt])([Pt]) 5 2
C(CC[Pt])([Pt]) 5 2
C([Pt])([Pt])([Pt]) 4 3
C([Pt])([Pt])([Pt])C 5 3
C(C[Pt])([Pt])([Pt]) 5 3
C=C 2 3
Etc.

Reaction Mechanism: State Model



- Reactions proceed from state to state
- “Species” = States
- Each state contains all the reactants or products
- Limited to the proposed reaction paths... Might not be comprehensive

Statistical Thermodynamics

The collective body of statistical mechanics is based on two main postulates:

Equal a priori probability postulate

- All microstates of the system of volume V that have the same energy and the same number of particles are equally probable

Ergodic hypothesis

- The (long) time average of any mechanical property in a macroscopic system is equal to the average value of that property over all the microscopic states of the system, each weighted with its probability of occurrence, provided that the microscopic states replicate the thermodynamic state and environment of the actual system

Statistical Thermodynamics:

Partition functions and thermodynamic properties

$$q = \sum_i e^{\frac{-\varepsilon_i}{kT}}$$

For canonical ensemble

$$Q(T, V, N) = \begin{cases} q^N & \text{for distinguishable systems} \\ \frac{q^N}{N!} & \text{for indistinguishable systems} \end{cases}$$

$$Q_{tot} = q_{trans} \cdot q_{rot} \cdot q_{vib} \cdot q_{elect} \cdot q_{nuclear}$$

$$U = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V, N}$$

$$H = kT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{V, N} + kTV \left(\frac{\partial \ln Q}{\partial V} \right)_{T, N}$$

$$S = k \ln Q + kT \left(\frac{\partial \ln Q}{\partial T} \right)_{V, N}$$

$$F(N, V, T) = -kT \ln Q(N, V, T)$$

$$\mu_i = -kT \left(\frac{\partial \ln Q}{\partial N_i} \right)_{T, V, N_{j \neq i}}$$

$$C_V = 2kT \left(\frac{\partial \ln Q}{\partial T} \right)_{V, N} + kT^2 \left(\frac{\partial^2 \ln Q}{\partial T^2} \right)_{V, N}$$

$$C_P = C_V - T \frac{\left(\frac{\partial P}{\partial T} \right)_V^2}{\left(\frac{\partial P}{\partial V} \right)_T}$$

Statistical Thermodynamics:

Macro thermodynamic properties-Heat Capacity

Linear molecules

$$\frac{C_p}{R} = \underbrace{\sum_i \left(\frac{\Theta_{v,i}}{T} \right)^2 \frac{e^{-\Theta_{v,i}/T}}{(1 - e^{-\Theta_{v,i}/T})^2}}_{\text{Vibrational contribution}} + \underbrace{\frac{3}{2}}_{\text{Rotational contribution}} + \underbrace{1}_{\text{Translational contribution}} + \underbrace{1}_{C_v \text{ to } C_p}$$

$$C_v = C_p + R$$

$$\frac{C_v}{R} = \frac{C_p}{R} + 1$$

Non-linear molecules

$$\frac{C_p}{R} = \underbrace{\sum_i \left(\frac{\Theta_{v,i}}{T} \right)^2 \frac{e^{-\Theta_{v,i}/T}}{(1 - e^{-\Theta_{v,i}/T})^2}}_{\text{Vibrational contribution}} + \underbrace{\frac{3}{2}}_{\text{Rotational contribution}} + \underbrace{\frac{3}{2}}_{\text{Translational contribution}} + \underbrace{1}_{C_v \text{ to } C_p}$$

$$C_v = C_p + R$$

$$\frac{C_v}{R} = \frac{C_p}{R} + 1$$

$$\Theta_{v,i} = \frac{\nu_i h}{k_B}; \nu_i = i^{\text{th}} \text{ vibration frequency [s}^{-1}\text{]}$$

Statistical Thermodynamics:

Macro thermodynamic properties-Enthalpy

Linear molecules

$$\frac{H}{RT} = \underbrace{\sum_i \frac{\Theta_{v,i}}{2T} + \frac{\Theta_{v,i}}{T} \frac{e^{-\Theta_{v,i}/T}}{1 - e^{-\Theta_{v,i}/T}}}_{\text{Vibrational contribution}} + \underbrace{\frac{3}{2}}_{\text{Rotational contribution}} + \underbrace{1}_{\text{Translational contribution}} + \underbrace{RT}_{\text{Convert U to H } H = U + PV} + \underbrace{E_{\text{zero point}} + E_{\text{dft total}}}_{\text{Energies from DFT}}$$

Non-linear molecules

$$\frac{H}{RT} = \underbrace{\sum_i \frac{\Theta_{v,i}}{2T} + \frac{\Theta_{v,i}}{T} \frac{e^{-\Theta_{v,i}/T}}{1 - e^{-\Theta_{v,i}/T}}}_{\text{Vibrational contribution}} + \underbrace{\frac{3}{2}}_{\text{Rotational contribution}} + \underbrace{\frac{3}{2}}_{\text{Translational contribution}} + \underbrace{RT}_{\text{Convert U to H } H = U + PV} + \underbrace{E_{\text{zero point}} + E_{\text{dft total}}}_{\text{Energies from DFT}}$$

$$\Theta_{v,i} = \frac{\nu_i h}{k_B}; \nu_i = i^{\text{th}} \text{ vibration frequency } [s^{-1}]$$

Statistical Thermodynamics:

Macro thermodynamic properties-Entropy

Linear molecules

$$\frac{S}{R} = \underbrace{\sum_i \frac{\Theta_{v,i}}{T} \frac{e^{-\Theta_{v,i}/T}}{1 - e^{-\Theta_{v,i}/T}} - \ln(1 - e^{-\Theta_{v,i}/T})}_{\text{Vibrational contribution}} + \underbrace{1 + \ln \frac{T}{\sigma \Theta_r}}_{\text{Rotational contribution}} + \underbrace{\frac{5}{2} + \ln \left[\left(\frac{2\pi \sum_i h \nu_i k_B T}{h^2} \right)^{\frac{3}{2}} \frac{1}{P} \right]}_{\text{Translational contribution}}$$

Non-linear molecules

$$\frac{S}{R} = \underbrace{\sum_i \frac{\Theta_{v,i}}{T} \frac{e^{-\Theta_{v,i}/T}}{1 - e^{-\Theta_{v,i}/T}} - \ln(1 - e^{-\Theta_{v,i}/T})}_{\text{Vibrational contribution}} + \underbrace{\frac{3}{2} + \ln \left(\frac{\sqrt{\pi}}{\sigma} \sqrt{\frac{T^3}{\Theta_x \Theta_y \Theta_z}} \right)}_{\text{Rotational contribution}} + \underbrace{\frac{5}{2} + \ln \left[\left(\frac{2\pi \sum_i m_i k_B T}{h^2} \right)^{\frac{3}{2}} \frac{1}{P} \right]}_{\text{Translational contribution}}$$

$$\Theta_{v,i} = \frac{v_i h}{k_B}; \quad v_i = i^{\text{th}} \text{ vibrational frequency } [s^{-1}]$$

$$\Theta_k = \frac{8\pi^2 I_k k_B}{h^2}; \quad I_k = \text{moment of inertia in the k-plane}$$

Transition State Theory:

Reaction barrier and Pre-exponential factor

Reaction Barrier

$$E_a = E^\ddagger - E^{IS}$$

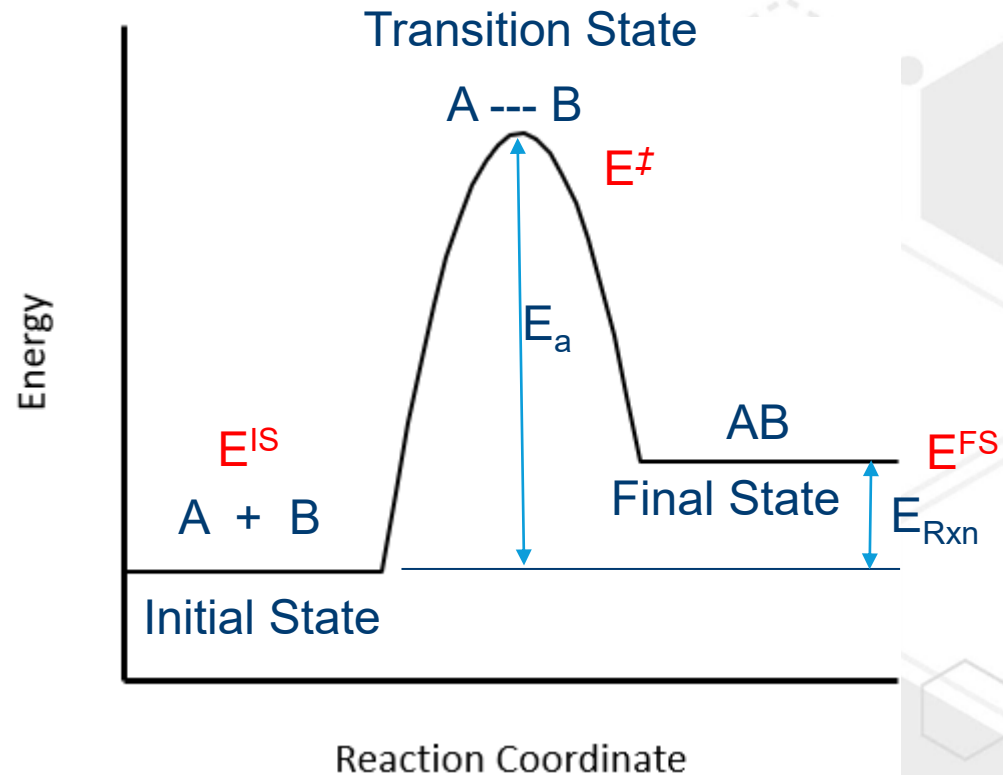
$$E_a = H^\ddagger - H^{IS}$$

$$E_a = G^\ddagger - G^{IS} \text{ Account for both enthalpic and entropic}$$

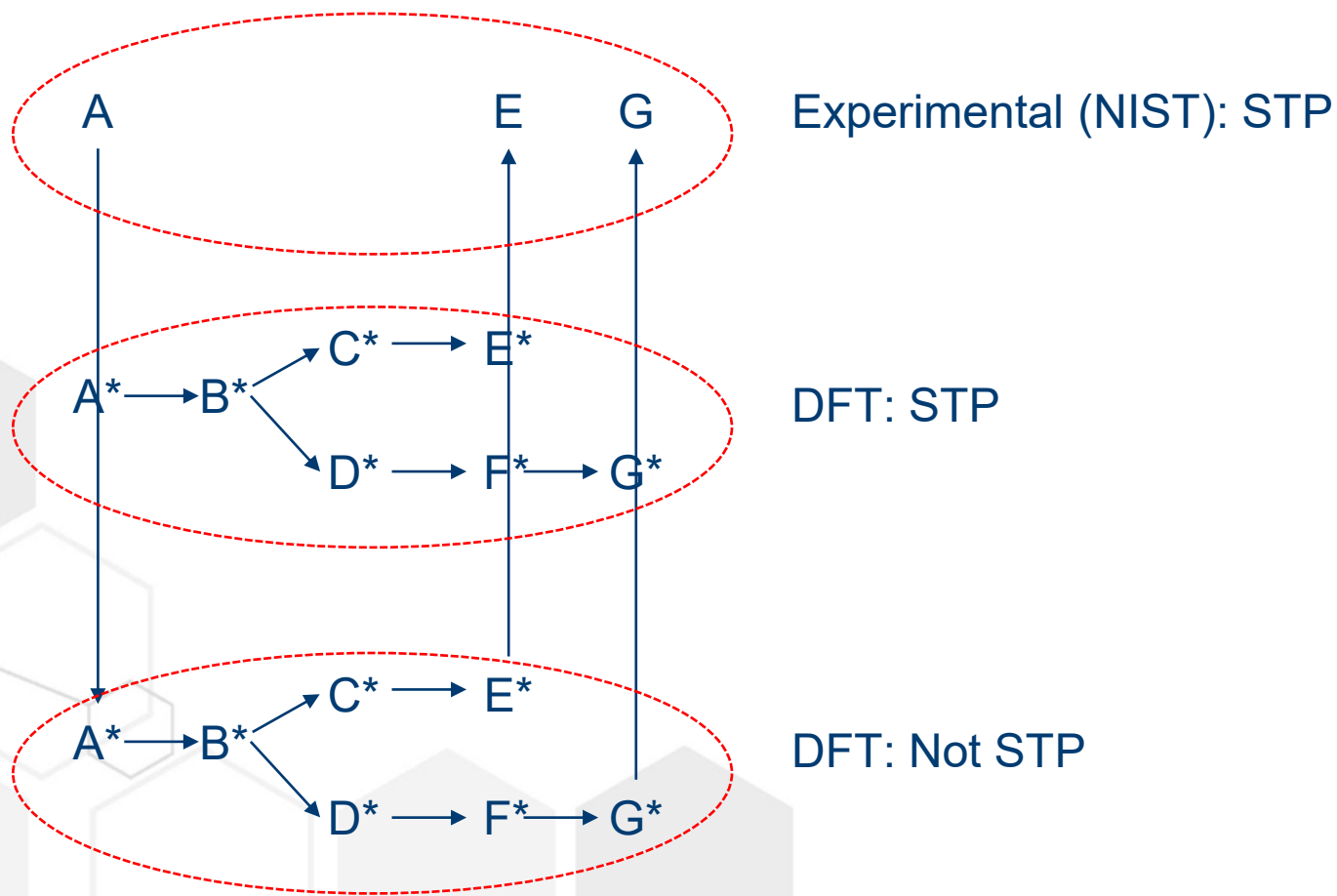
Pre-exponential factor

$$A = \frac{k_B T}{h} \exp(-\Delta S^\ddagger)$$

$$A = \frac{k_B T}{h} \frac{q^\ddagger}{\prod q_{i,IS}}$$



Miscellaneous: Re-referencing



- DFT derived thermochemistry is not at standard conditions
 - Misstates energy
- Need to atomistically adjust DFT derived thermochemistry to account for:
 - Standard temperature
 - Atomistic formation energies
 - Error in DFT
- Methods:
 - Use known adsorption energies regressed to constituent atoms to shift DFT data
 - Use DFT computed vs experimental thermochemistry for reference gases regressed to constituent atoms to shift DFT data

Miscellaneous: Re-referencing

Name	NIST Enthalpy (kcal/mol)
CH ₄	-17.89
CH ₃ OH	-49.0
CH ₃ CH ₃	-20.0
CH ₂ CH ₂	12.54
CH ₃ CH ₂ OH	-56.0
H ₂ O	-57.798
CO ₂	-94.051
H ₂	0.0

$$\varepsilon_i = H_{i,NIST} - H_{i,DFT}$$

$$\begin{bmatrix} 1 & 4 & 0 \\ 1 & 4 & 1 \\ 2 & 6 & 0 \\ 2 & 4 & 0 \\ 3 & 6 & 1 \\ 0 & 2 & 1 \\ 1 & 0 & 2 \\ 0 & 2 & 0 \end{bmatrix}$$

C H O

$$\cdot \begin{bmatrix} C \\ H \\ O \end{bmatrix} =$$

$$\begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \\ \varepsilon_7 \\ \varepsilon_8 \end{bmatrix}$$

\Rightarrow

$$\begin{bmatrix} C \\ H \\ O \end{bmatrix} =$$

Pseudo-inverse

$$\begin{bmatrix} 1 & 4 & 0 \\ 1 & 4 & 1 \\ 2 & 6 & 0 \\ 2 & 4 & 0 \\ 3 & 6 & 1 \\ 0 & 2 & 1 \\ 1 & 0 & 2 \\ 0 & 2 & 0 \end{bmatrix}^+$$

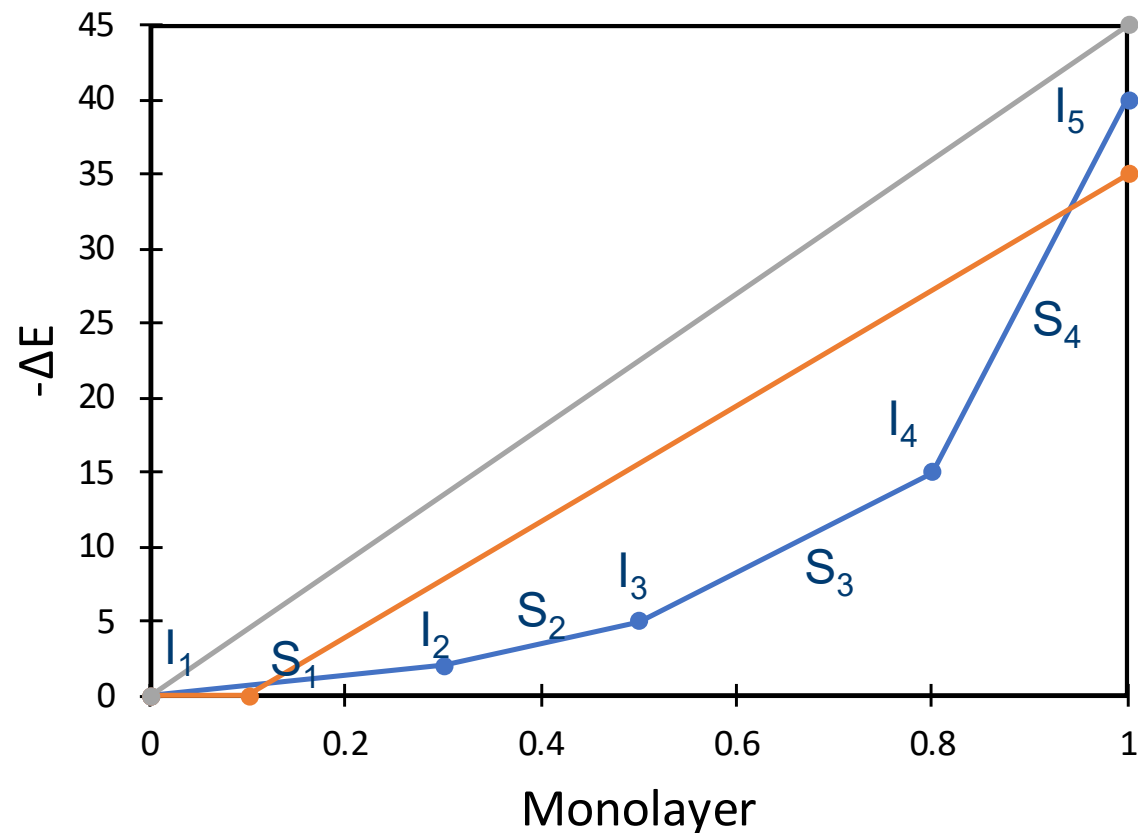
\cdot

$$\begin{bmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \\ \varepsilon_7 \\ \varepsilon_8 \end{bmatrix}$$

Apparent contribution
to error per atom

Miscellaneous: Lateral Interactions

- Multiple species adsorbed on the surface of a heterogeneous catalyst can impact their energy
- Some modeling tools (KMC) that track the position of all surface species provide multiple energies for all species based on 1st, 2nd, nth nearest neighbors.
- Mean field model do not track exact adsorbate positions must rely on average surface coverages.
- These corrections are often critical to model accuracy by not overstating adsorbate coverages.
- These are expressed as the impact pairs of adsorbates have on each other using one or more linear relationships



Miscellaneous: Empirical Relationships

- Simpler representation of thermodynamic property as function of temperature
- Fitted using statistical thermodynamic or experimental data
- Required by many material modeling programs

Shomate Polynomials (NIST)

$$C_p^o = A + Bt + Ct^2 + Dt^3 + E\frac{1}{t^2}$$

$$H^o - H_{298.15}^o = At + B\frac{t^2}{2} + C\frac{t^3}{3} + D\frac{t^4}{4} - E\frac{1}{t} + F - H$$

$$S^o = A\ln(t) + Bt + C\frac{t^2}{2} + D\frac{t^3}{3} - E\frac{1}{2t^2} + G$$

$$t = \frac{T}{1000 \text{ K}}$$

NASA Polynomials (7-coefficient)

$$\frac{C_p}{R} = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4$$

$$\frac{H}{RT} = a_1 + a_2\frac{T}{2} + a_3\frac{T^2}{3} + a_4\frac{T^3}{4} + a_5\frac{T^4}{5} + a_6\frac{1}{T}$$

$$\frac{S}{R} = a_1\ln T + a_2T + a_3\frac{T^2}{2} + a_4\frac{T^3}{3} + a_5\frac{T^4}{4} + a_7$$

NASA Polynomials (9-coefficient)

$$\frac{C_p}{R} = a_1T^{-2} + a_2T^{-1} + a_3 + a_4T + a_5T^2 + a_6T^3 + a_7T^4$$

$$\frac{H}{RT} = -a_1T^{-2} + a_2\frac{\ln T}{T} + a_3 + \frac{a_4}{2}T + \frac{a_5}{3}T^2 + \frac{a_6}{4}T^3 + \frac{a_7}{5}T^4 + \frac{a_8}{T}$$

$$\frac{S}{R} = -\frac{a_1}{2}T^{-2} - a_2T^{-1} + a_3\ln T + a_4T + \frac{a_5}{2}T^2 + \frac{a_6}{3}T^3 + \frac{a_7}{4}T^4 + a_9$$

Interesting pMuTT and pGrAdd Examples

- Error propagation in kinetic models
- Dynamic catalysis

Error Propagation in Kinetic Models¹

Motivation:

- Kinetic model parameter uncertainty can result in uncertainty in model quantities of interest (Reaction rates, apparent activation energy, reaction orders, etc.)
- Thermodynamic parameters (and associated kinetic parameters) are a key source of uncertainty in models
- **Challenge:** Can we use a distribution of thermodynamic parameter uncertainty to model quantity of interest uncertainty understanding that thermodynamic values are correlated between molecules?

(1) Wittreich, G. R.; et al. Uncertainty Quantification and Error Propagation in the Enthalpy and Entropy of Surface Reactions Arising from a Single DFT Functional. *J. Phys. Chem. C* **2021**, 125 (33), 18187–18196.

Error Propagation in Kinetic Models

Approach:

- Since group additivity predicts molecule thermodynamics via groups and those groups are shared among molecules
- Group additivity could allow us to model thermodynamic uncertainty by attributing the uncertainty to groups in a way consistent with the overall model uncertainty
- Develop a probability distribution for groups
- Select a demonstration mechanism
- Develop a process to parameterize a large number of MKM's with thermodynamic and kinetic properties from the distribution

Error Propagation in Kinetic Models

$$\mathbf{Y}_P = \mathbf{X}_P \hat{\boldsymbol{\beta}} + \boldsymbol{\varepsilon}_{\text{Fit}} + \hat{\boldsymbol{\varepsilon}}_{\text{Random}} + \boldsymbol{\varepsilon}_{\text{Random Estimation}} ; \quad \boldsymbol{\varepsilon}_{\text{Fit,RE}} = \boldsymbol{\varepsilon}_{\text{Fit}} + \boldsymbol{\varepsilon}_{\text{Random Estimation}}$$

$$\text{Var}(\mathbf{Y}_P) = \text{Var}(\mathbf{X}_P \hat{\boldsymbol{\beta}} + \hat{\boldsymbol{\varepsilon}}_{\text{Random}} + \boldsymbol{\varepsilon}_{\text{Fit,RE}}) = \text{Var}(\mathbf{X}_P \hat{\boldsymbol{\beta}} + \boldsymbol{\varepsilon}_{\text{Fit,RE}}) + \text{Var}(\hat{\boldsymbol{\varepsilon}}_{\text{Random}})$$

$$\text{Var}(\mathbf{Y}_P) = \underbrace{\text{Var}(\mathbf{X}_P \hat{\boldsymbol{\beta}} + \boldsymbol{\varepsilon}_{\text{Fit,RE}})}_{\text{Var}(\hat{\mathbf{Y}}_P)} + \underbrace{\sigma^2 \mathbf{I}_{N_P}}_{\text{Var}(\hat{\boldsymbol{\varepsilon}}_{\text{Random}})}$$

$$\mathbf{P}(\mathbf{Y}_P | \mathbf{X}_T, \mathbf{Y}_T, \mathbf{X}_P) \approx \mathcal{N}\left(\mathbf{E}(\mathbf{X}_P \hat{\boldsymbol{\beta}} + \hat{\boldsymbol{\varepsilon}}_{\text{Random}} + \boldsymbol{\varepsilon}_{\text{Fit,RE}}), \text{Var}(\mathbf{X}_P \hat{\boldsymbol{\beta}} + \hat{\boldsymbol{\varepsilon}}_{\text{Random}} + \boldsymbol{\varepsilon}_{\text{Fit,RE}})\right)$$

$$\mathbf{P}(\mathbf{Y}_P | \mathbf{X}_T, \mathbf{Y}_T, \mathbf{X}_P) \approx \mathcal{N}\left(\underbrace{\mathbf{E}(\mathbf{X}_P \hat{\boldsymbol{\beta}})}_{\mathbf{X}_P \hat{\boldsymbol{\beta}}}, \underbrace{\mathbf{E}(\hat{\boldsymbol{\varepsilon}}_{\text{Random}} + \boldsymbol{\varepsilon}_{\text{Fit,RE}})}_0, \underbrace{\text{Var}(\mathbf{X}_P \hat{\boldsymbol{\beta}} + \boldsymbol{\varepsilon}_{\text{Fit,RE}})}_{\text{Var}(\hat{\mathbf{Y}}_P) = \hat{\sigma}^2 \mathbf{H}_P} + \underbrace{\text{Var}(\hat{\boldsymbol{\varepsilon}}_{\text{Random}})}_{\hat{\sigma}^2 \mathbf{I}_{N_P}}\right)$$

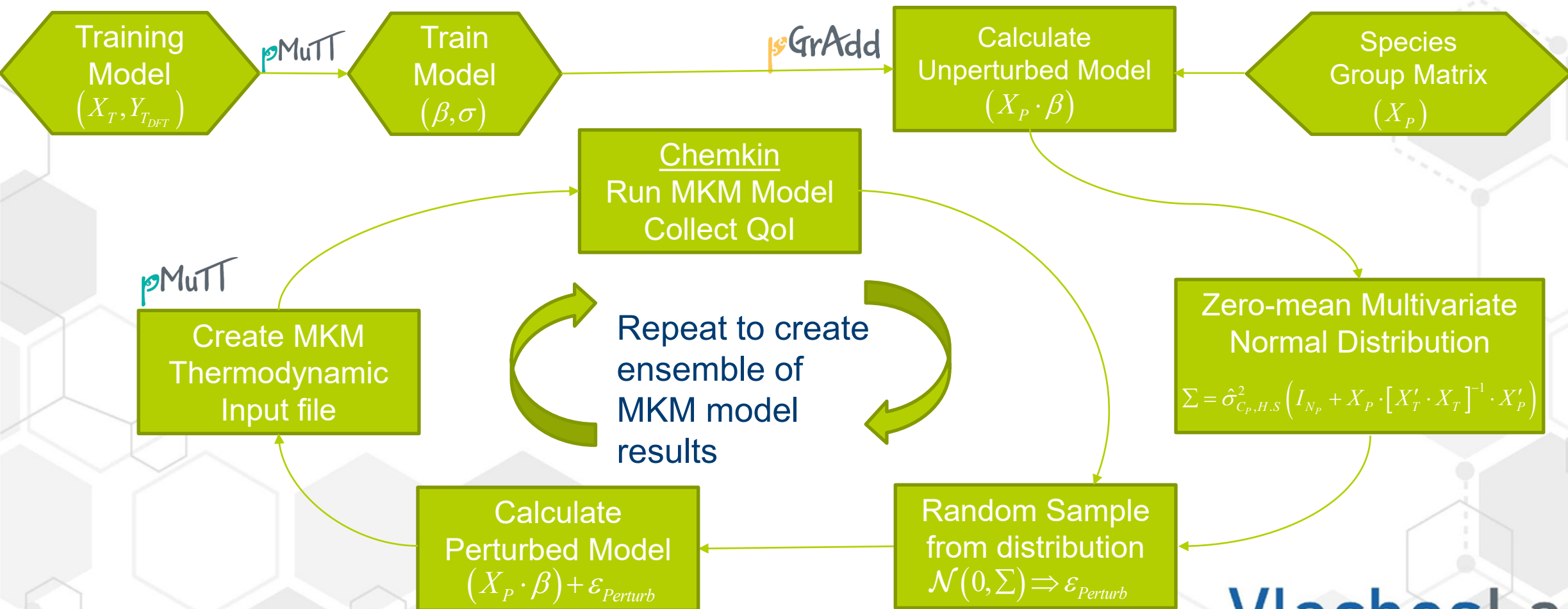
Covariance is zero for independent distributions

$$\mathbf{P}(\mathbf{Y}_P | \mathbf{X}_T, \mathbf{Y}_T, \mathbf{X}_P) \approx \mathcal{N}(\mathbf{X}_P \hat{\boldsymbol{\beta}}, \hat{\sigma}^2 \mathbf{H}_P + \hat{\sigma}^2 \mathbf{I}_{N_P})$$

$$\mathbf{P}(\mathbf{Y}_P | \mathbf{X}_T, \mathbf{Y}_T, \mathbf{X}_P) \approx \mathcal{N}(\mathbf{X}_P \hat{\boldsymbol{\beta}}, \hat{\sigma}^2 (\mathbf{H}_P + \mathbf{I}_{N_P}))$$

$$\mathcal{N}(\mathbf{X}_P \hat{\boldsymbol{\beta}}, \hat{\sigma}^2 (\mathbf{I}_{N_P} + \mathbf{H}_P)) = \underbrace{\mathbf{X}_P \hat{\boldsymbol{\beta}}}_{\text{Unperturbed Values}} + \underbrace{\mathcal{N}(\mathbf{0}_{N_P}, \hat{\sigma}^2 (\mathbf{I}_{N_P} + \mathbf{H}_P))}_{\text{Zero-mean multi-variate normal distribution}}$$

Error Propagation in Kinetic Models

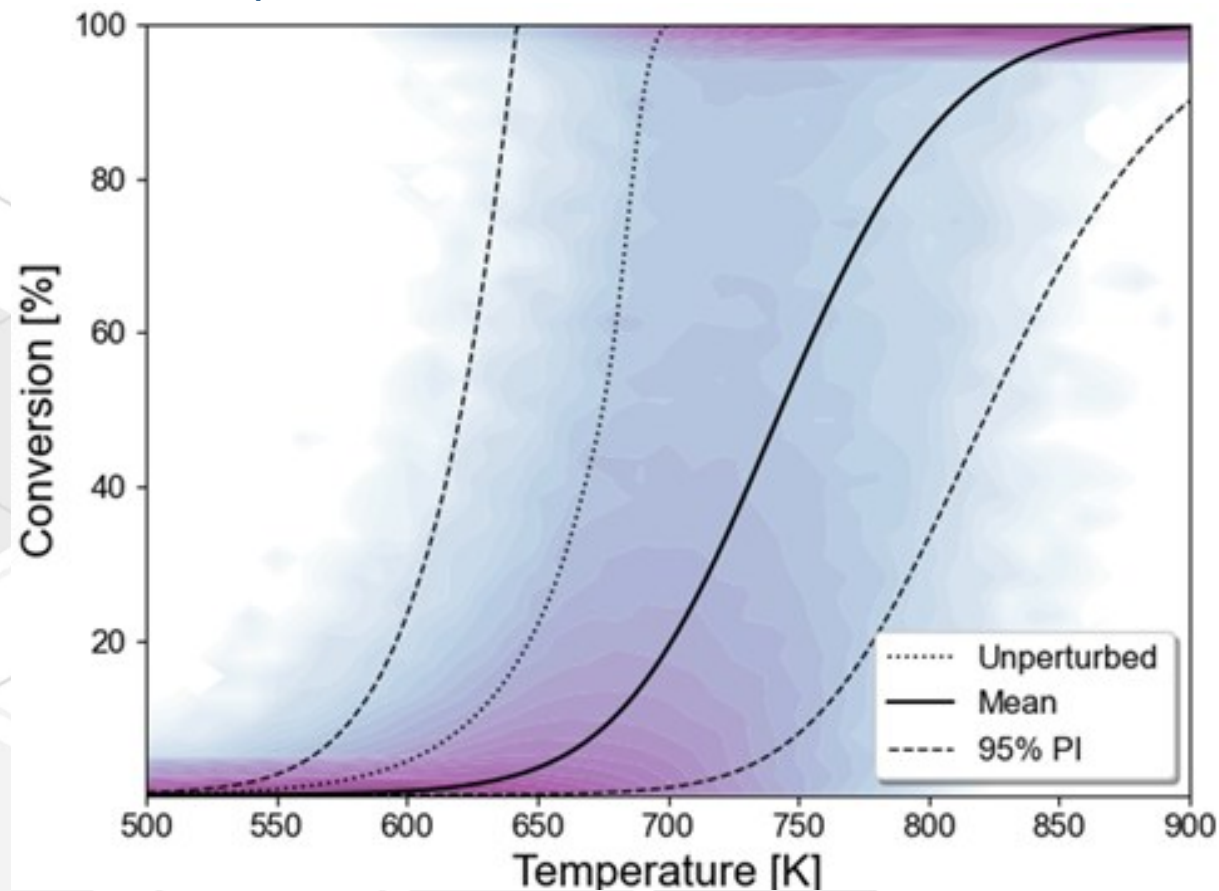


$$\sigma_{\text{enthalpy}} = 4.5 \text{ kcal/mol}$$

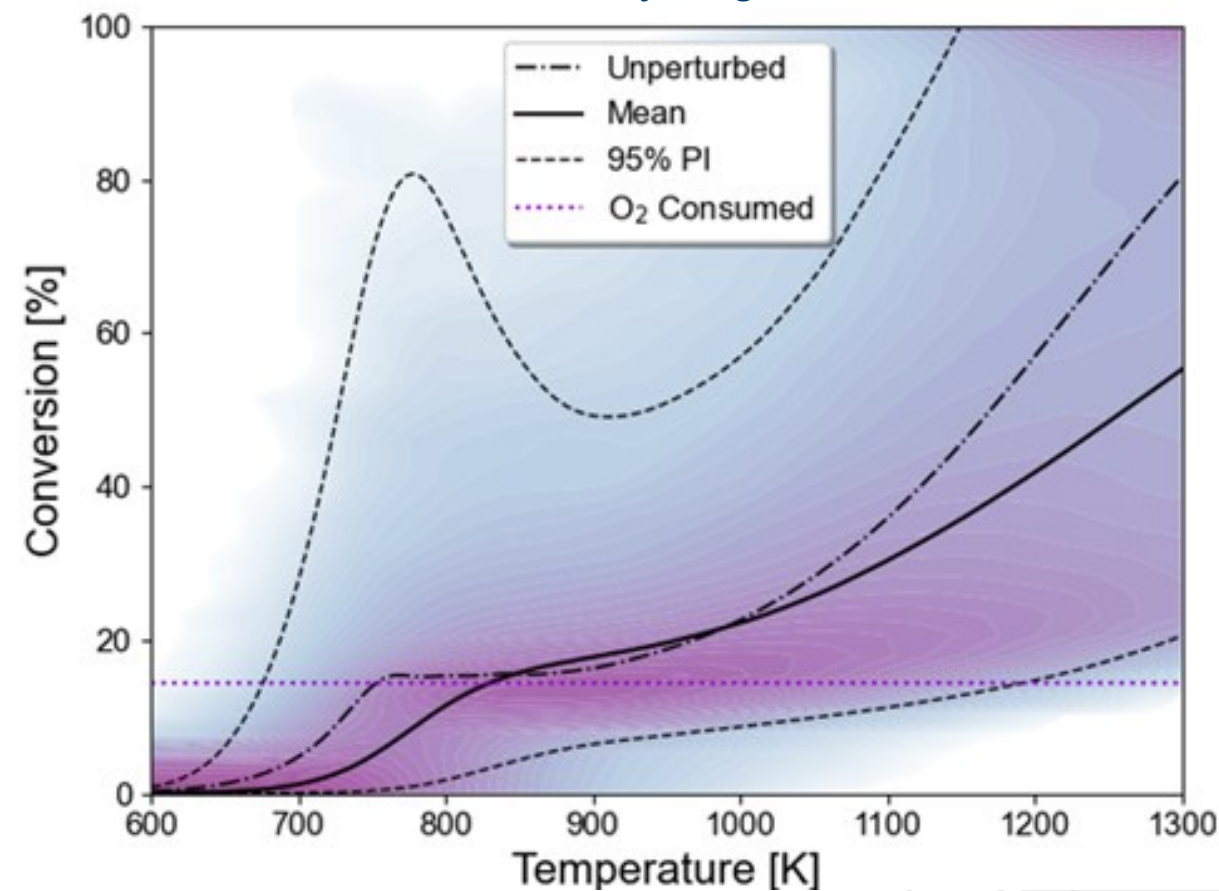
$$\sigma_{\text{entropy}} = 2.1 \text{ cal/mol}\cdot\text{K}$$

Conversion Distribution vs Temperature

Propane Oxidation



Ethane Oxidative Dehydrogenation



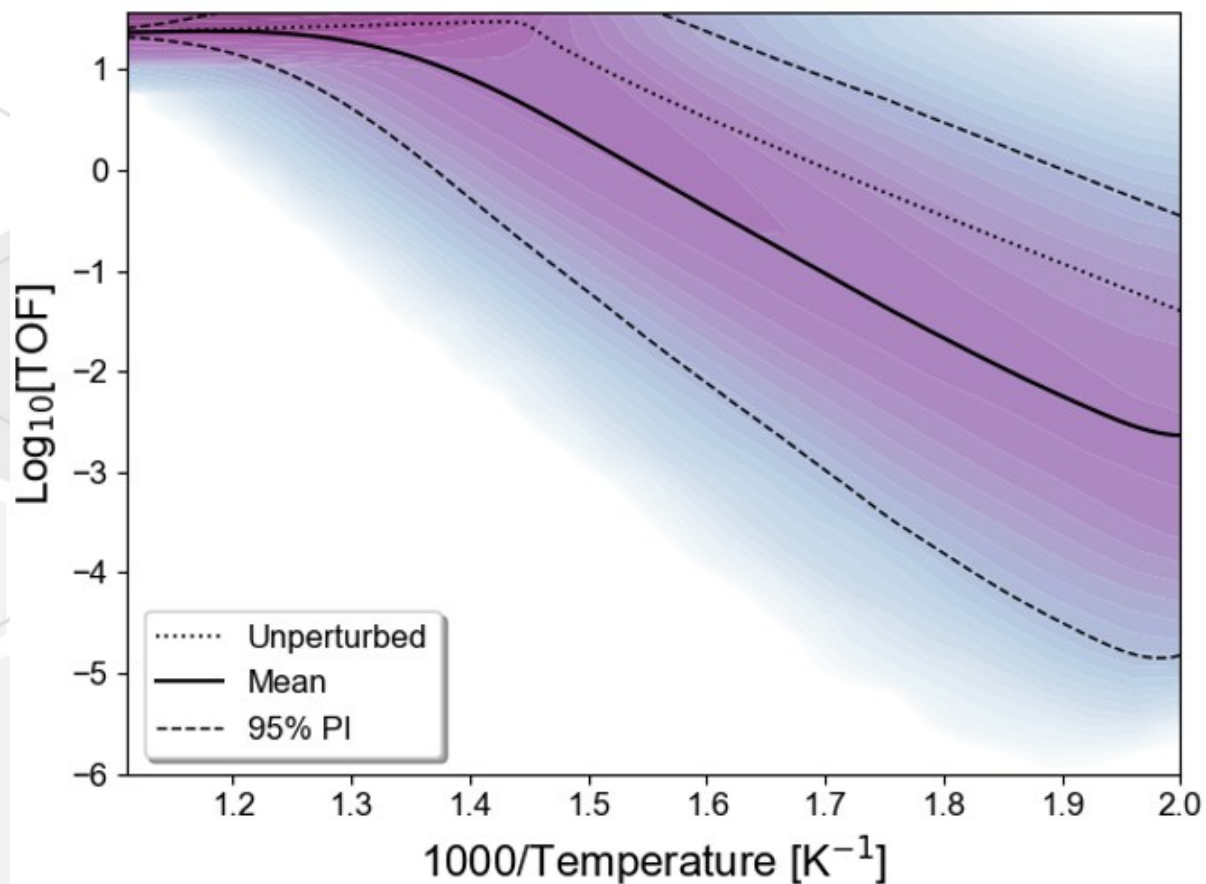
Propane--Feed: 1 mole $\text{CH}_3\text{CH}_2\text{CH}_3$ + 5 moles O_2 (as air), $T = 500\text{-}900 \text{ K}$, $P = 5 \text{ atm}$, $\tau = 235 \text{ msec}$, Pt catalysts at 200 cm^{-1} loading
 Ethane ODH--Feed: 1 mole CH_3CH_3 + 0.5 moles O_2 , $T = 600\text{-}1300 \text{ K}$, $P = 1 \text{ atm}$, $\tau = 20 \text{ msec}$, Pt catalysts at 200 cm^{-1} loading

TOF Distribution vs Temperature

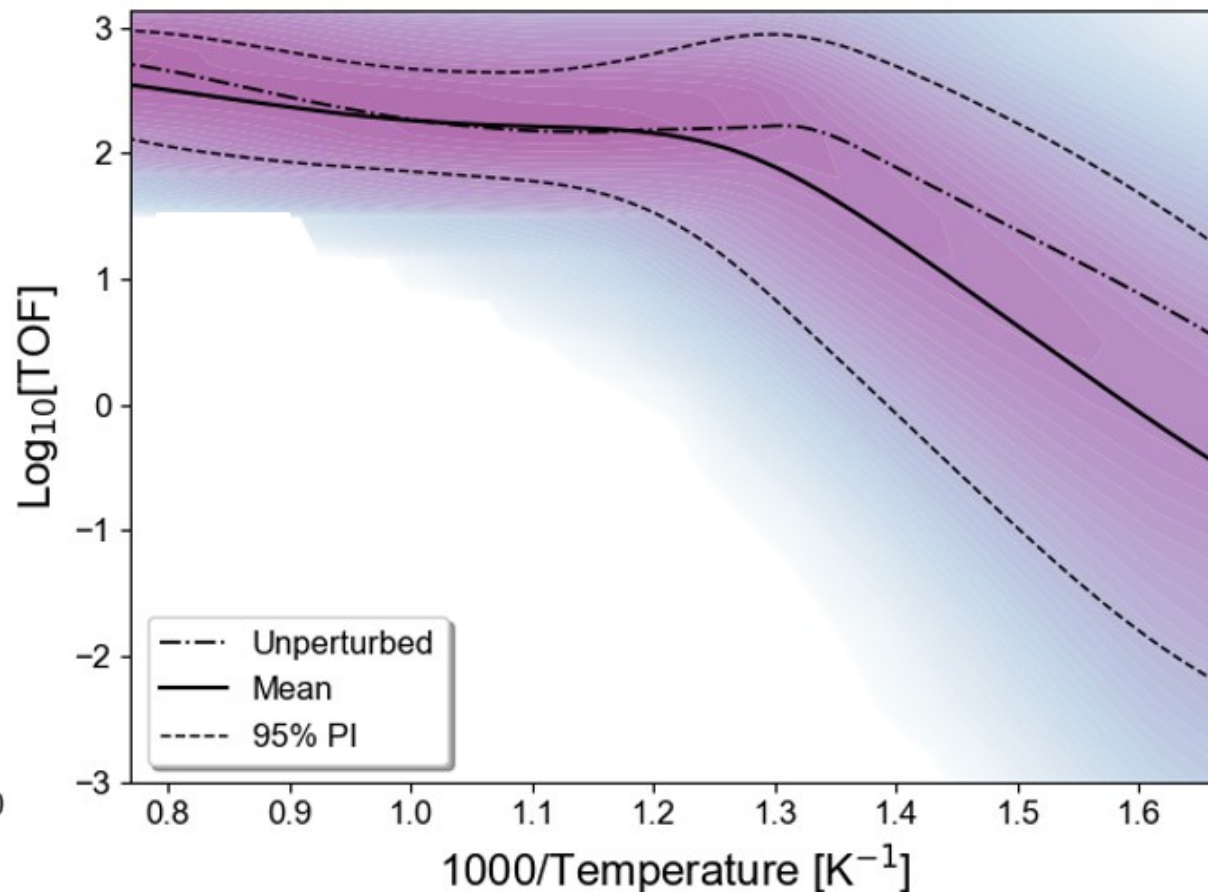
$$\sigma_{\text{enthalpy}} = 4.5 \text{ kcal/mol}$$

$$\sigma_{\text{entropy}} = 2.1 \text{ cal/mol}\cdot\text{K}$$

Propane Oxidation



Ethane Oxidative Dehydrogenation



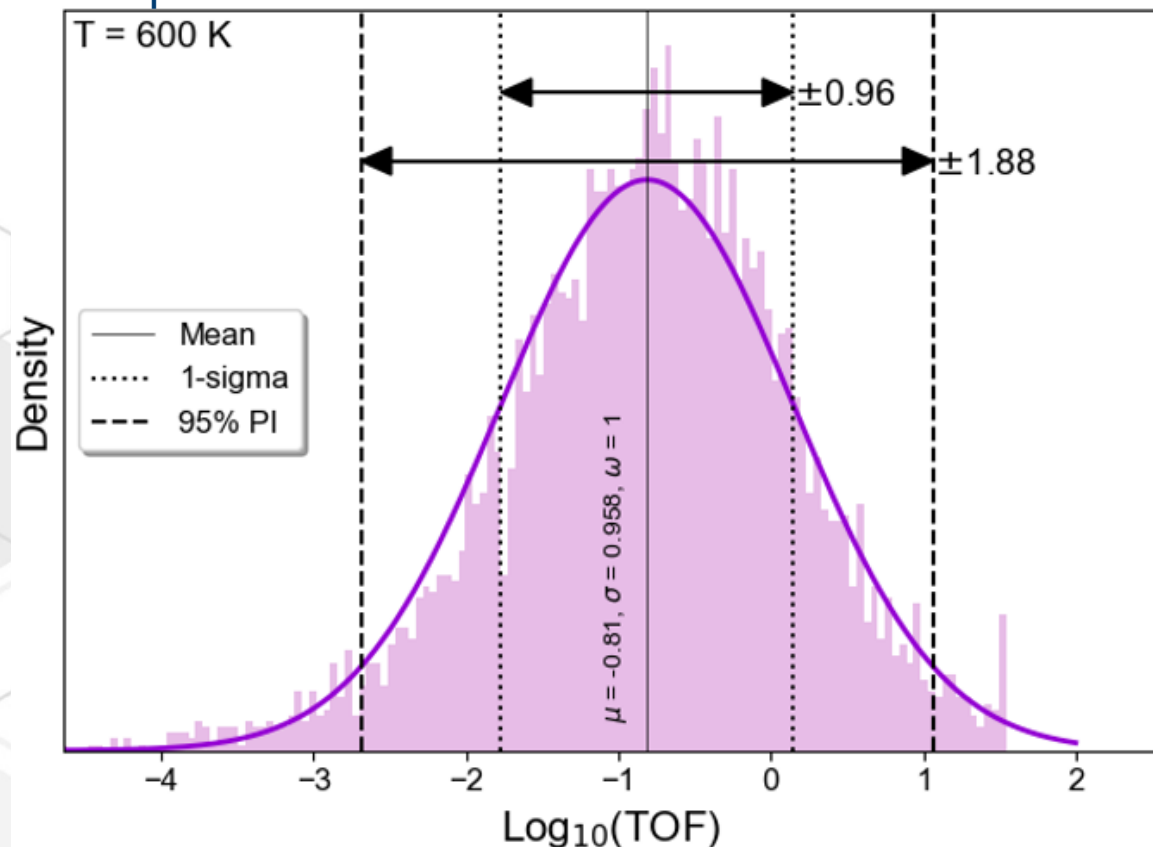
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 Ethane ODH--Feed: 1 mole CH_3CH_3 + 0.5 moles O_2 , $T = 600\text{-}1300 \text{ K}$, $P = 1 \text{ atm}$, $\tau = 20 \text{ msec}$, Pt catalysts at 200 cm^{-1} loading

$$\sigma_{\text{enthalpy}} = 4.5 \text{ kcal/mol}$$

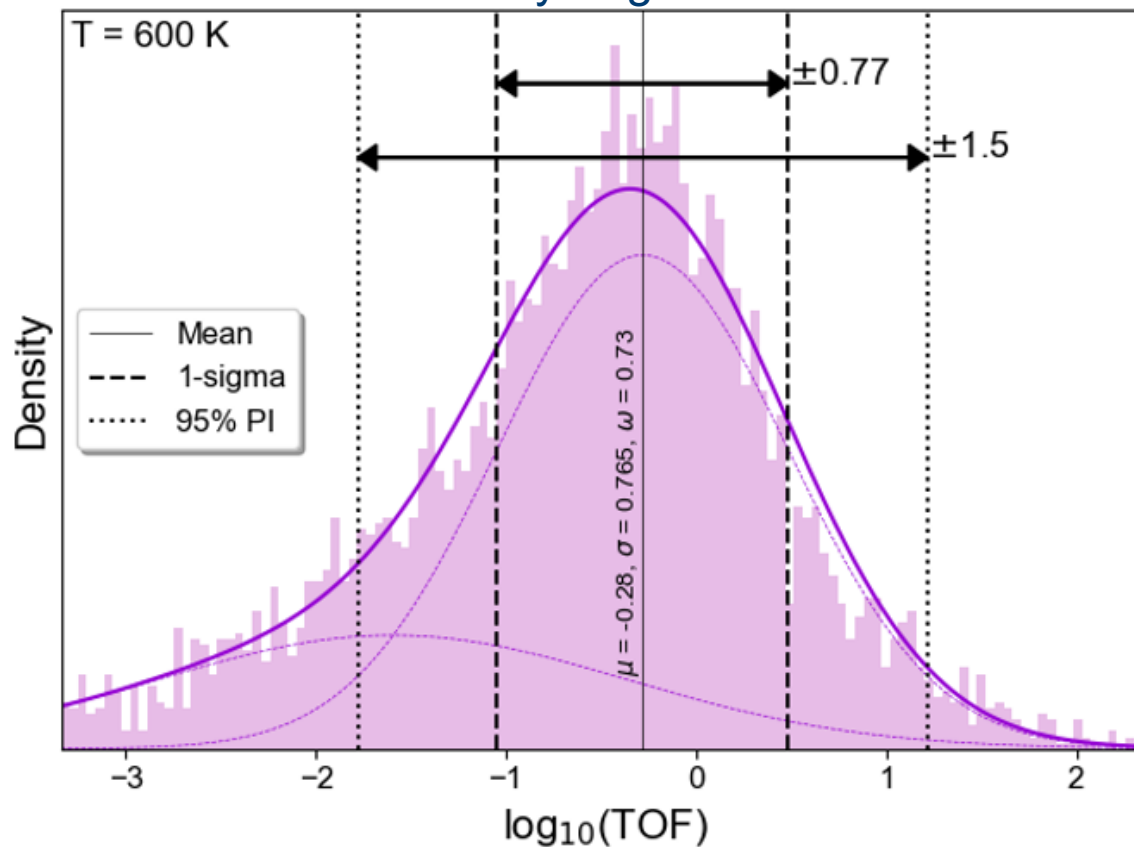
$$\sigma_{\text{entropy}} = 2.1 \text{ cal/mol}\cdot\text{K}$$

TOF Distribution vs Temperature

Propane Oxidation



Ethane Oxidative Dehydrogenation



Reaction rate uncertainty can be as high ± 2.0 orders-of-magnitude for larger molecules (propane) and higher $E_{a,app}$ to ± 1.5 orders-of-magnitude for smaller molecules and lower $E_{a,app}$.

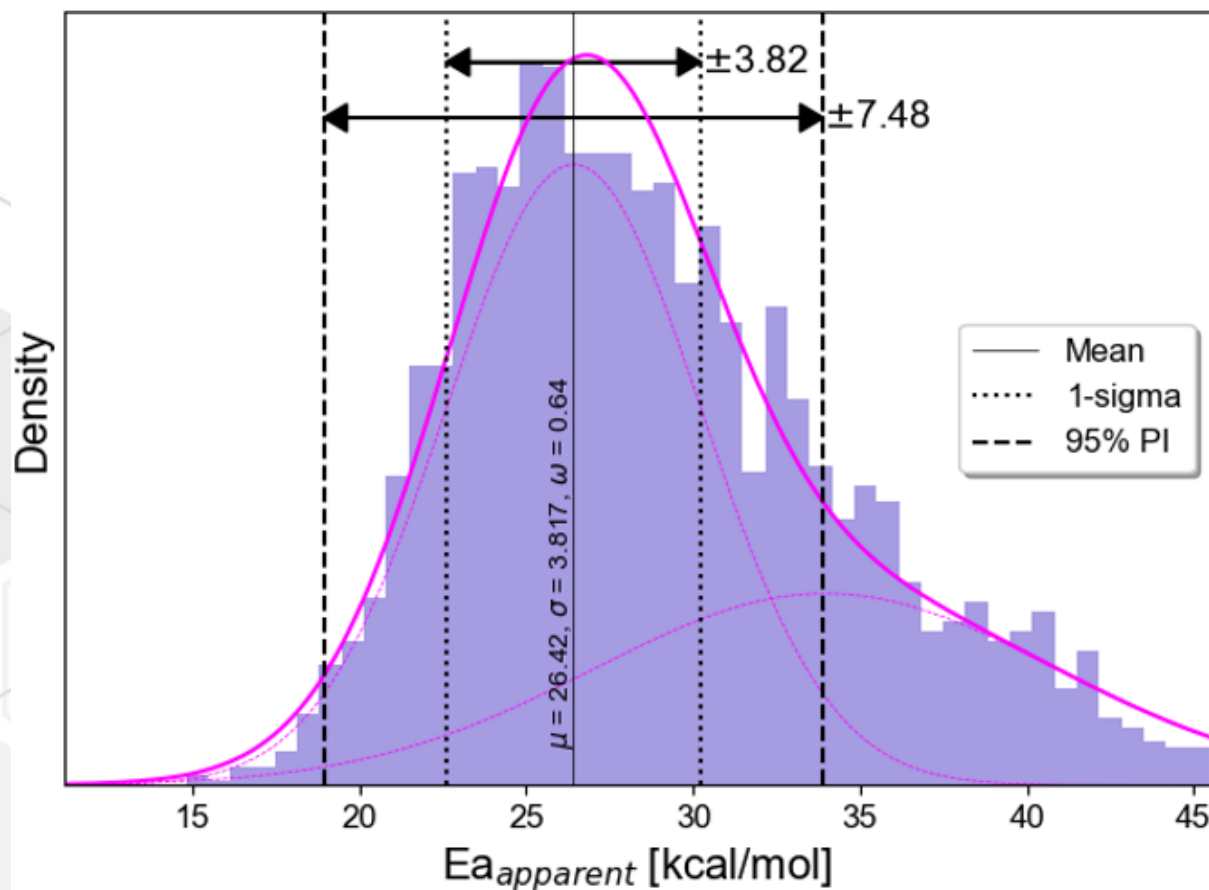
Propane--Feed: 1 mole $\text{CH}_3\text{CH}_2\text{CH}_3$ + 5 moles O_2 (as air), T = 600 K, P = 5 atm, τ = 235 msec, Pt catalysts at 200 cm^{-1} loading
Ethane ODH--Feed: 1 mole CH_3CH_3 + 0.5 moles O_2 , T = 600 K, P = 1 atm, τ = 20 msec, Pt catalysts at 200 cm^{-1} loading

$$\sigma_{\text{enthalpy}} = 4.5 \text{ kcal/mol}$$

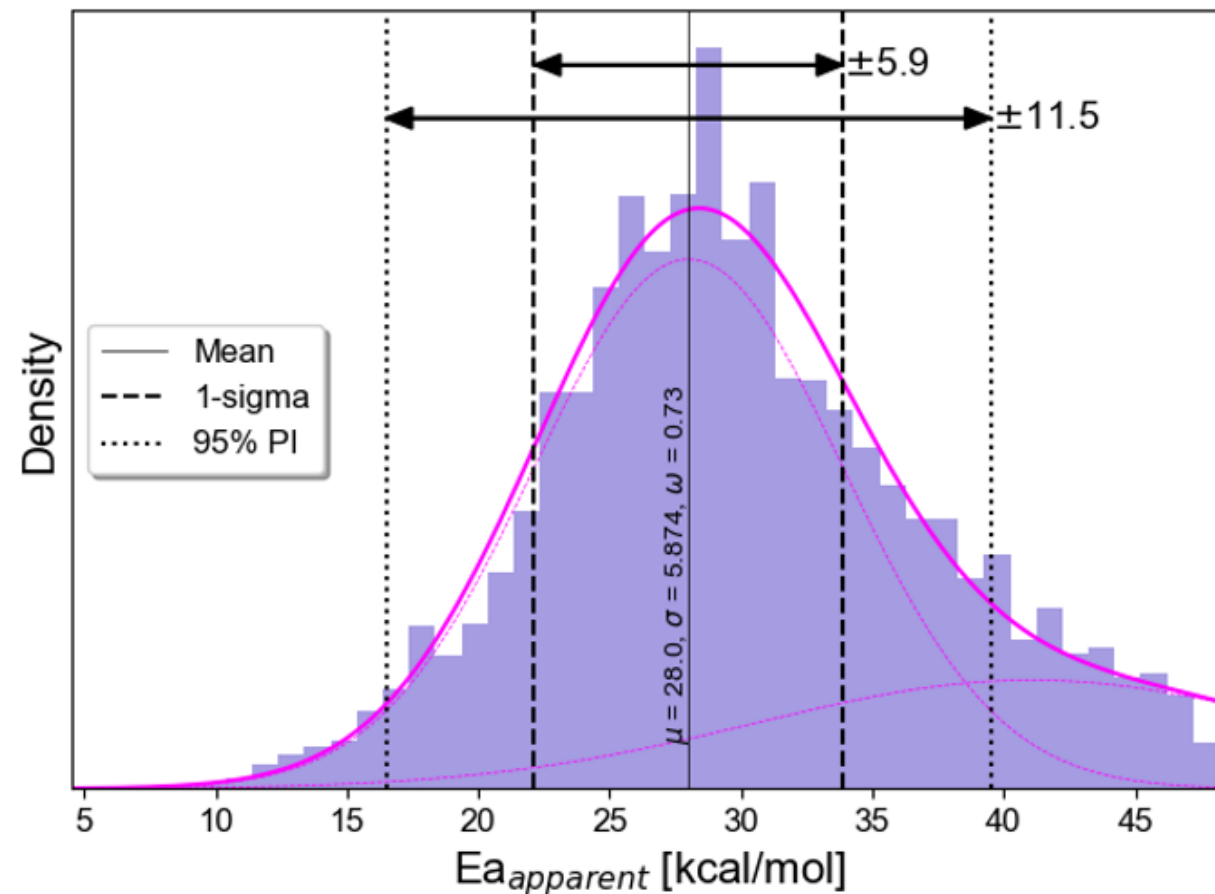
$$\sigma_{\text{entropy}} = 2.1 \text{ cal/mol}\cdot\text{K}$$

Apparent Activation Energy Distribution

Propane Oxidation



Ethane Oxidative Dehydrogenation



Propane--Feed: 1 mole $\text{CH}_3\text{CH}_2\text{CH}_3$ + 5 moles O_2 (as air), $T = 500\text{-}900 \text{ K}$, $P = 5 \text{ atm}$, $\tau = 235 \text{ msec}$, Pt catalysts at 200 cm^{-1} loading

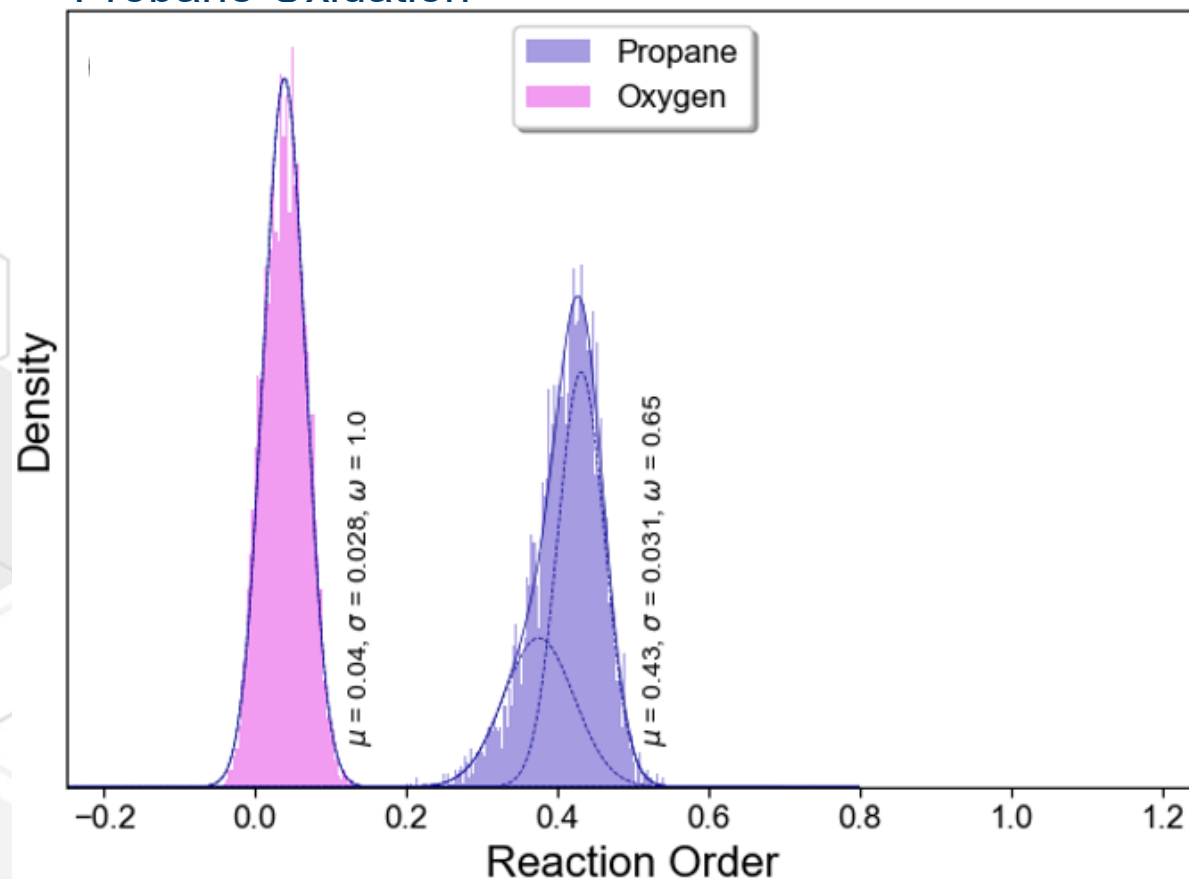
Ethane ODH--Feed: 1 mole CH_3CH_3 + 0.5 moles O_2 , $T = 600\text{-}1300 \text{ K}$, $P = 1 \text{ atm}$, $\tau = 20 \text{ msec}$, Pt catalysts at 200 cm^{-1} loading

$$\sigma_{\text{enthalpy}} = 4.5 \text{ kcal/mol}$$

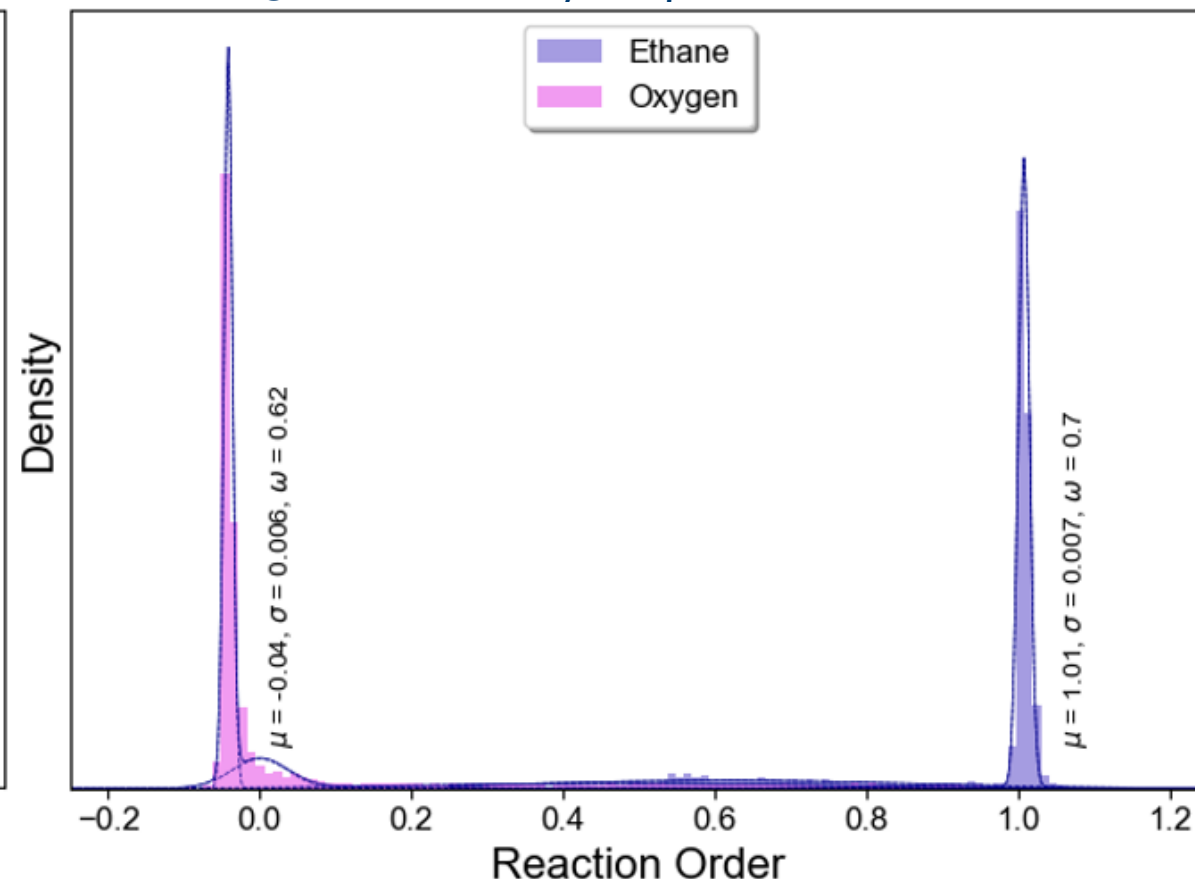
$$\sigma_{\text{entropy}} = 2.1 \text{ cal/mol}\cdot\text{K}$$

Reaction Order Distribution

Propane Oxidation



Ethane Oxidative Dehydrogenation



A more complex multimodal distribution

Propane--Feed: 1 mole $\text{CH}_3\text{CH}_2\text{CH}_3$ + 5 moles O_2 (as air), $T = 500\text{-}900 \text{ K}$, $P = 5 \text{ atm}$, $\tau = 235 \text{ msec}$, Pt catalysts at 200 cm^{-1} loading
 Ethane ODH--Feed: 1 mole CH_3CH_3 + 0.5 moles O_2 , $T = 600\text{-}1300 \text{ K}$, $P = 1 \text{ atm}$, $\tau = 20 \text{ msec}$, Pt catalysts at 200 cm^{-1} loading

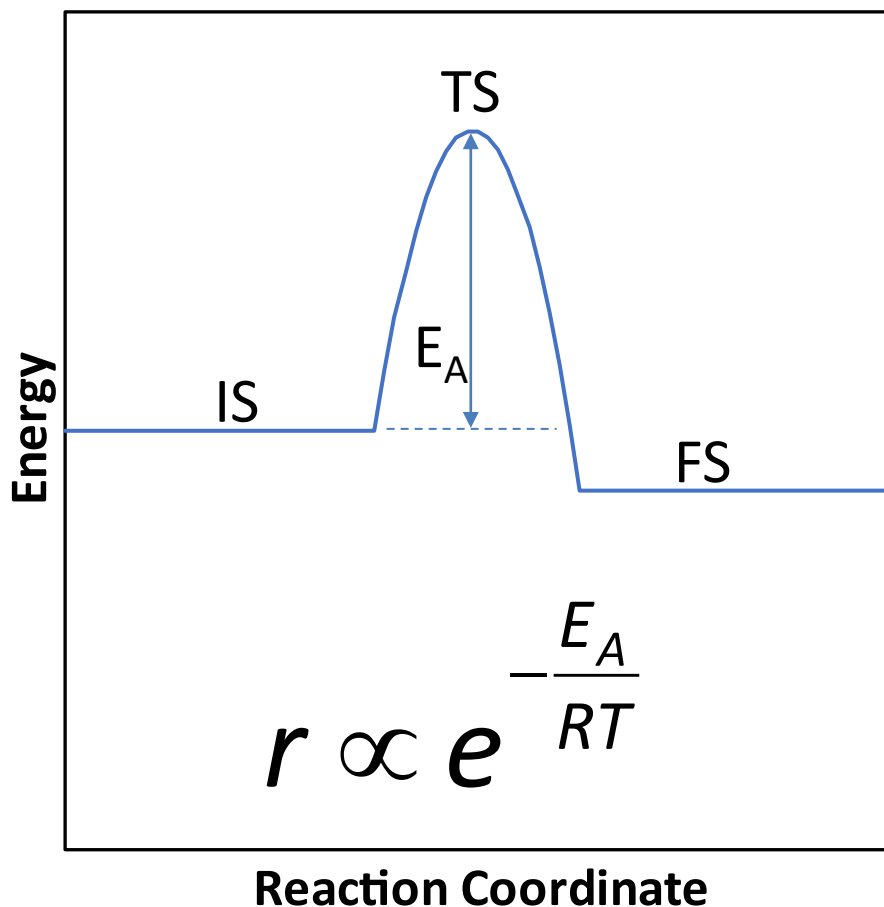
Dynamic Catalysis¹

Motivation:

- Many kinetic models are executed assuming isothermal conditions (or minimal temperature changes) and catalysts are static
- Could we drive catalytic reactions to different rates (beyond Sabatier limits) and beyond equilibrium by rapidly varying key reaction parameters such as temperature or species binding energies?

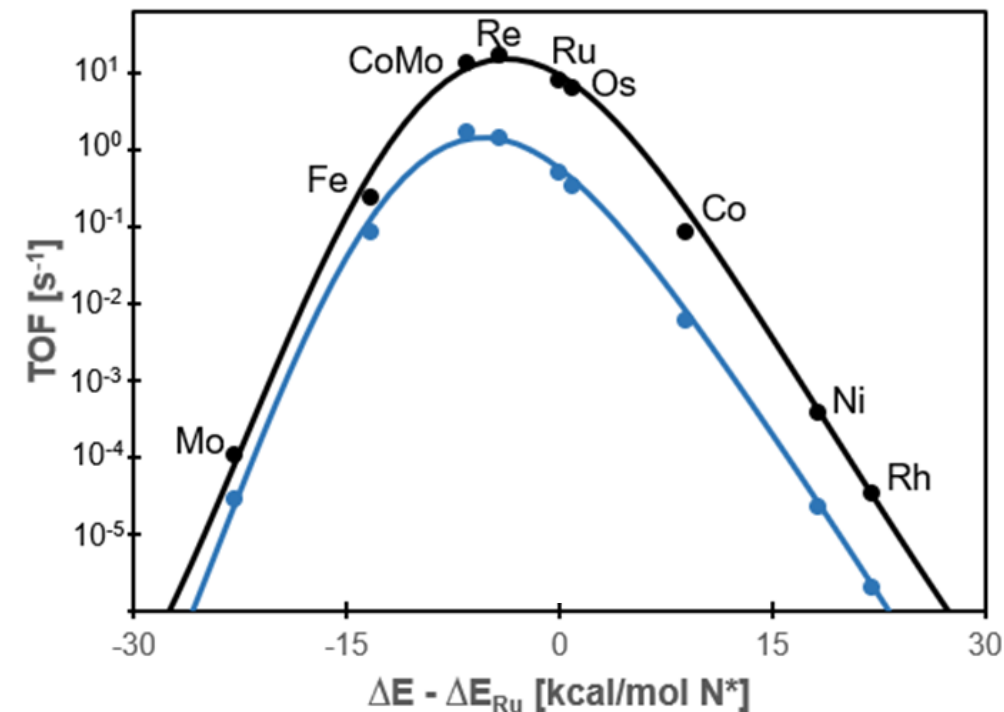
(1) Wittreich, G. R.; et al. Catalytic Resonance of Ammonia Synthesis by Simulated Dynamic Ruthenium Crystal Strain. *Sci. Adv.* **2022**, 8 (4), 1–12.
<https://doi.org/10.1126/sciadv.abl6576>.

Dynamic catalysis: Motivation-Role of catalyst/Sabatier Limit

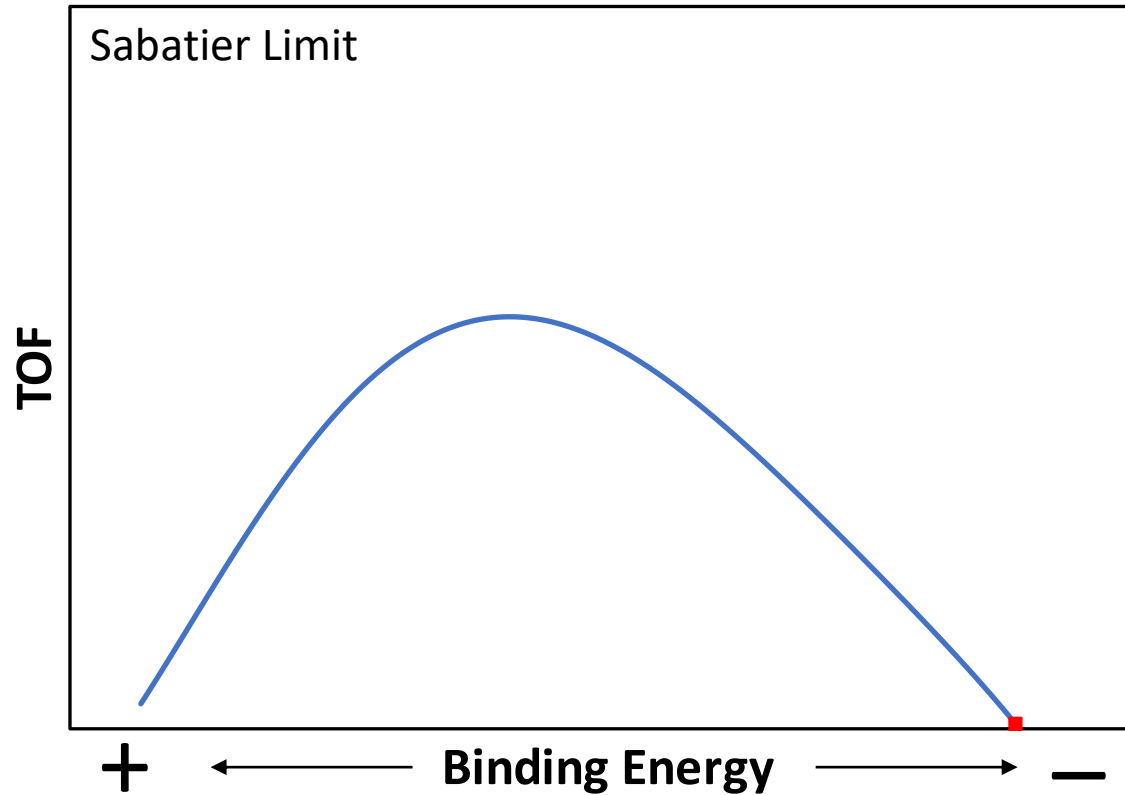


IS = Initial state
TS = Transition state
FS = Final state
 E_A = Reaction barrier

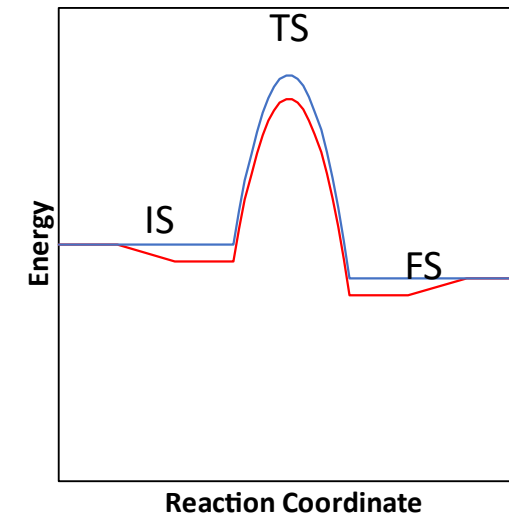
Role of the catalyst is to stabilize the transition state lowering the reaction barrier



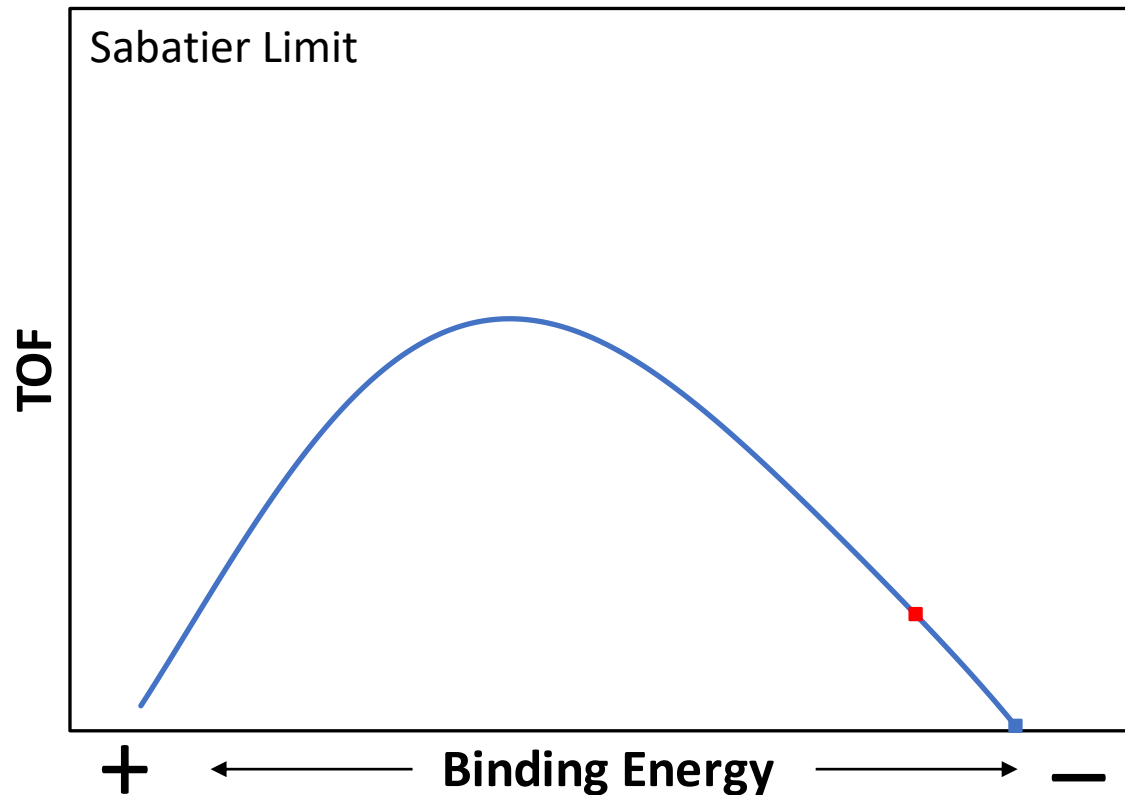
Dynamic catalysis: Motivation-Sabatier limit



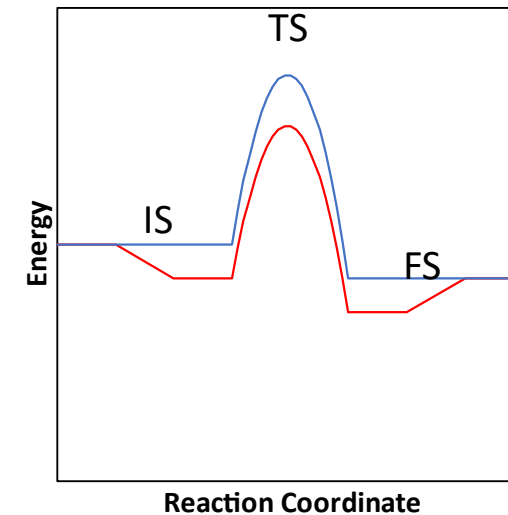
Reactants are adsorbed on the catalyst surface, transition states is stabilized, and the reaction barrier is lowered



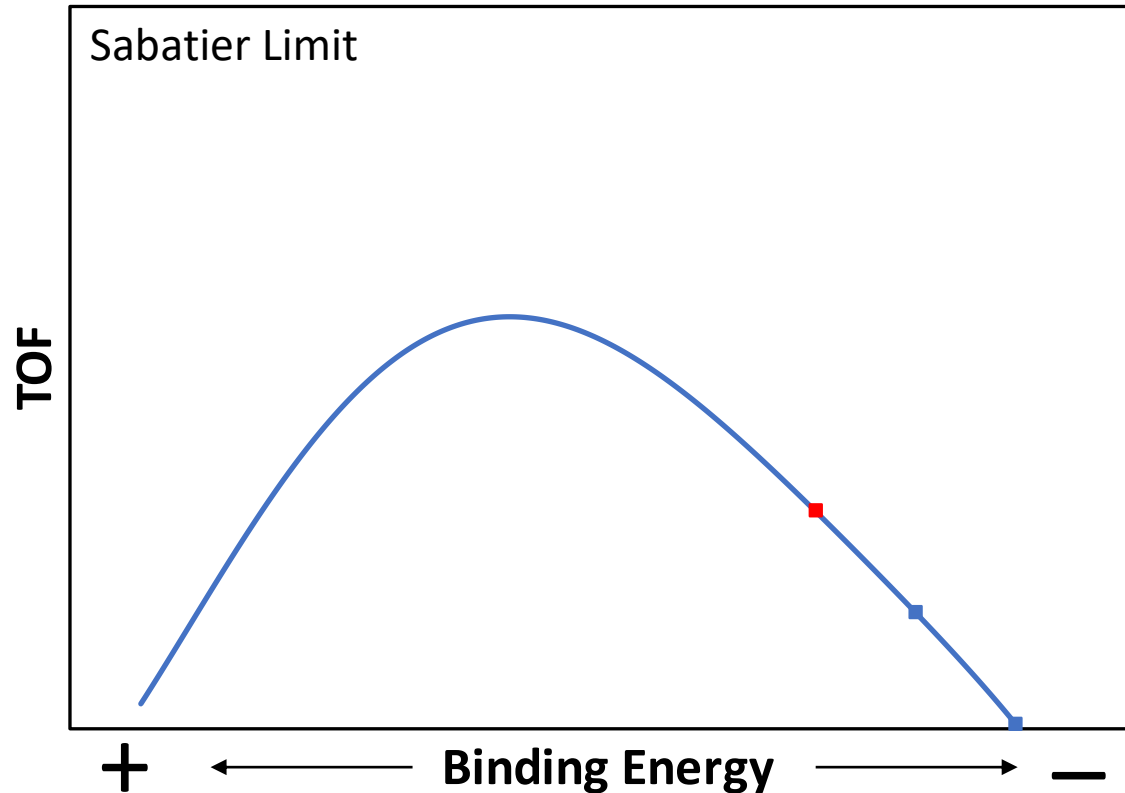
Dynamic catalysis: Motivation-Sabatier limit



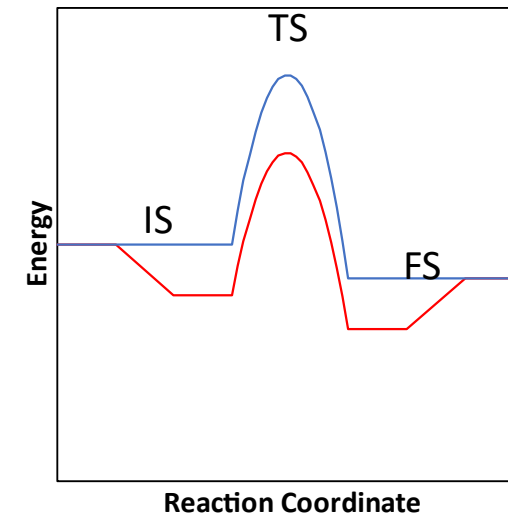
More tightly bound adsorbates result in better transition state stabilization and lower reaction barrier.



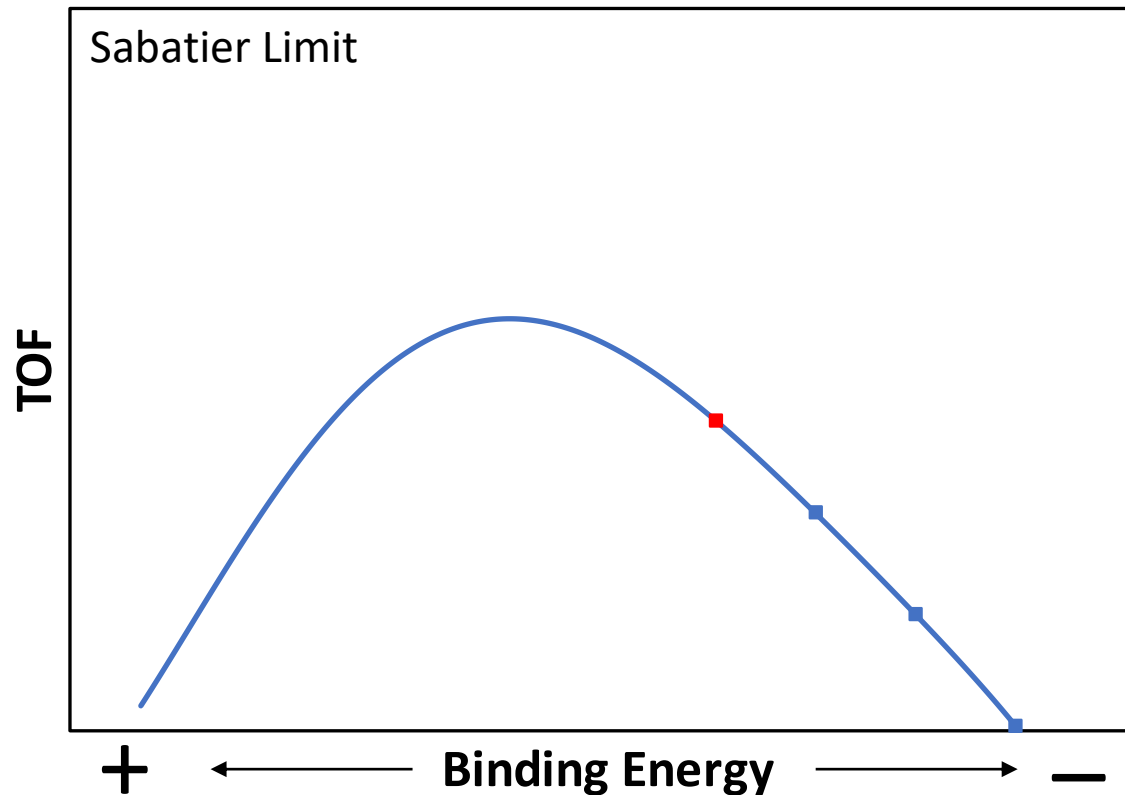
Dynamic catalysis: Motivation-Sabatier limit



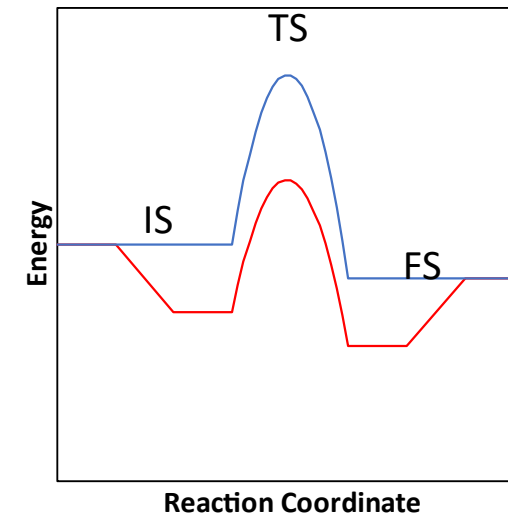
More tightly bound adsorbates result in better transition state stabilization and lower reaction barrier.



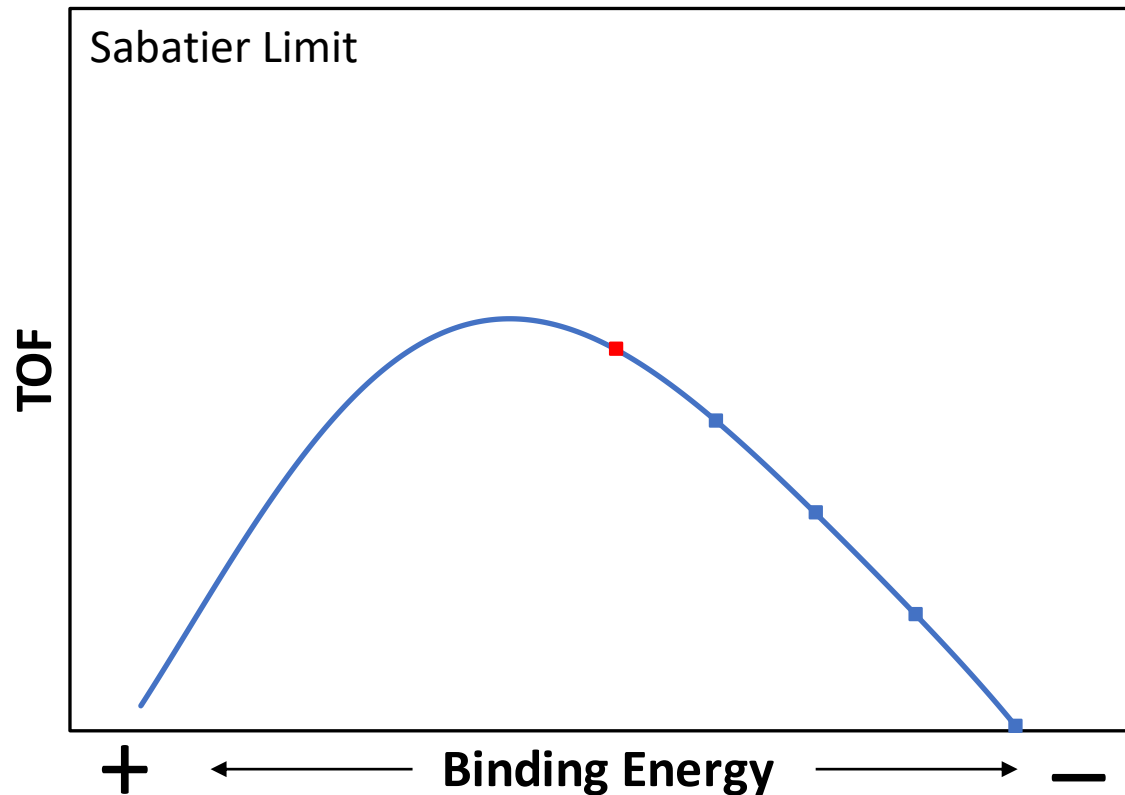
Dynamic catalysis: Motivation-Sabatier limit



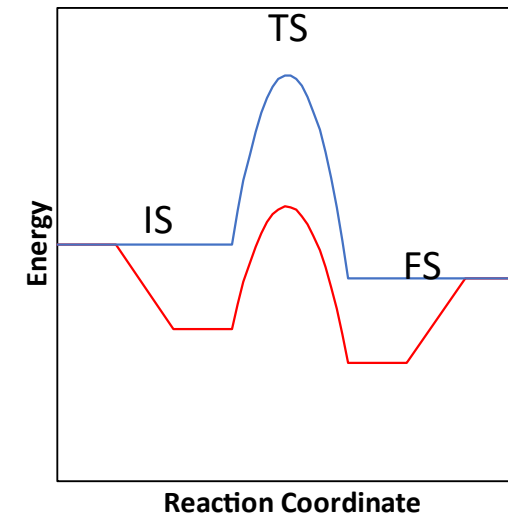
More tightly bound adsorbates result in better transition state stabilization and lower reaction barrier.



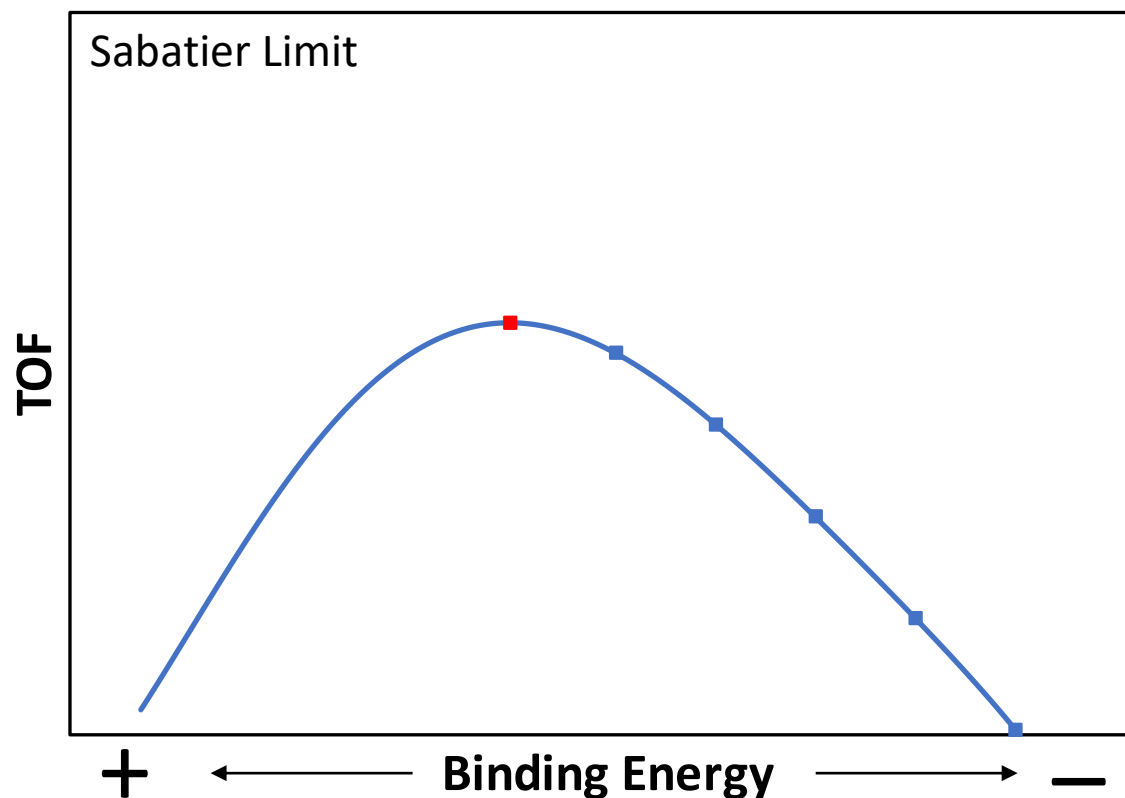
Dynamic catalysis: Motivation-Sabatier limit



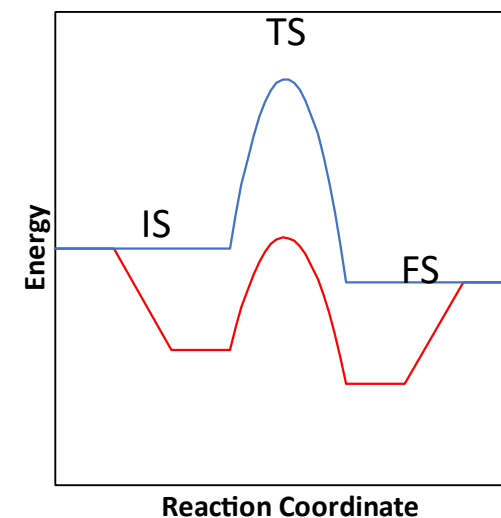
More tightly bound adsorbates result in better transition state stabilization and lower reaction barrier.



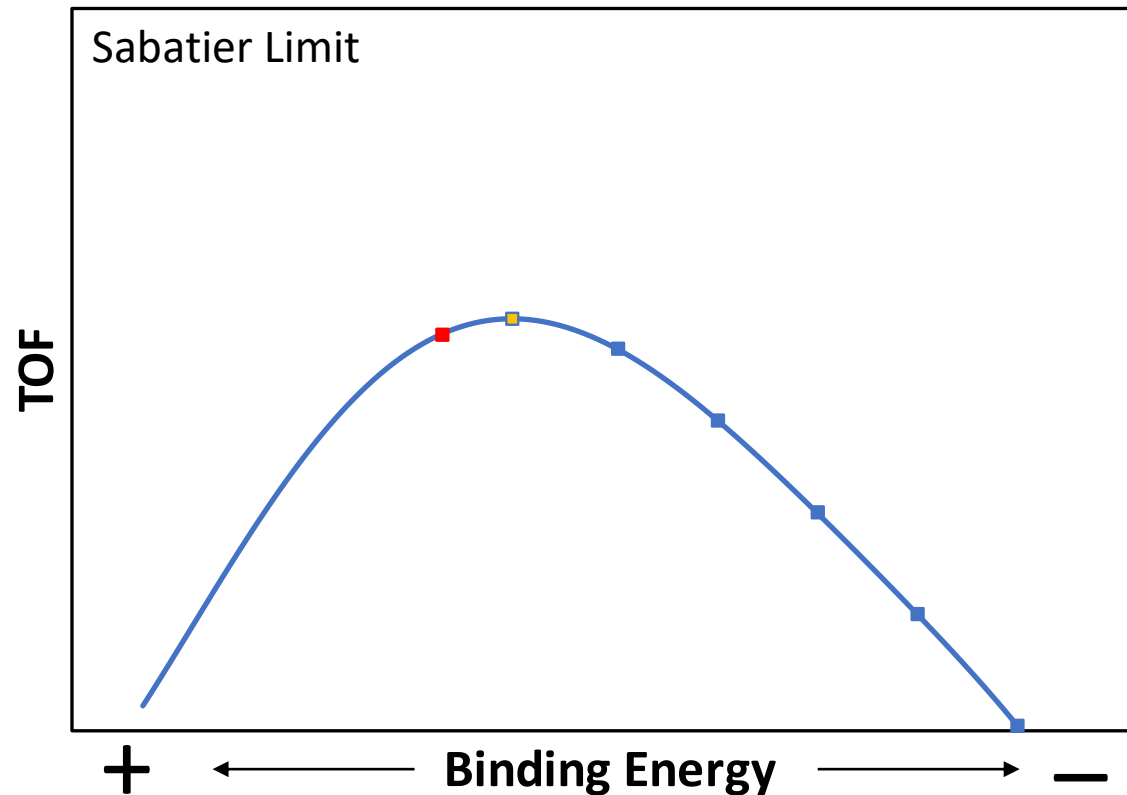
Dynamic catalysis: Motivation-Sabatier limit



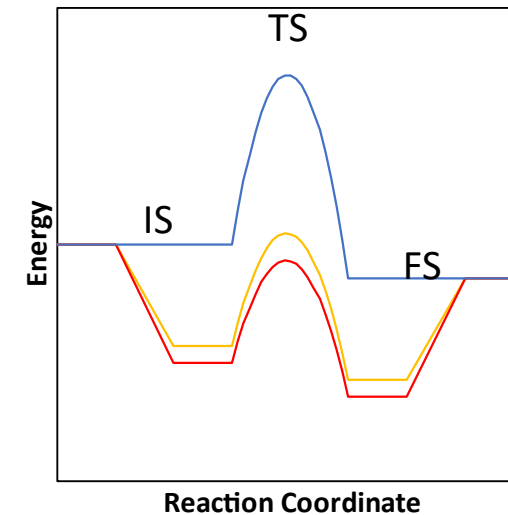
At some binding energy the benefit of TS stabilization is overshadowed by product desorption and a maximum benefit is achieved.



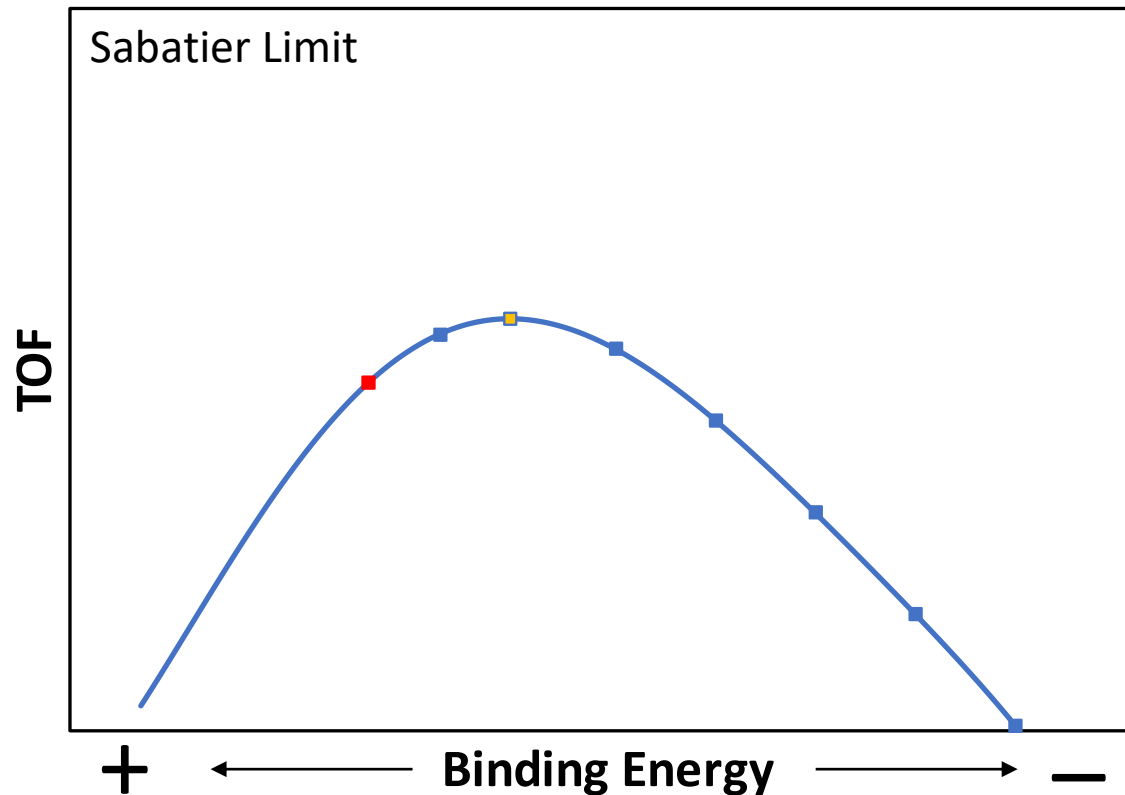
Dynamic catalysis: Motivation-Sabatier limit



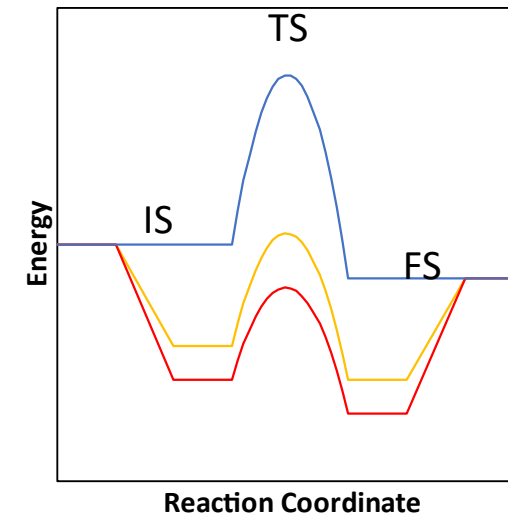
Higher binding energies now hinder overall reaction rates as desorption limitations define reaction rate.



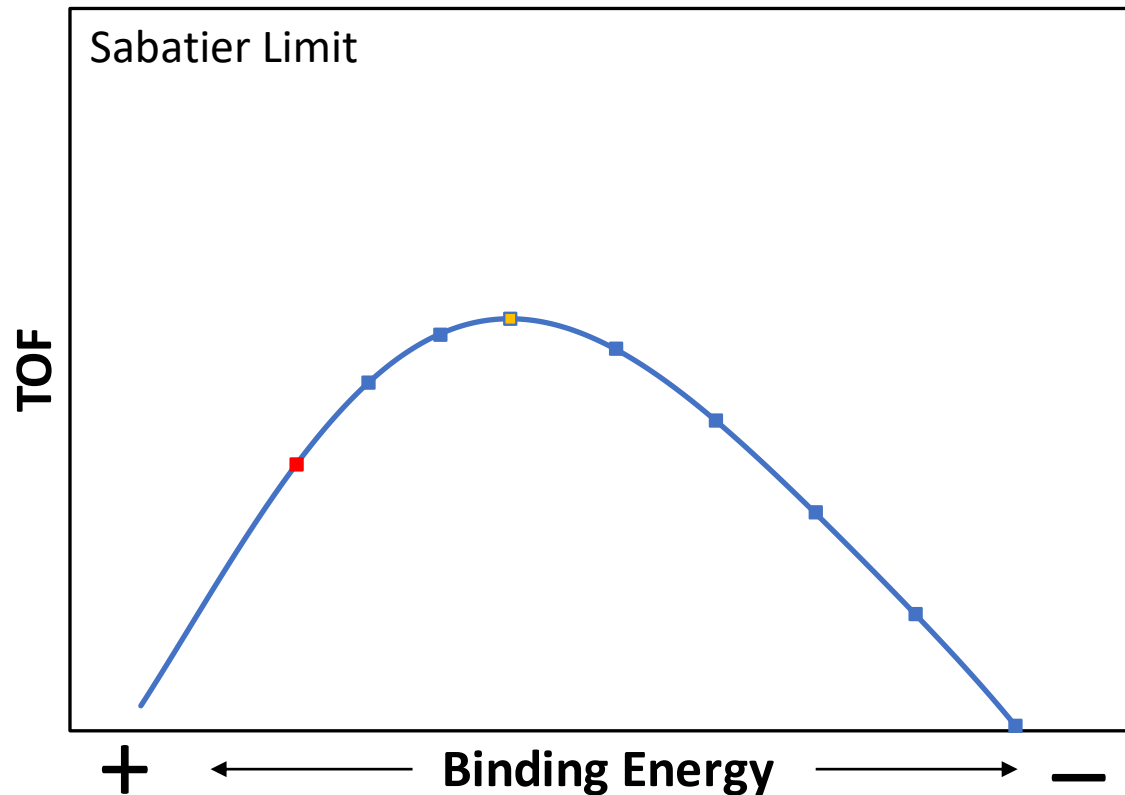
Dynamic catalysis: Motivation-Sabatier limit



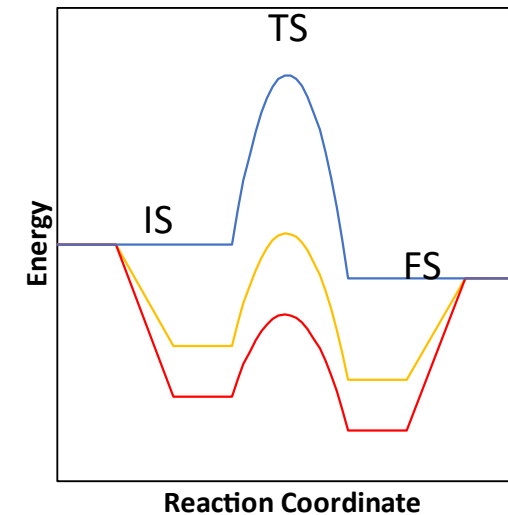
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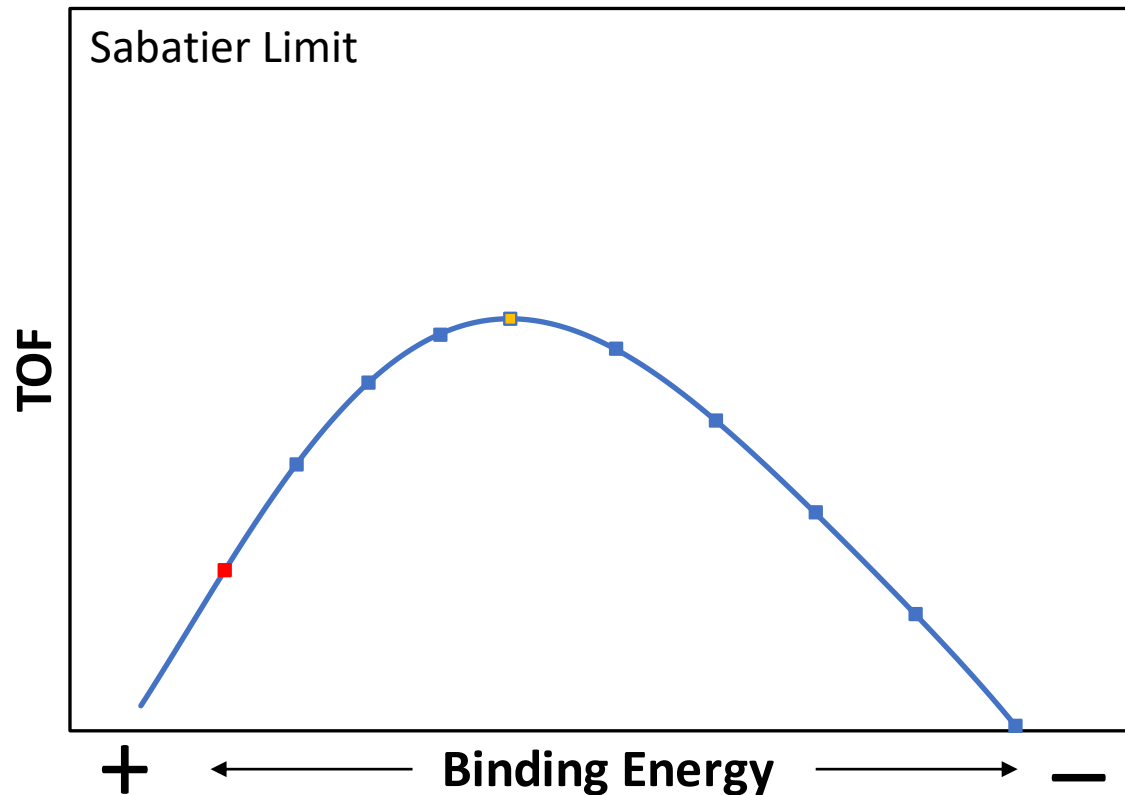
Dynamic catalysis: Motivation-Sabatier limit



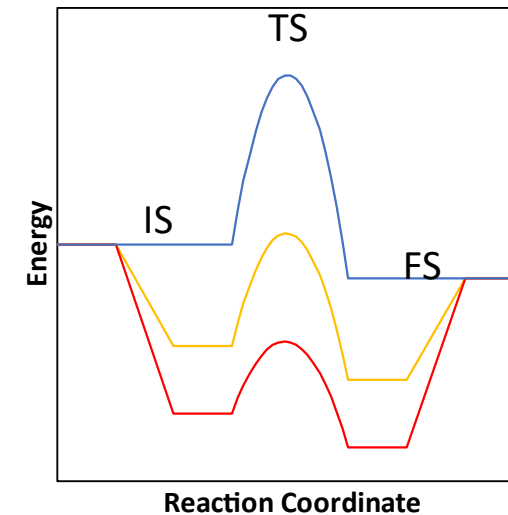
Higher binding energies now hinder overall reaction rates as desorption limitations define reaction rate.



Dynamic catalysis: Motivation-Sabatier limit

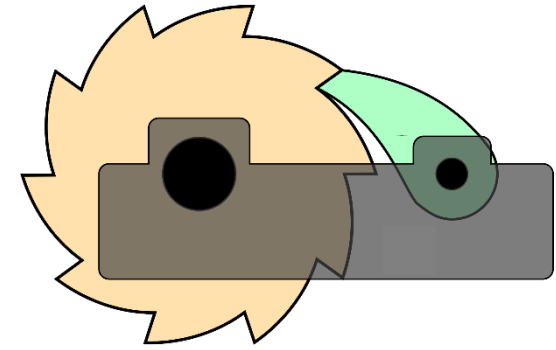
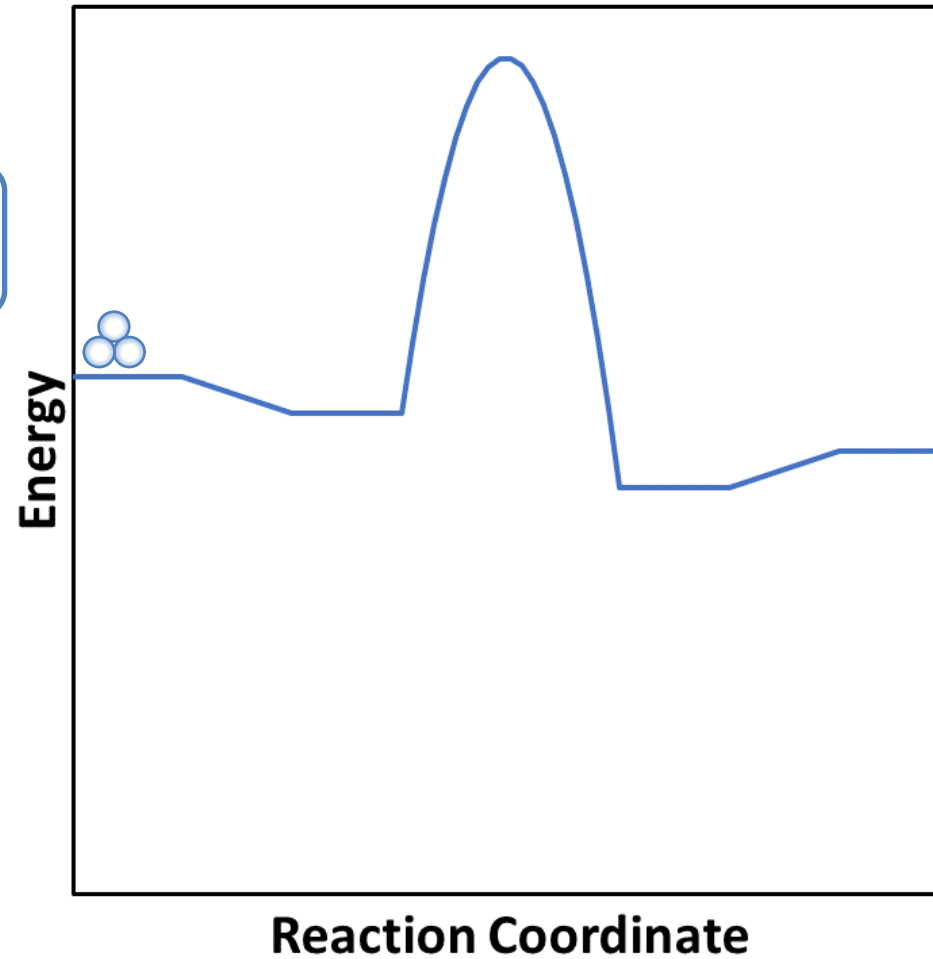


Higher binding energies now hinder overall reaction rates as desorption limitations define reaction rate.



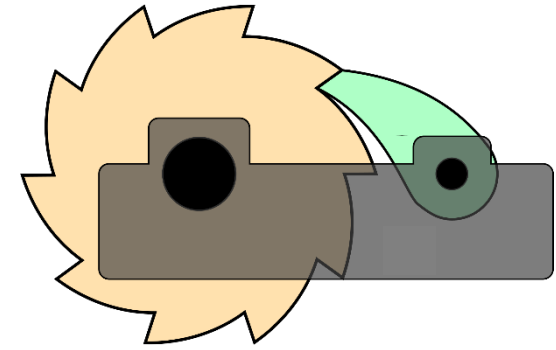
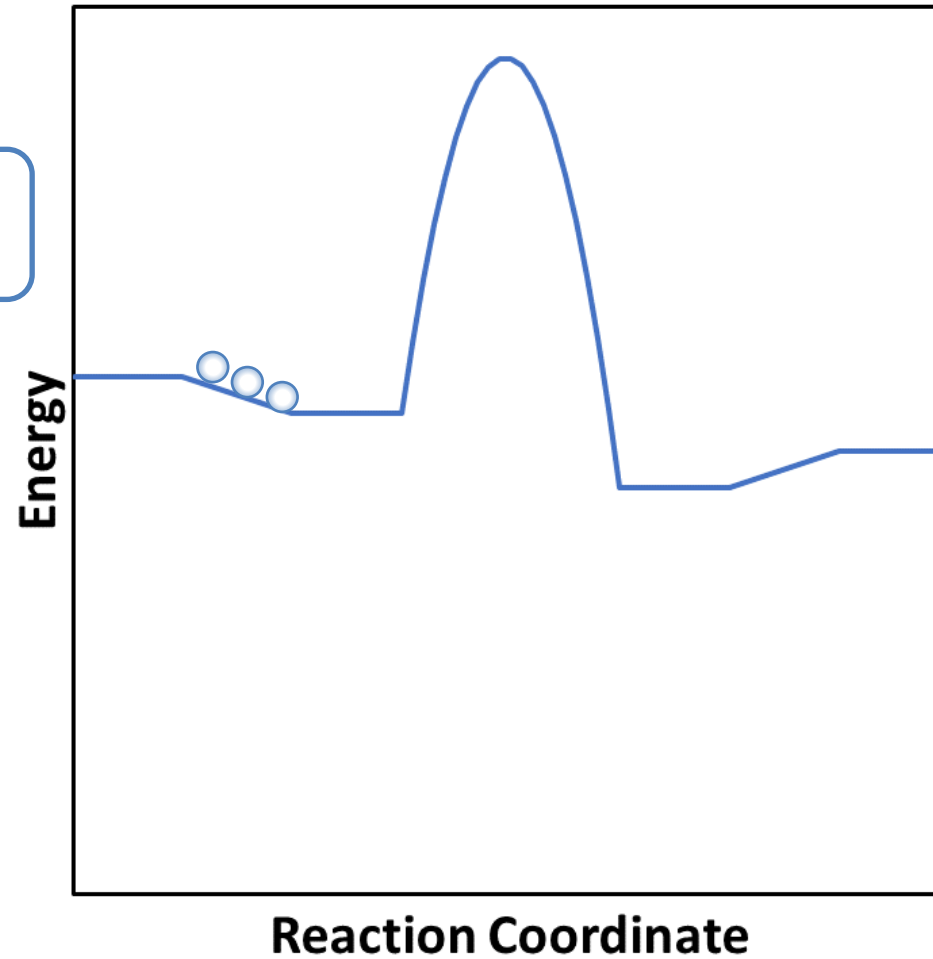
Dynamic catalysis: Motivation-Molecular ratchet

Gas phase reactants
in the initial state



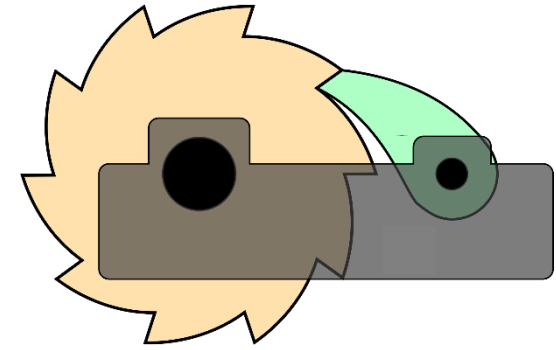
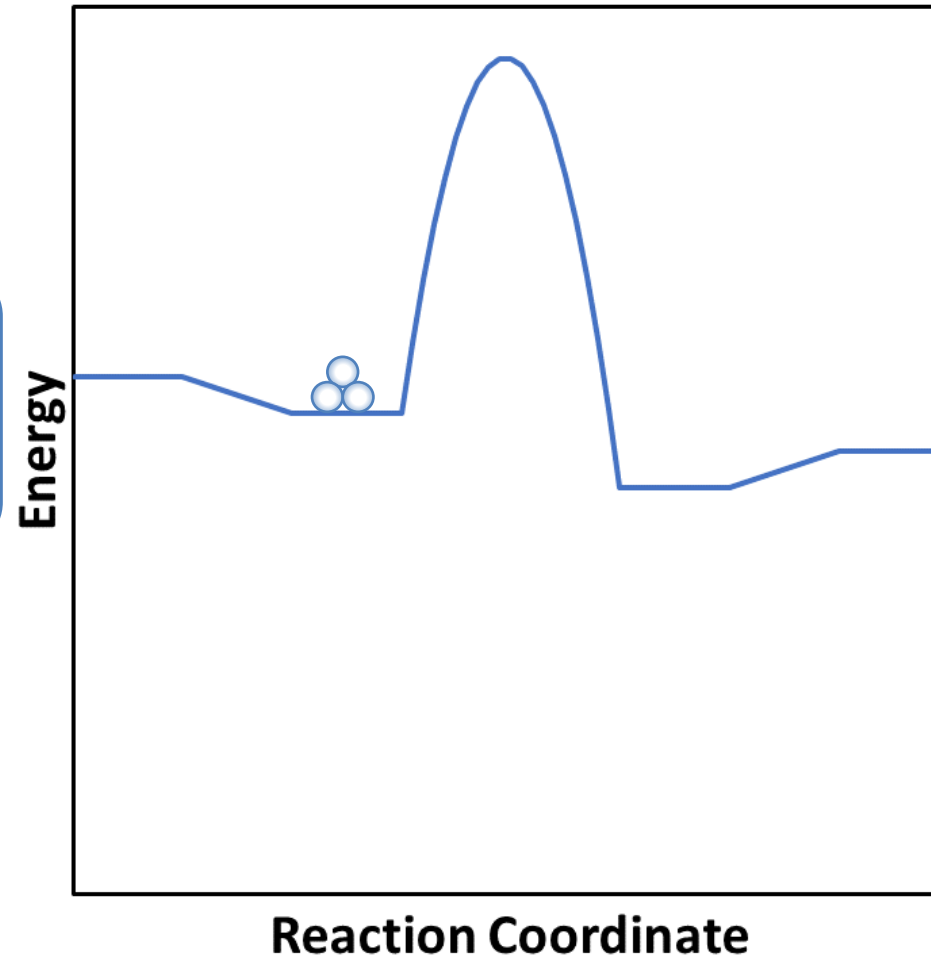
Dynamic catalysis: Motivation-Molecular ratchet

Adsorption on to the catalyst surface.

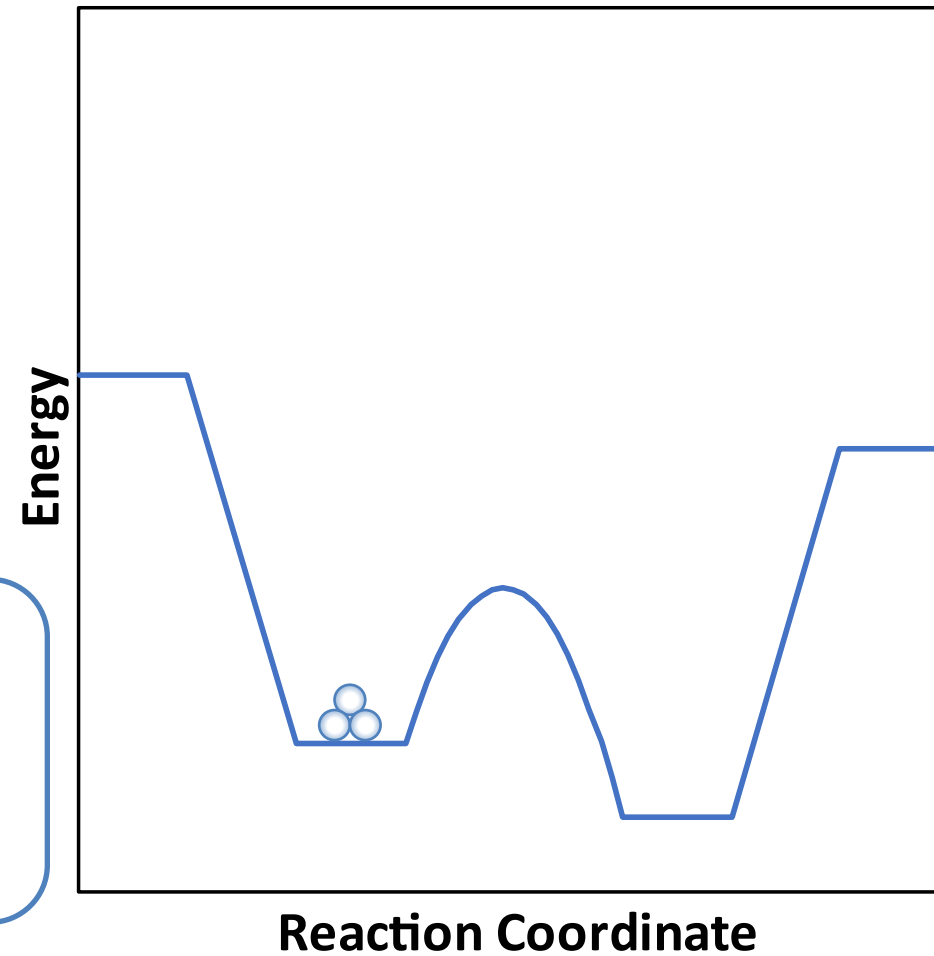
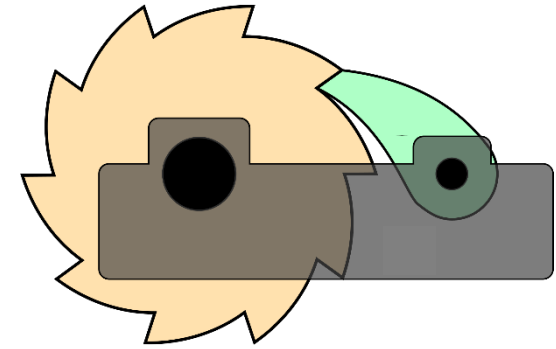


Dynamic catalysis: Motivation-Molecular ratchet

Reactants adsorbed
on the catalyst
surface with low
binding energy

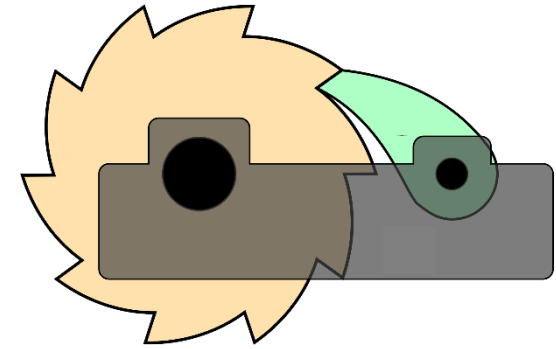


Dynamic catalysis: Motivation-Molecular ratchet

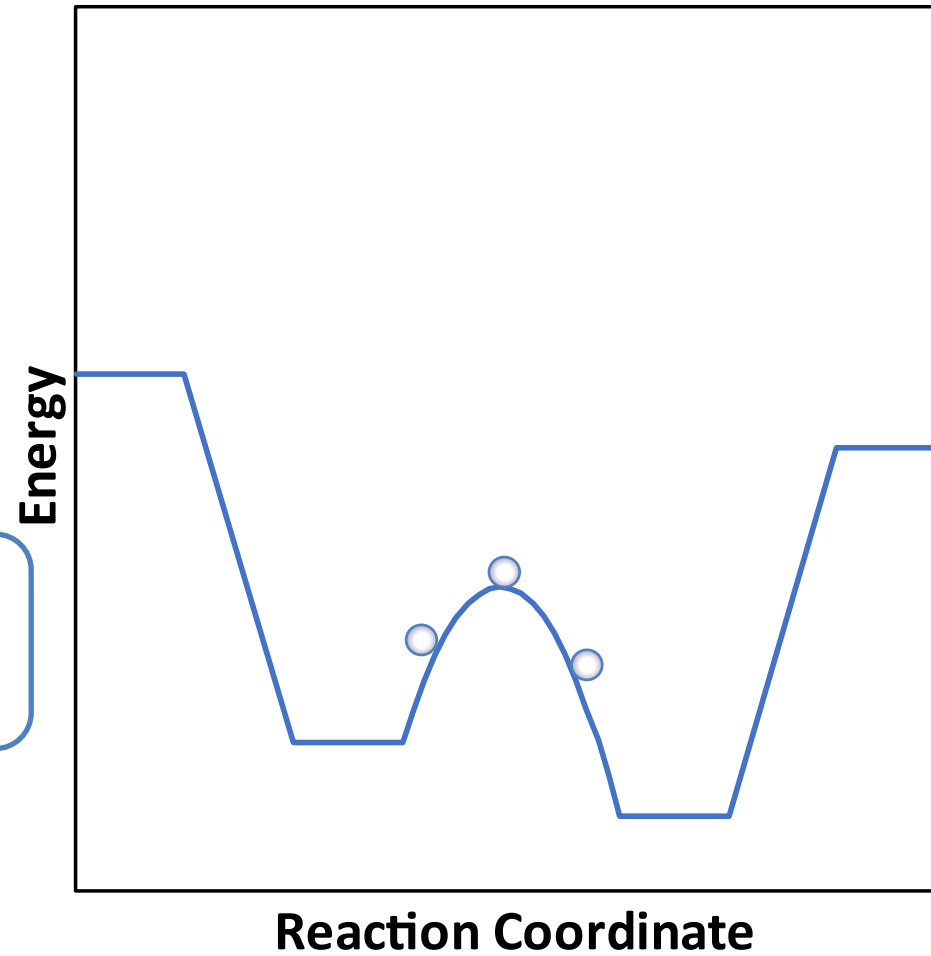


Binding energy rises,
transition state is
stabilized, and
reaction barrier
lowered

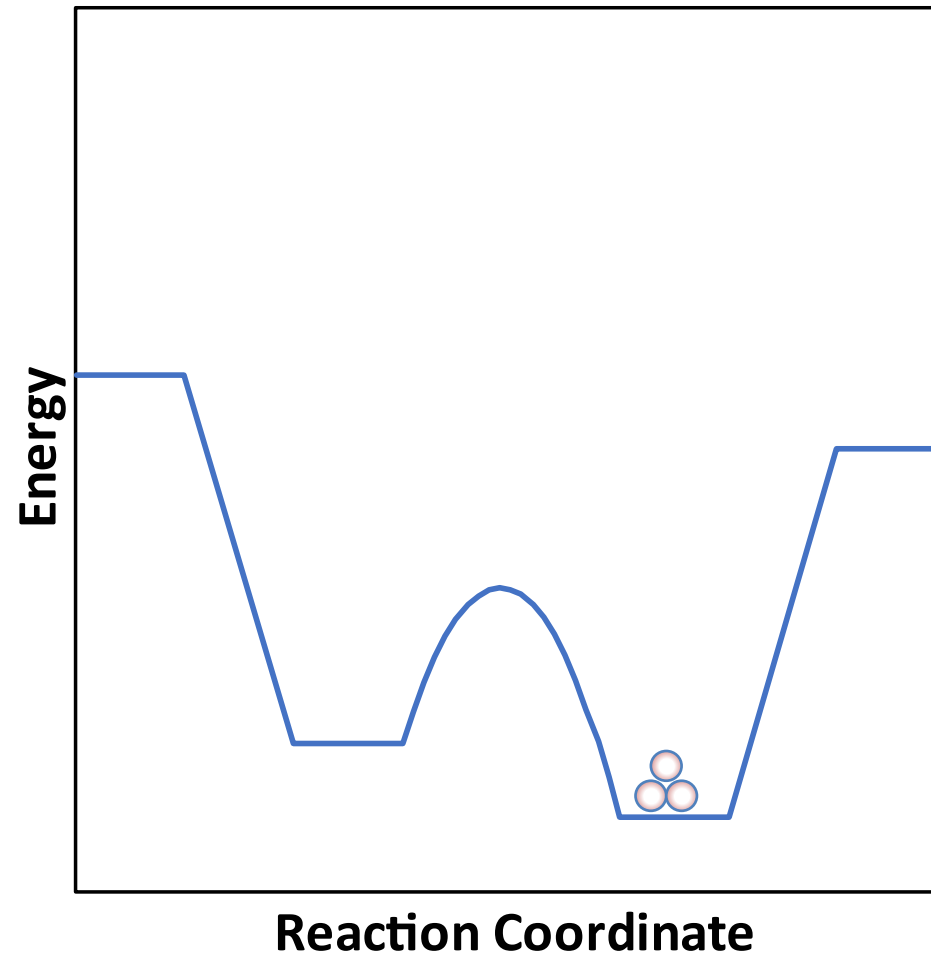
Dynamic catalysis: Motivation-Molecular ratchet



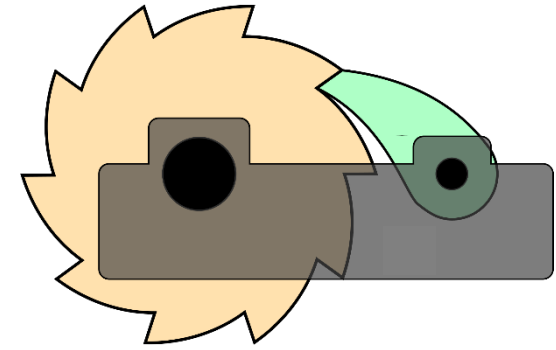
Reactants proceed
through the lowered
transition state



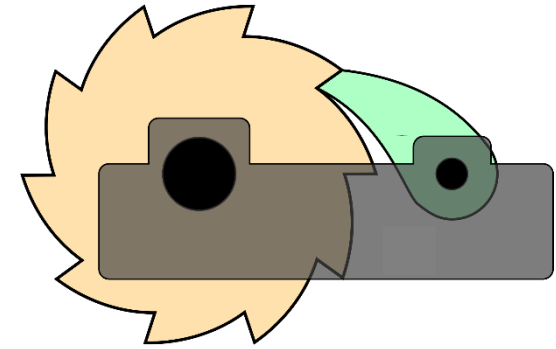
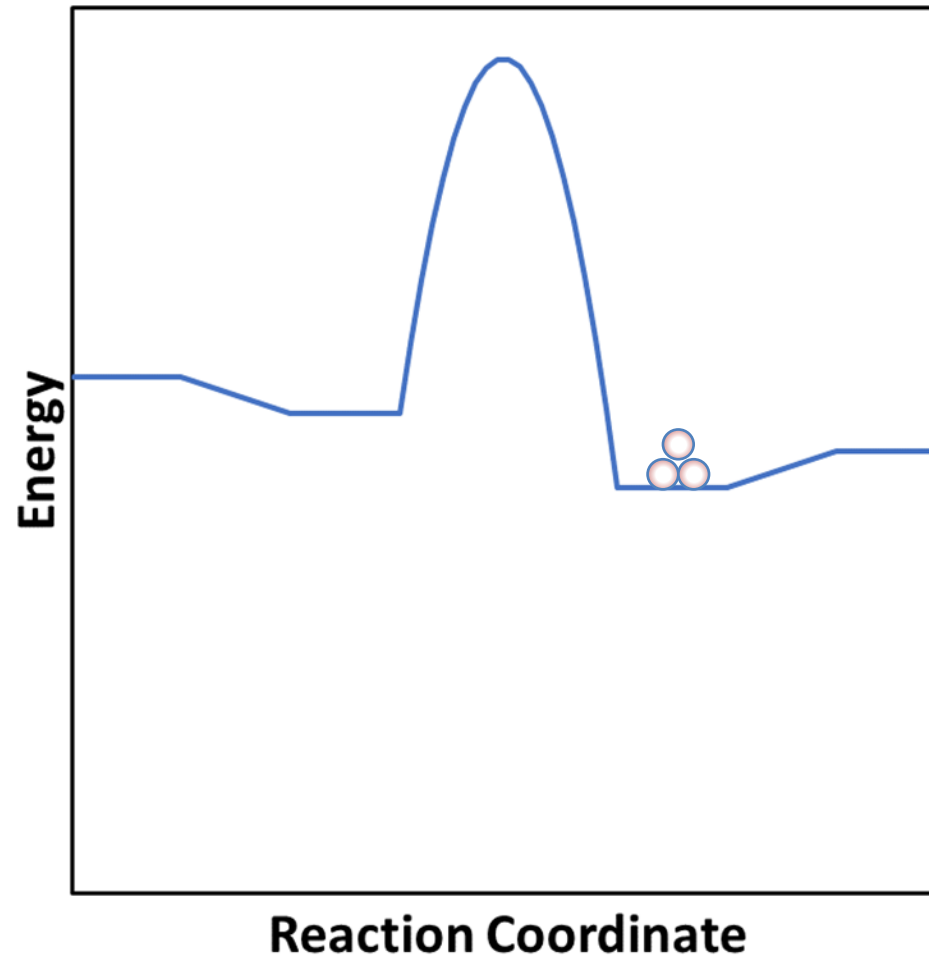
Dynamic catalysis: Motivation-Molecular ratchet



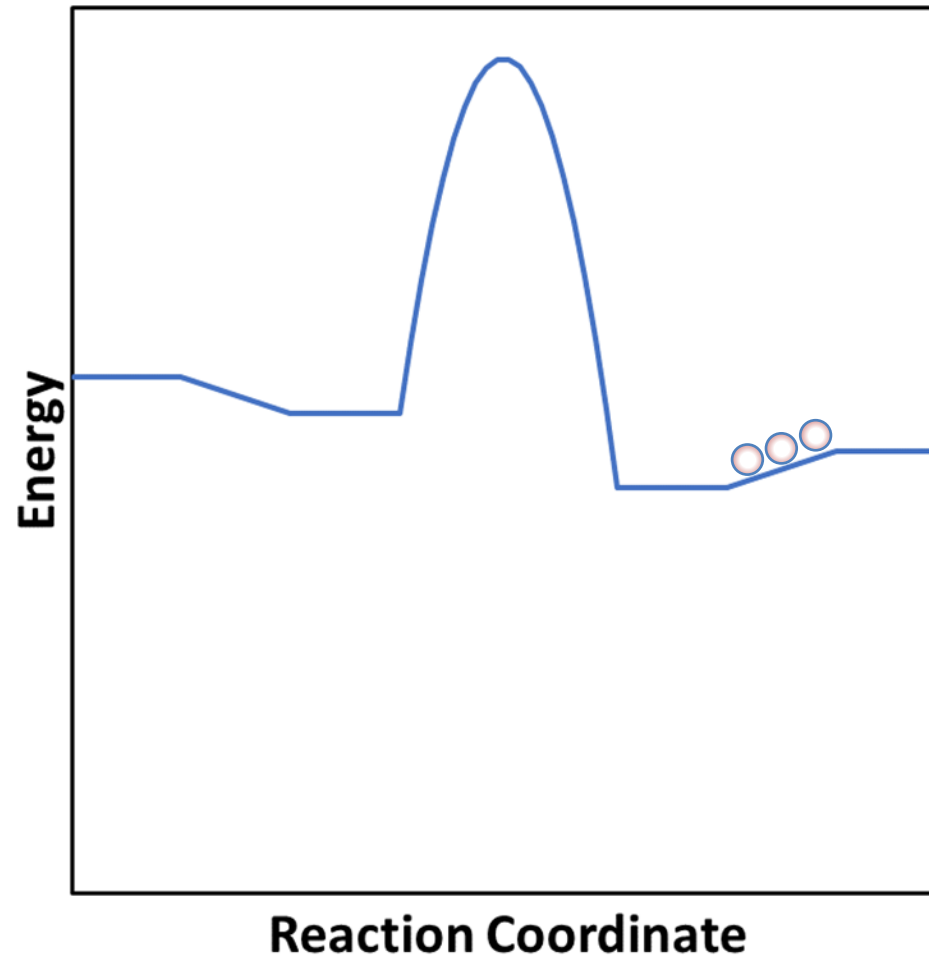
Product forms on
the catalyst surface
but is tightly bound



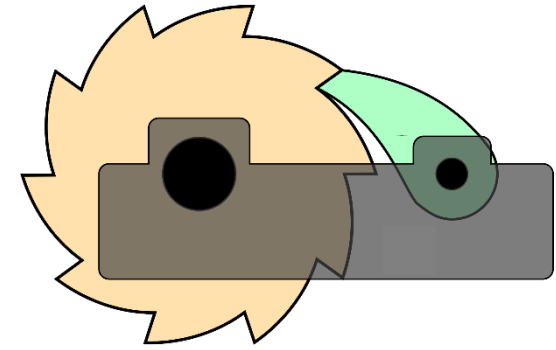
Dynamic catalysis: Motivation-Molecular ratchet



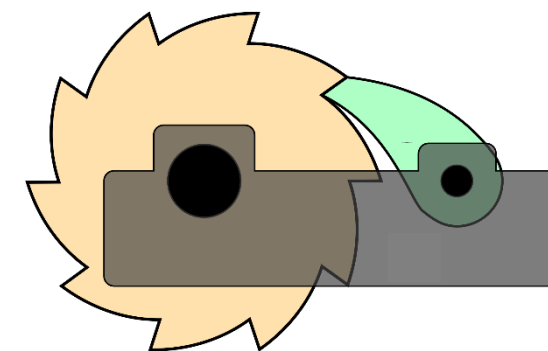
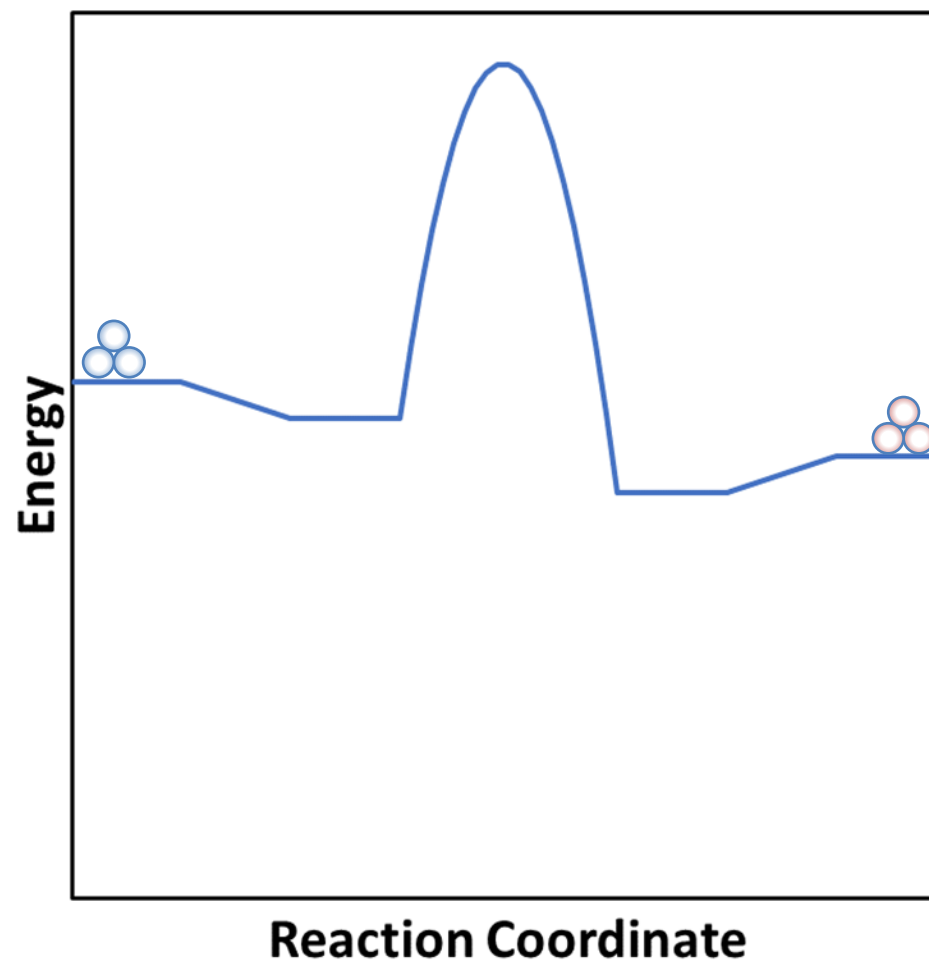
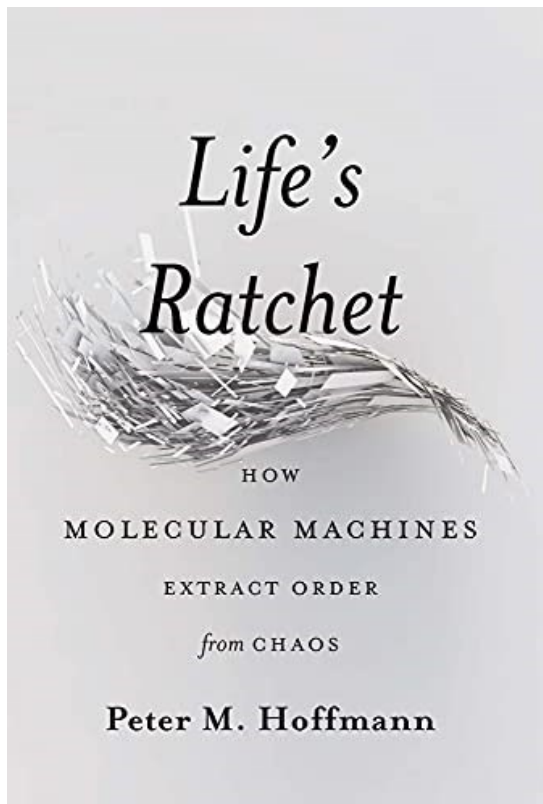
Dynamic catalysis: Motivation-Molecular ratchet



Products desorb from the catalyst surface more easily at the lower binding energy



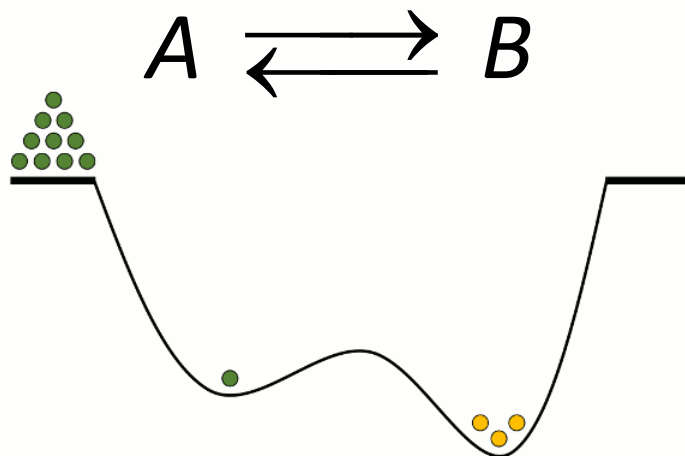
Dynamic catalysis: Motivation-Molecular ratchet



Final state product is now in the gas phase and additional reactants can proceed on the next oscillation.

¹ Hoffman, P. M. *Life's Ratchet. How Molecular Machines Extract Order from Chaos*, 1st ed.; Basic Books, 2012.

Dynamic catalysis: Gaps and Challenges



Paul Dauenhauer, et al., University of Minnesota¹

Gaps

- “Toy” problem.
 - Unconstrained thermodynamic and kinetic parameters
 - Constrained reaction path
 - Lacks complexity of real world reaction

Challenges: Demonstrate dynamic catalysis with real world conditions

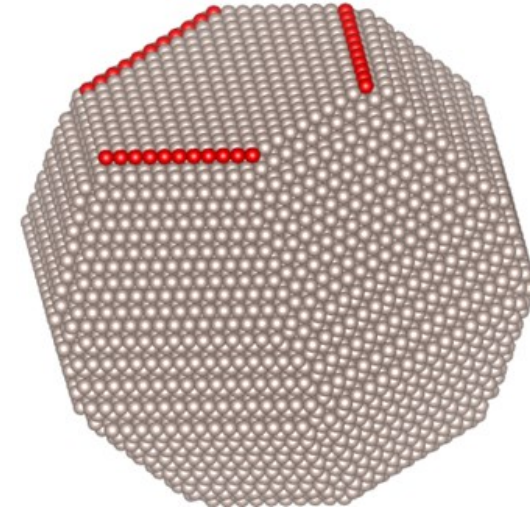
- How do we oscillate binding energy?
- Multiple reaction paths
- Multiple reaction active sites with diffusion between sites
- Thermodynamics and kinetics tied to binding energy
- Co-adsorbate interactions
- Meaningful reaction

¹ Ardagh, M. A.; Dauenhauer, P. J.; et al. Catalytic Resonance Theory: SuperVolcanoes, Catalytic Molecular Pumps, and Oscillatory Steady State. *Catal. Sci. Technol.* **2019**, 9 (18), 5058–5076.

Dynamic catalysis: NH₃ synthesis on Ru model



1 Adsorption/Desorption	Surface Diffusion	Surface Reactions
$N_2 + *(T) \rightleftharpoons N_2(T)$	$N(T) + *(S) \rightleftharpoons N(S) + *(T)$	$N_2(T) + *(T) \rightleftharpoons 2N(T)$
$H_2 + 2*(T) \rightleftharpoons 2H(T)$	$N(T) + *(S_L) \rightleftharpoons N(S_L) + *(T)$	$N_2(S) + *(S_L) \rightleftharpoons N(S) + N(S_L)$
$NH_3 + *(T) \rightleftharpoons NH_3(T)$	$NH(T) + *(S) \rightleftharpoons NH(S) + *(T)$	$N(T) + H(T) \rightleftharpoons NH(T) + *(T)$
$N_2 + *(S) \rightleftharpoons N_2(S)$	$NH_2(T) + *(S) \rightleftharpoons NH_2(S) + *(T)$	$NH(T) + H(T) \rightleftharpoons NH_2(T) + *(T)$
$H_2 + 2*(S) \rightleftharpoons 2H(S)$	$NH_3(T) + *(S) \rightleftharpoons NH_3(S) + *(T)$	$NH_2(T) + H(T) \rightleftharpoons NH_3(T) + *(T)$
$NH_3 + *(S) \rightleftharpoons NH_3(S)$		$N(S) + H(S) \rightleftharpoons NH(S) + *(S)$
		$NH(S) + H(S) \rightleftharpoons NH_2(S) + *(S)$
		$NH_2(S) + H(S) \rightleftharpoons NH_3(S) + *(S)$



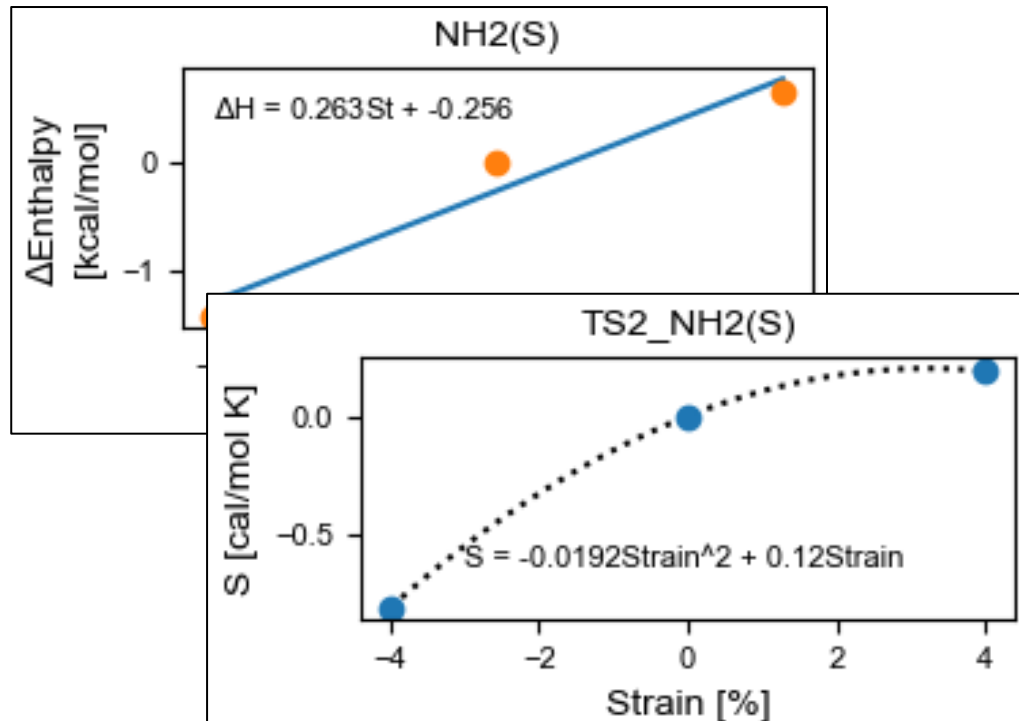
Ru HCP Nanoparticle

- Largest volume, high energy cost, critical to feeding the world, potential high density energy storage
- Sufficiently complex: Multiple active sites, multiple reaction pathways
- Severe reaction conditions required: 200 atm, 673K

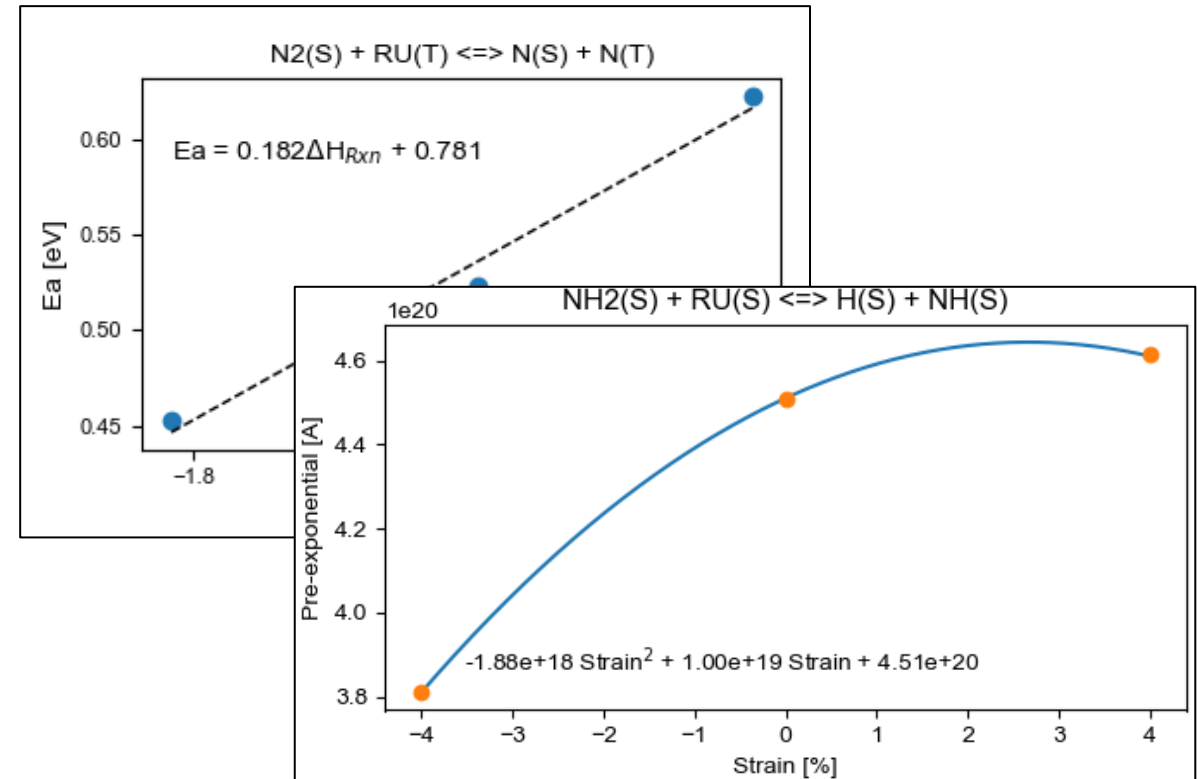
¹ <https://kids.kiddle.co/Ammonia>

Dynamic catalysis: Scaling relationships

Thermodynamic

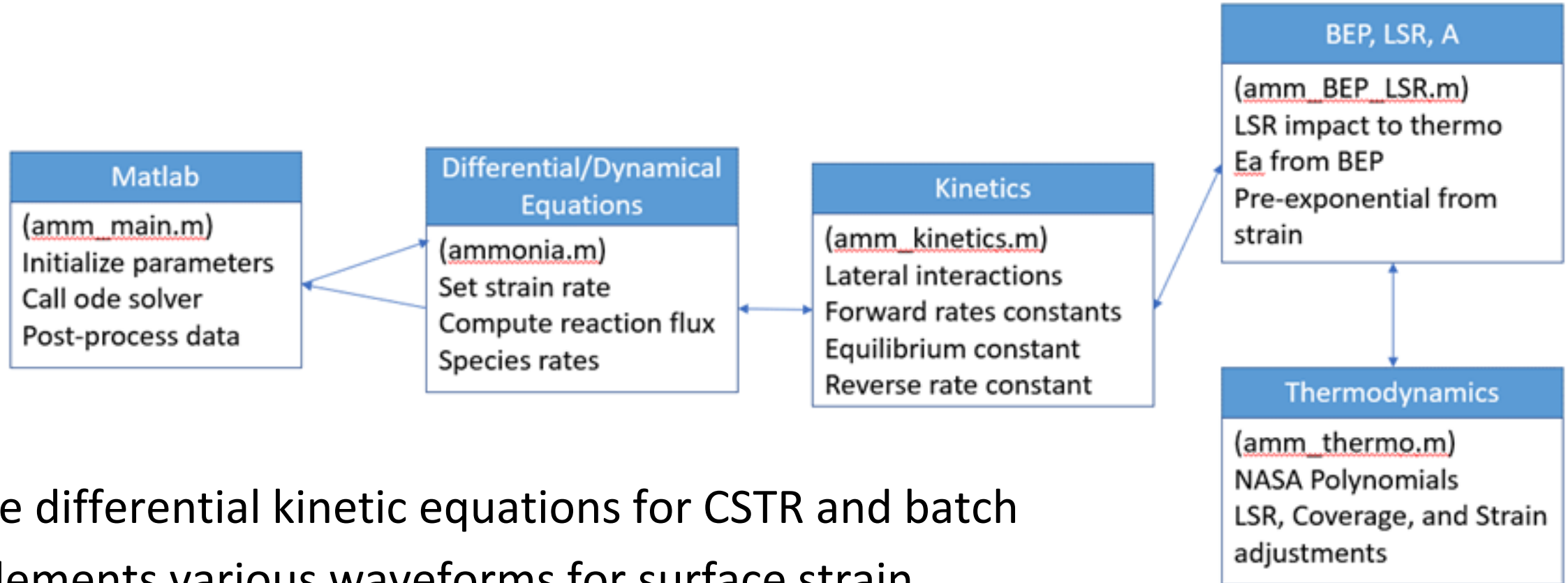


Kinetic



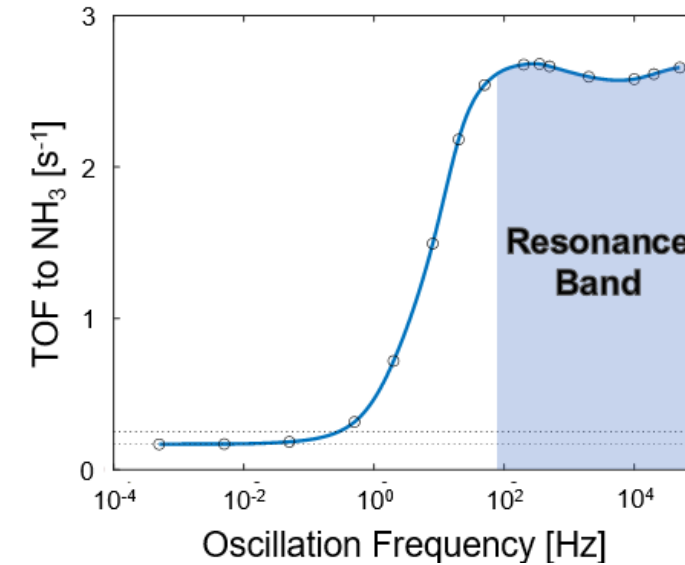
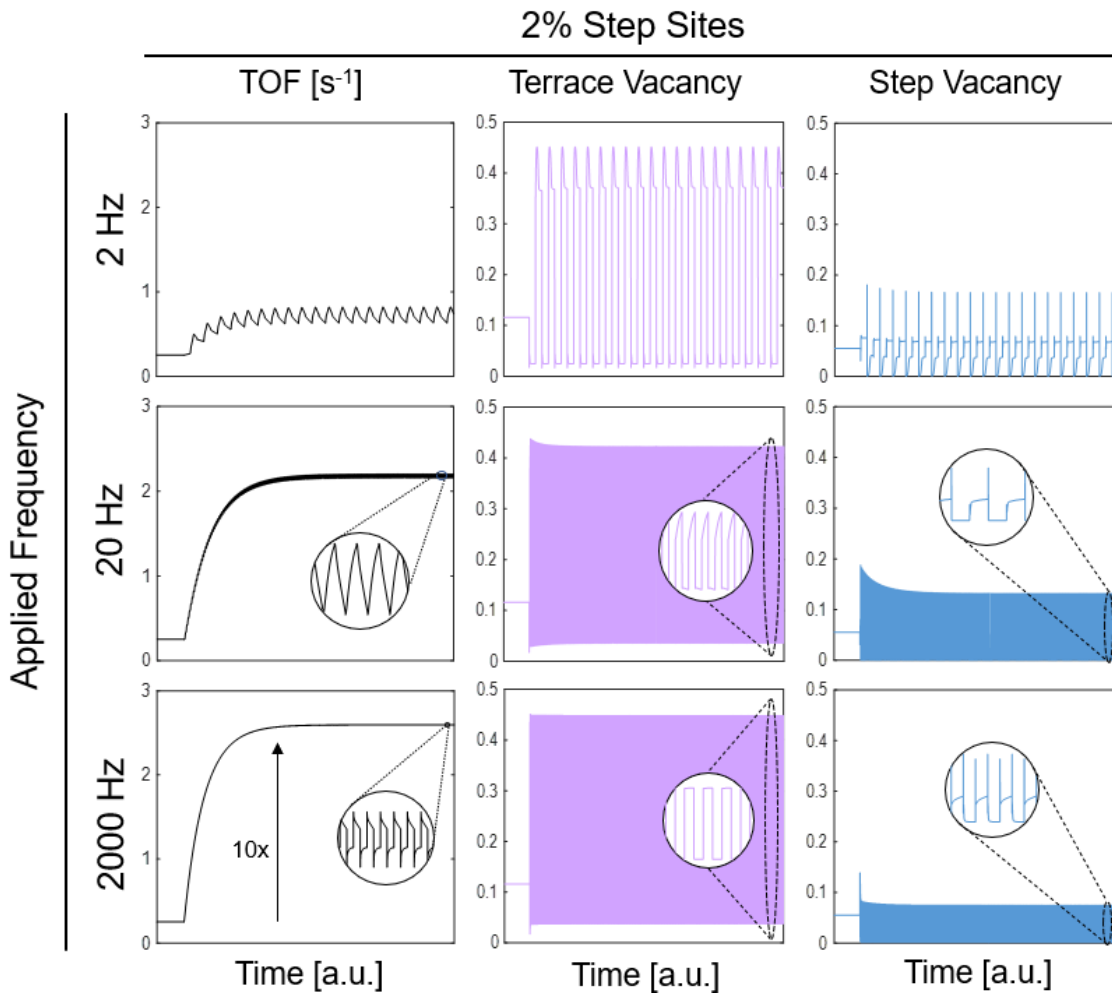
- Scaling relationships provides a continuum of thermodynamic and kinetic values across the full spectrum of lattice strain
- Computed for lattice strain

Dynamic catalysis: Matlab Dynamic Catalysis Kinetic Model



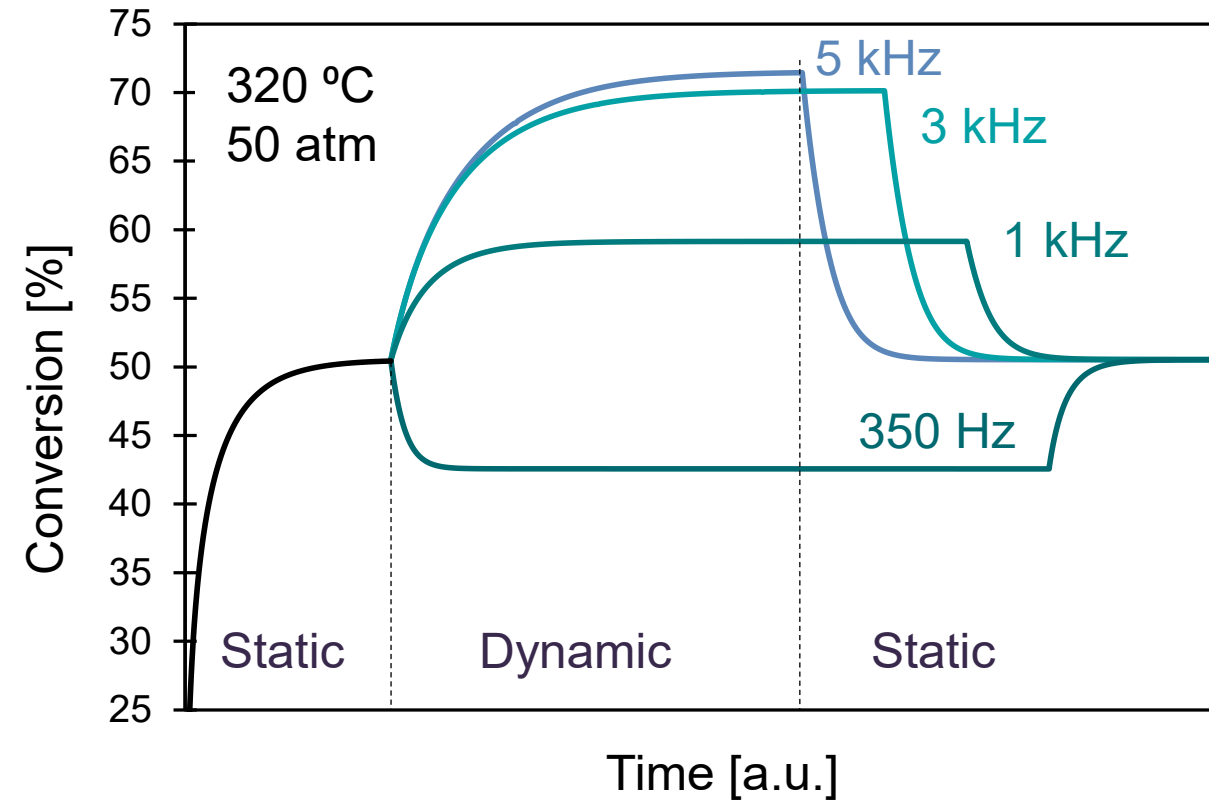
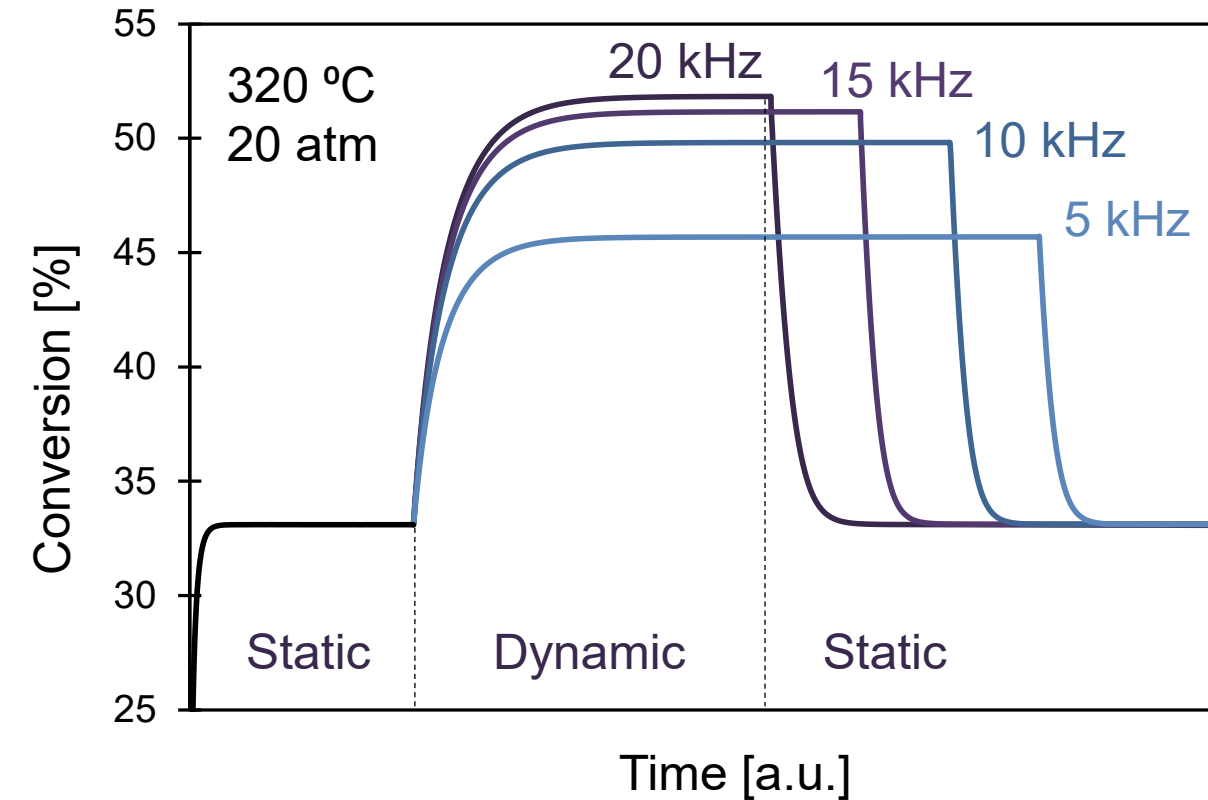
- Solve differential kinetic equations for CSTR and batch
- Implements various waveforms for surface strain
- Updates thermodynamic and kinetic parameters based on strain
- Manages extended computation time and memory

Dynamic catalysis: Dynamic strain



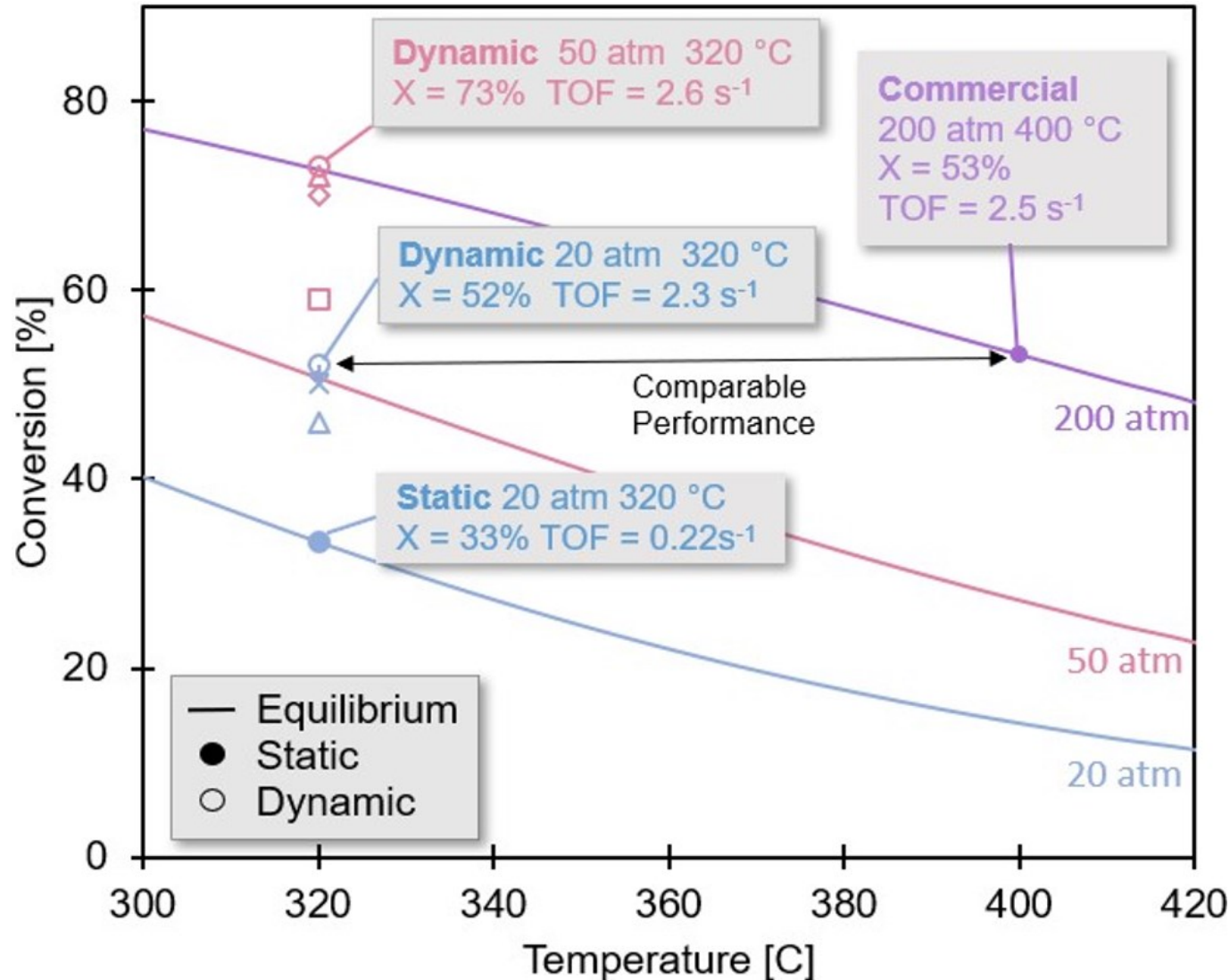
- Square-wave oscillations
- TOF increases reaching a maximum at 200 Hz+. One order-of-magnitude higher than static catalysis.
- Adsorbate surface coverage \sim 0-50% during oscillations. Lower on steps

Dynamic catalysis: Equilibrium conversion



- The molecular ratchet allows us to drive equilibrium beyond the thermodynamic limit

Dynamic catalysis: NH_3 synthesis on Ru model



- Combining TOF and equilibrium improvements we can operate a NH_3 synthesis reaction with the same TOF and conversion as a commercial Haber-Bosch process but at milder conditions.

T → 320 vs 400 C

P → 20 vs 200 atm