



# 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
- Bronsted-Evans-Polyani (BEP) Relationships
- Linear Scaling Relationships (LSR)

## Python Group Additivity (pGrAdd)

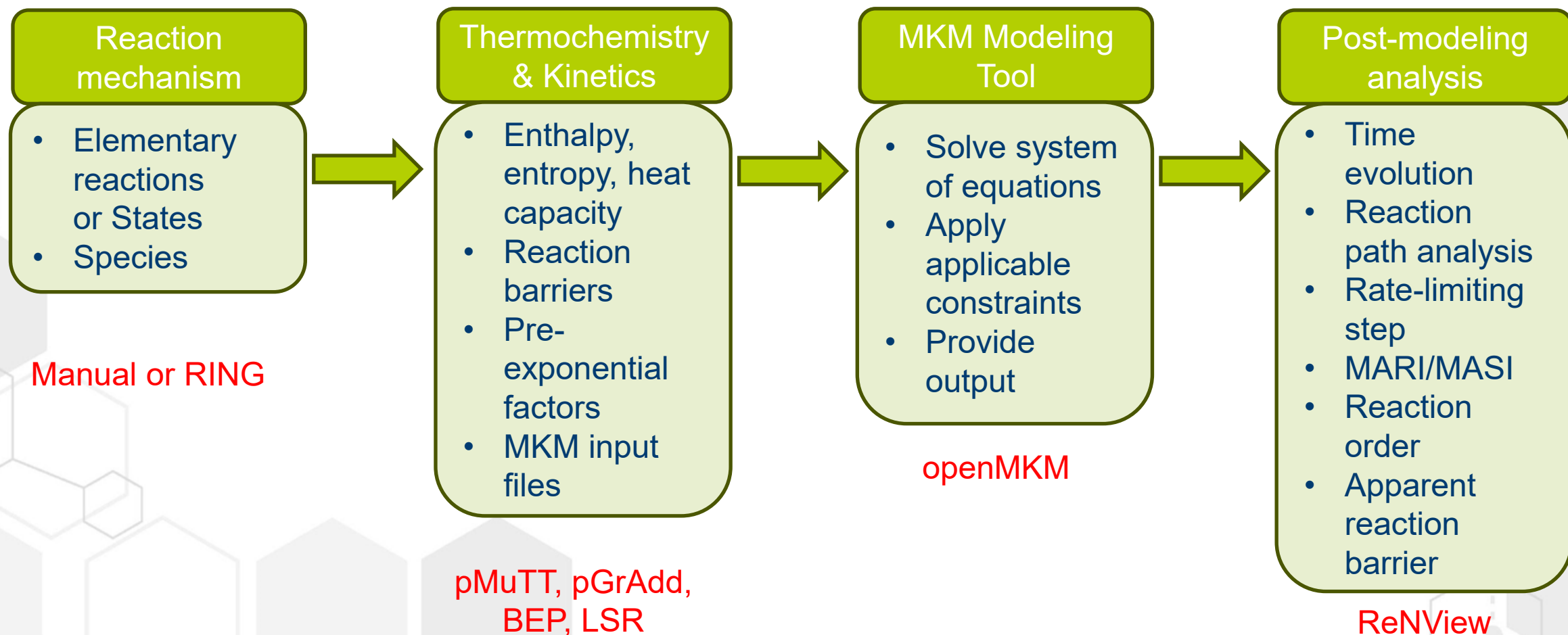
- Code demonstration



## 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 (CH<sub>4</sub>, NH<sub>3</sub>)
- 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



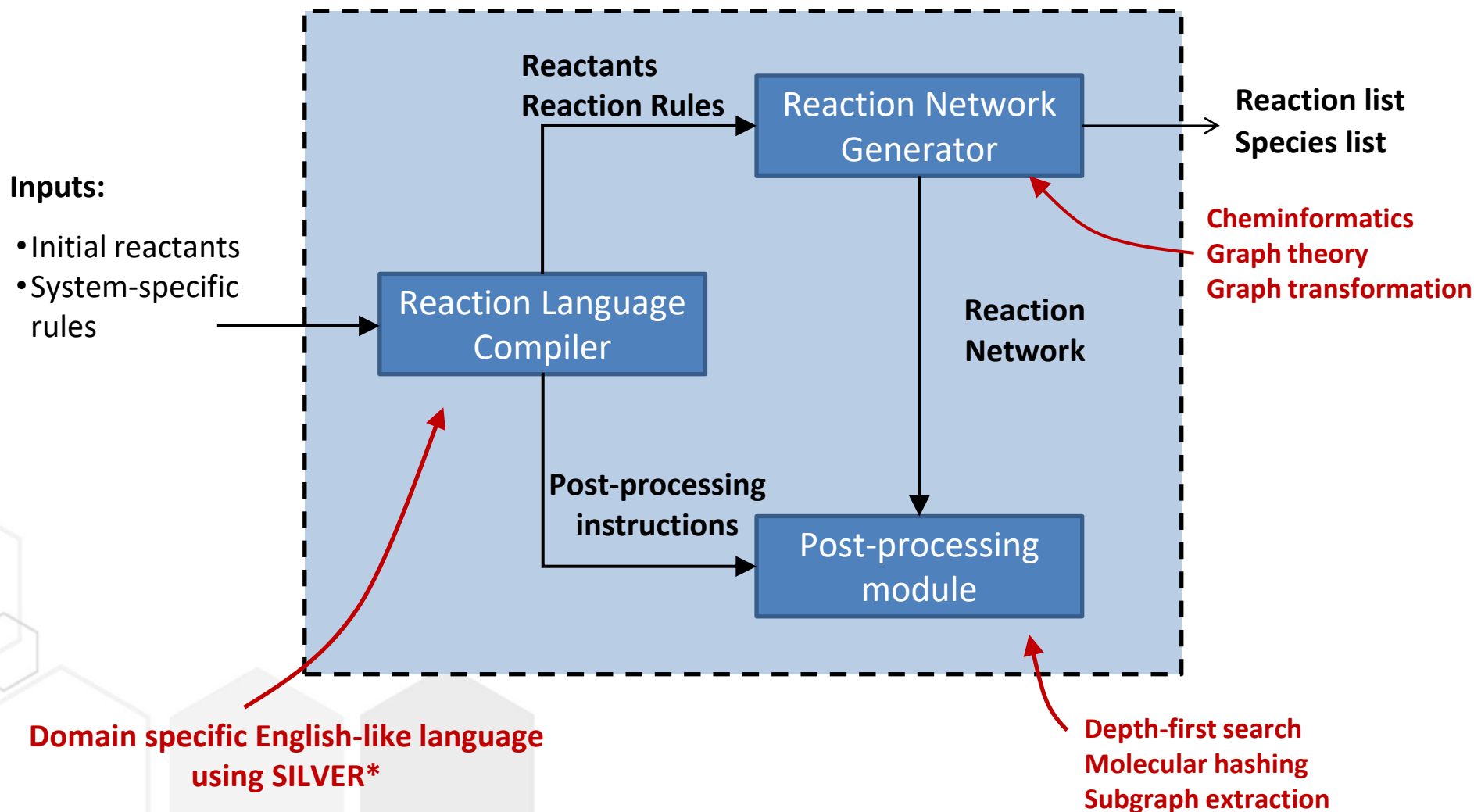
# Reaction Mechanism: Large Site Model

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

<sup>1</sup> Combustion and Flame 2009, 156 (1), 181; <sup>2</sup> Mol Syst Biol. 2007, 3, 121; <sup>3</sup> 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"**

REACTAN  
TS

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}

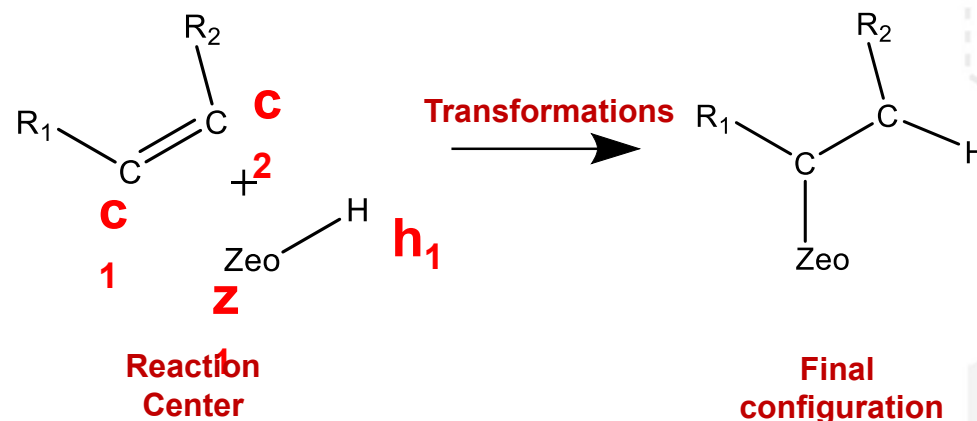
REACTION  
CENTER

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

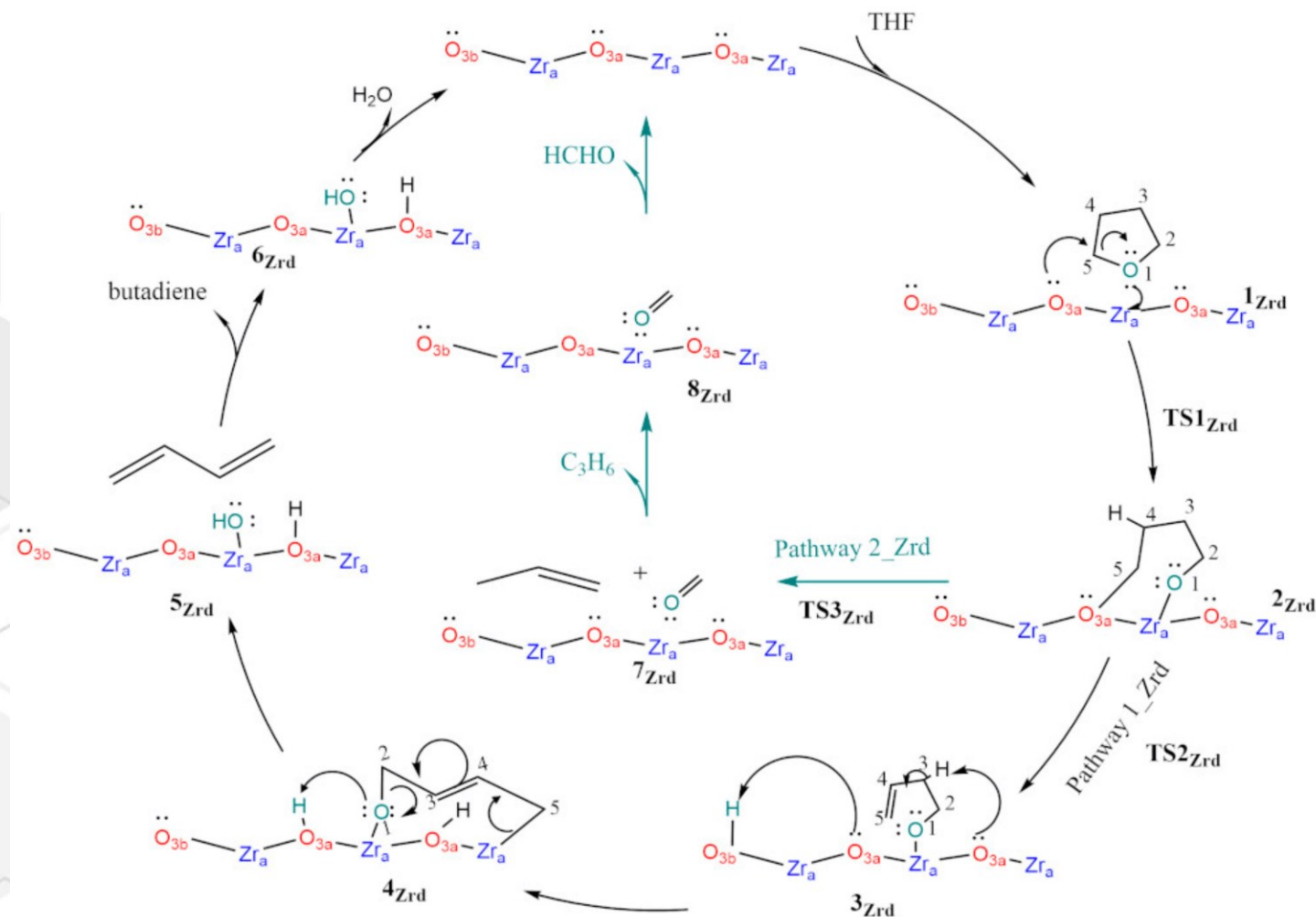
## Reactions (144)

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

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

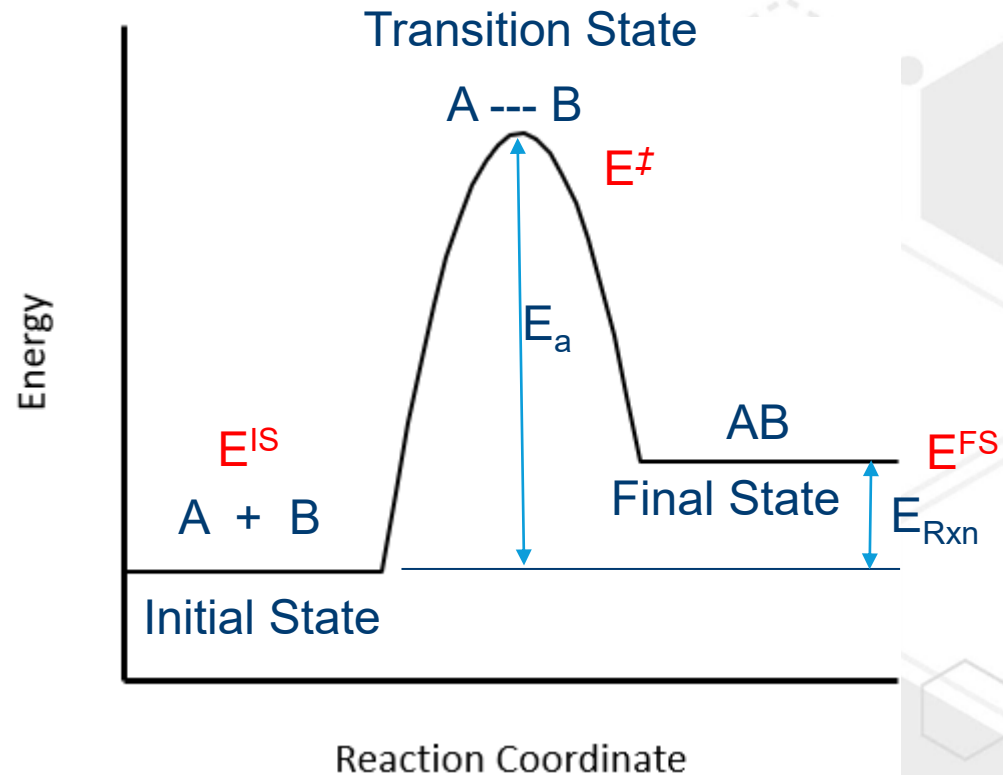
$$E_a = H^\ddagger - H^{IS}$$

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

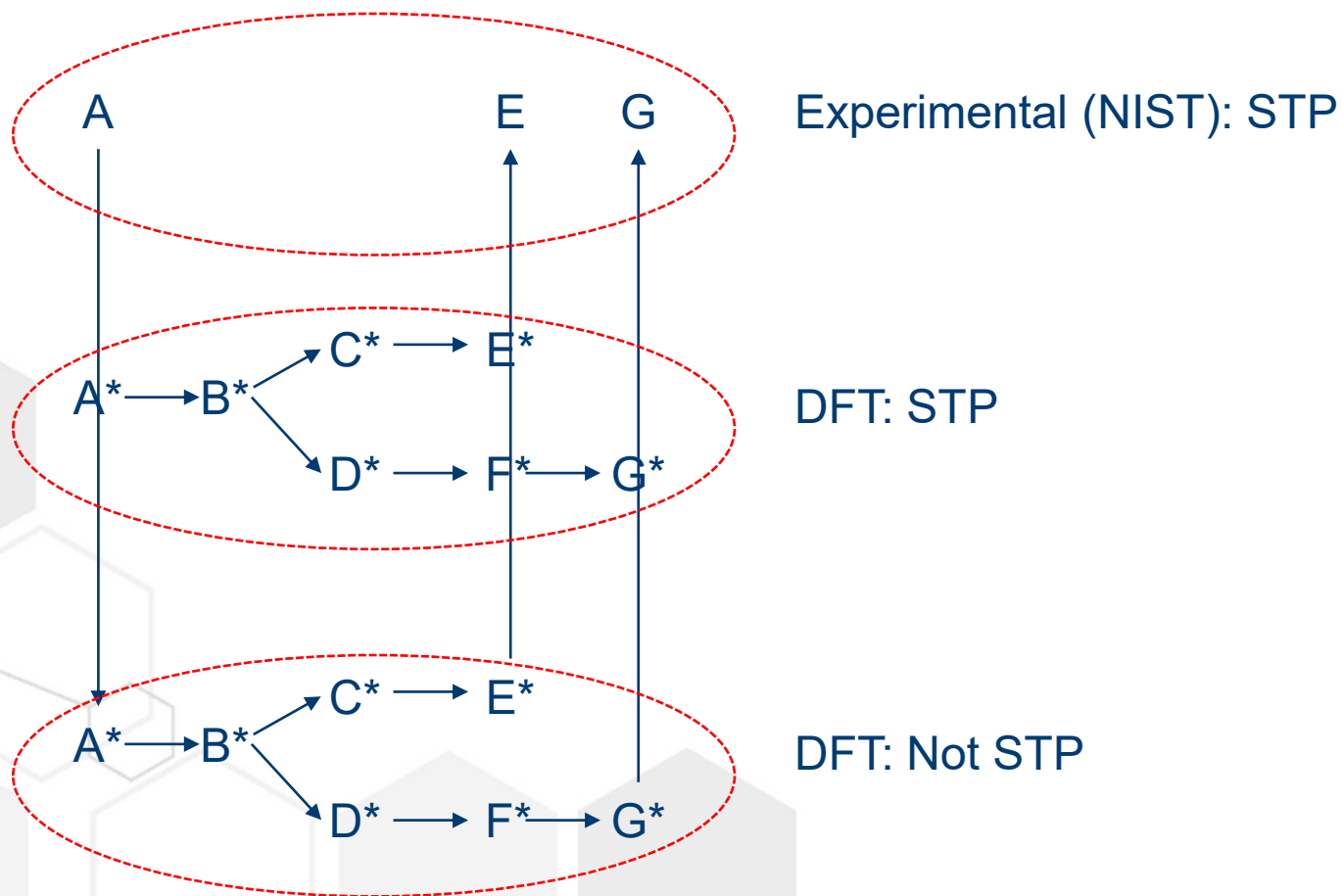
### Pre-exponential factor

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

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



# 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 <sub>4</sub>	-17.89
CH <sub>3</sub> OH	-49.0
CH <sub>3</sub> CH <sub>3</sub>	-20.0
CH <sub>2</sub> CH <sub>2</sub>	12.54
CH <sub>3</sub> CH <sub>2</sub> OH	-56.0
H <sub>2</sub> O	-57.798
CO <sub>2</sub>	-94.051
H <sub>2</sub>	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

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

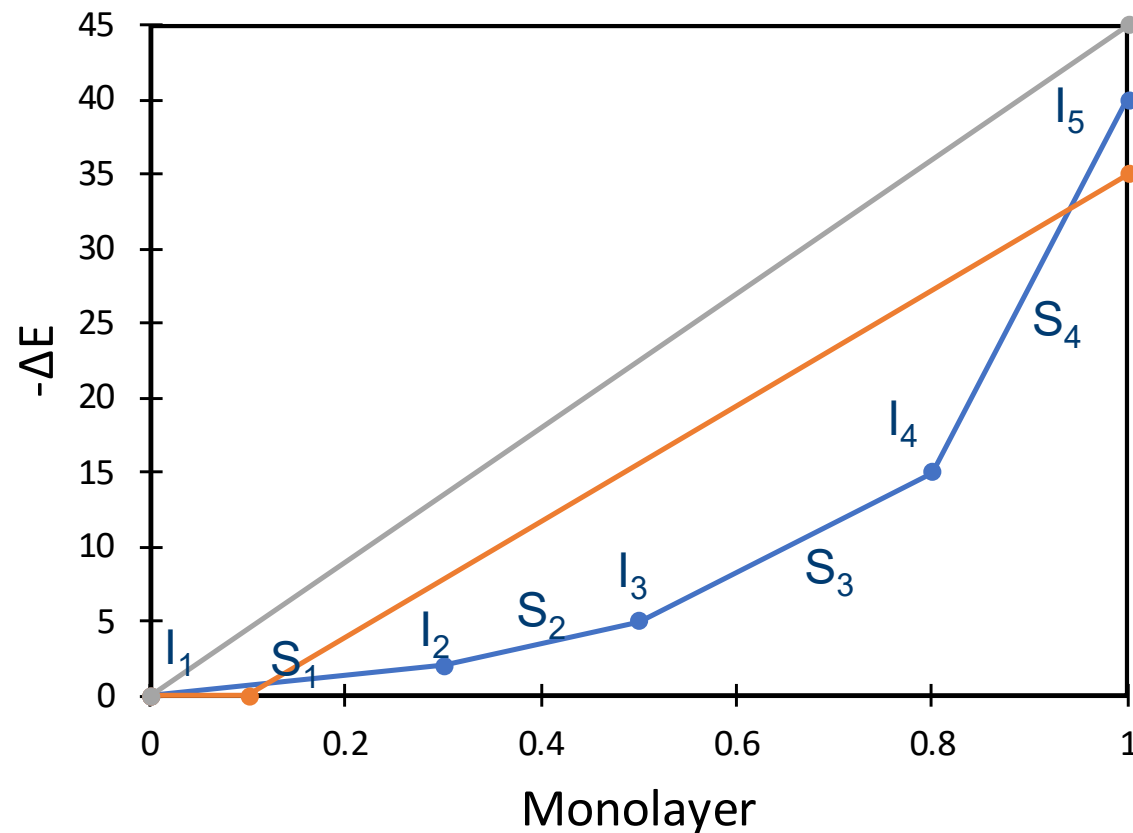
$\cdot$

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

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 1<sup>st</sup>, 2<sup>nd</sup>, n<sup>th</sup> 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)

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

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

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