

Tools for Kinetic Modeling

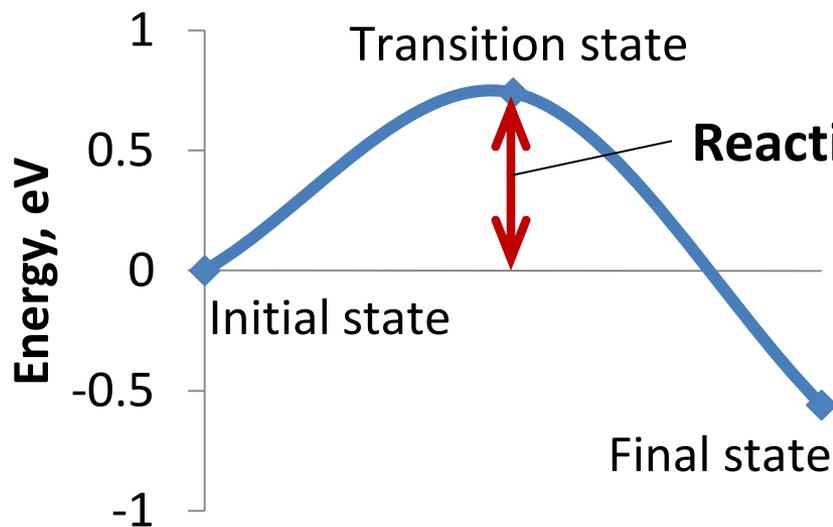
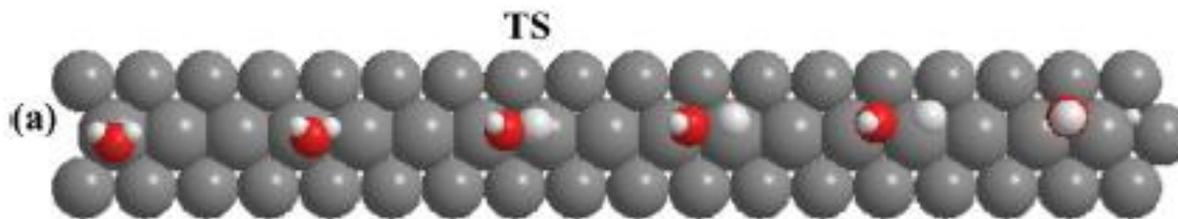
November 4, 2014

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Jonathan Sutton

Dionisios G. Vlachos

From DFT to Reaction Rates



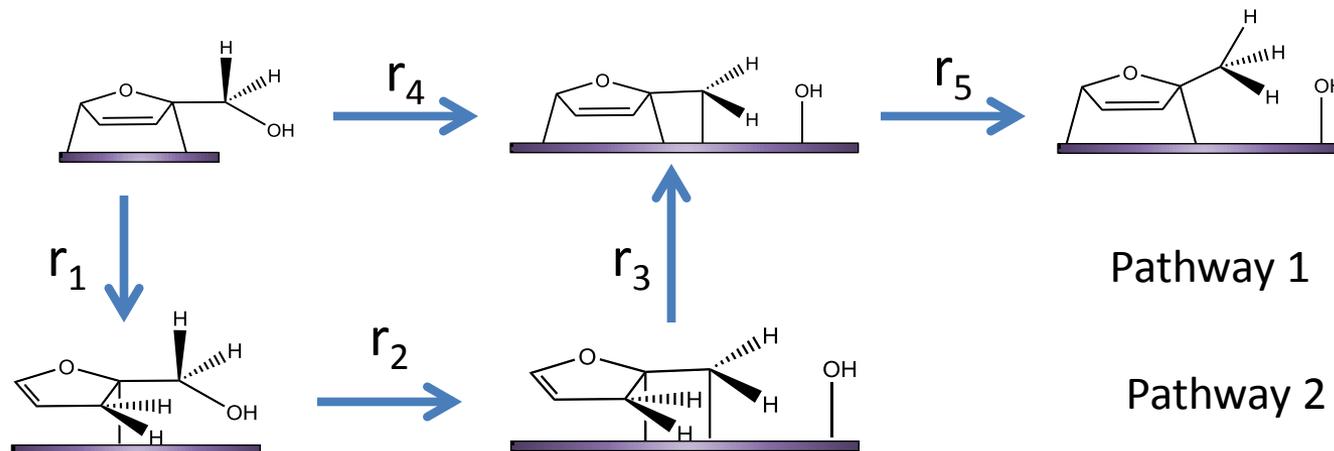
$$r = A \times e^{-\frac{E_a}{RT}} [\text{H}_2\text{O}]$$

$$r_{reverse} = A \times e^{-\frac{E_a,r}{RT}} [\text{H}][\text{OH}]$$

How fast is the reaction in the experiment?

Both energetics and concentrations determine the reaction rate

Reaction Paths

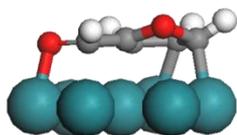


Which pathway is dominant? What is the **rate-controlling step**?

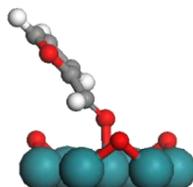
Microkinetic model gives an answer

Rates can be compared to experiment for model validation

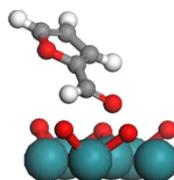
0 ML O/Ru



0.25 ML O/Ru



0.5 ML O/Ru



Activity and adsorption mode depend on oxygen coverage

Surface oxygen is produced in the reaction

Microkinetic model can predict reactivity as a function of surface environment

Limitation of Mean Field Microkinetic Models (MKM)



$$r = A \times e^{-\frac{E_a, r}{RT}} \underbrace{[H][OH]}$$

Product of species concentrations/probabilities

MKM

		B	A
	A		B
B		A	
A			B

$$r \propto \theta_A \theta_B$$

~~MKM~~

A		A	
	B	B	B
A	B	B	B
	B	B	A

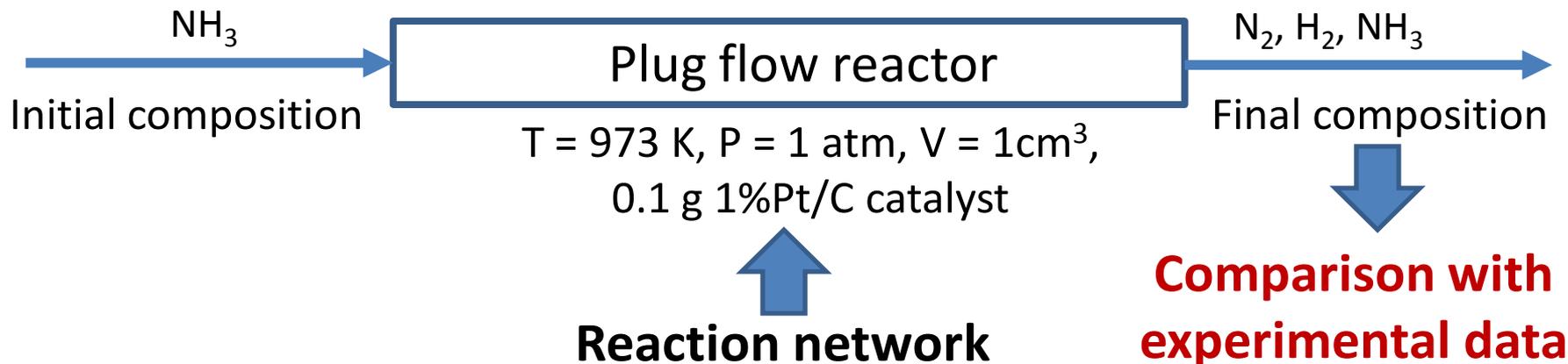
$$r < \theta_A \theta_B$$

MKM is applicable for well-mixed systems with low degree of order

Toy Problem



- What is the predicted **NH₃ conversion**?
- What is **the reaction mechanism**?
- What is **the rate-controlling step**?
- How does the **surface** look like under **reaction conditions**?

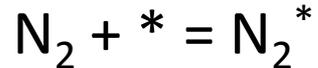
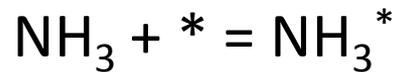


Toy Problem

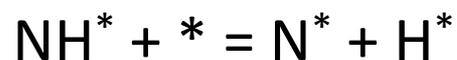
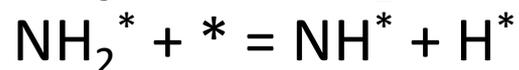
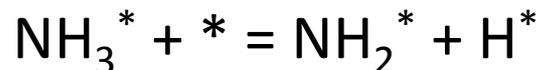


$T = 973 \text{ K}$, $P = 1 \text{ atm}$, $V = 1 \text{ cm}^3$,
 0.1 g 1%Pt/C catalyst

Adsorption:



Surface reactions:



Example of a mass balance for N^* species:

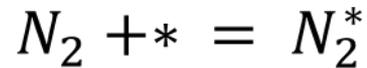
$$\begin{aligned}
 \frac{dN_{\text{N}^*}}{dt} = & \overbrace{2k_4[\text{N}_2][\text{Pt}]}^{\text{rates}} - \frac{k_4}{K_{c4}} [\text{N}^*]^2 + \\
 & + k_7[\text{NH}^*][\text{Pt}] - \frac{k_7}{K_{c7}} [\text{N}^*][\text{H}^*]
 \end{aligned}$$

Parameters needed:

- Forward rate constants k
- Equilibrium constants K_c
- Number of catalytic sites

How can we get the parameters? Predict them!

Equilibrium Constants



K_c can be related to
thermodynamic state functions:

$$K_c = \frac{[N_2^*]}{[N_2][Pt]} = \left(\frac{P_{atm}}{RT}\right)^{-1} \Gamma_0 K_a$$

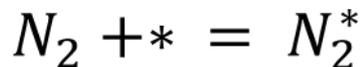
Surface site density, mol/cm²

$$K_a = \exp\left(\frac{\Delta G}{RT}\right) = \exp\left(\frac{S_{N_2^*} - S_{N_2}}{R} - \frac{H_{N_2^*} - H_{N_2}}{RT}\right)$$

NIST database

How can we calculate S and H
for surface species?

Equilibrium Constants



$$H_{N_2^*} = U_{N_2^*} = RT \left[\sum_{i=1}^{3n} \left(\underbrace{\frac{\theta_{v,i}}{2T}}_{\text{Zero-point energy}} + \underbrace{\frac{\theta_{v,i}}{T} \frac{e^{-\theta_{v,i}/T}}{1 - e^{-\theta_{v,i}/T}}}_{\text{Temperature correction}} \right) \right] + \underbrace{\epsilon_{elect}}_{\text{DFT energy}}$$

$$\theta_{v,i} = \frac{\hbar \nu_i}{k}$$

Zero-point energy (ZPE; $\neq f(T)$)

Temperature correction ($= f(T)$)

DFT energy

Vibrational frequencies from DFT

$$S_{N_2^*} = R \left[\sum_{i=1}^{3n} \left(\frac{\theta_{v,i}}{T} \frac{e^{-\theta_{v,i}/T}}{1 - e^{-\theta_{v,i}/T}} - \ln(1 - e^{-\theta_{v,i}/T}) \right) \right]$$

Key assumption: only vibrational degrees of freedom (n) are present in surface species

N/Pt(111): 3 degrees of freedom: 425, 382, 372 cm^{-1}

Equilibrium constants can be calculated from DFT energies and vibrational frequencies

Thermodynamic Consistency

OH/Ru(0001)

DFT energy: -593.5 eV $-$

slab energy: -582.2 eV $-$

ZPE: $+0.34 \text{ eV}$ $+$

T correction: $+0.09 \text{ eV}$ $+$

-10.9 eV

or -1049 kJ/mol

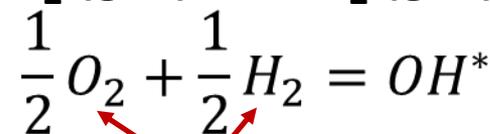
Not physical

- Needs to be converted to thermodynamically meaningful quantity
- Reference state** must be chosen

$$H_{O^*} = \text{ZPE} + \text{T correction} + \text{DFT energy}$$

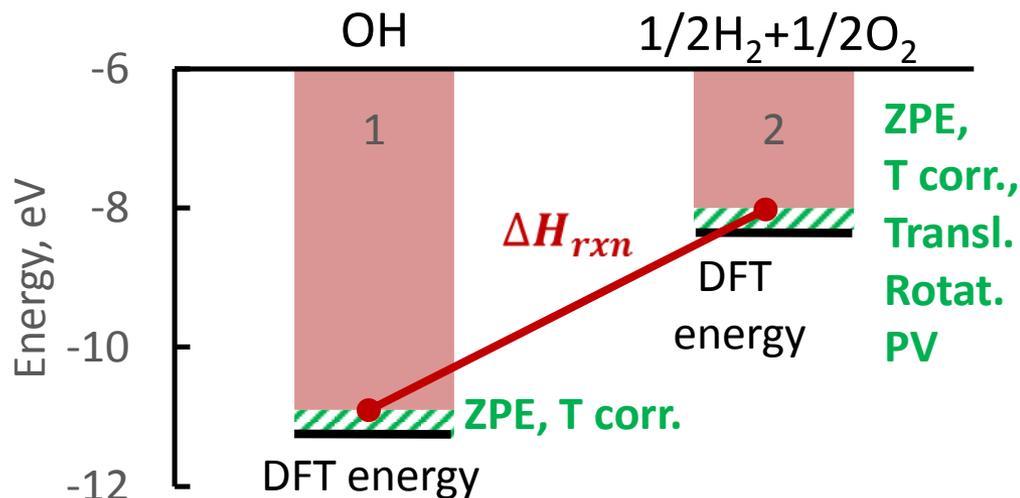
One reference choice:

O_2 (gas) and H_2 (gas)



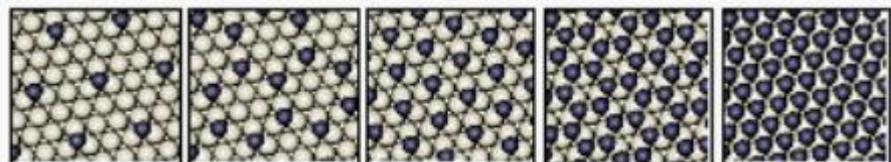
$\Delta H^0 = 0 @ 25^\circ\text{C}, 1 \text{ atm}$

$$\Delta H_{OH^*}^0 = \Delta H_{rxn}$$



Use of the same reference set for all species guarantees thermodynamic consistency

Lateral interactions



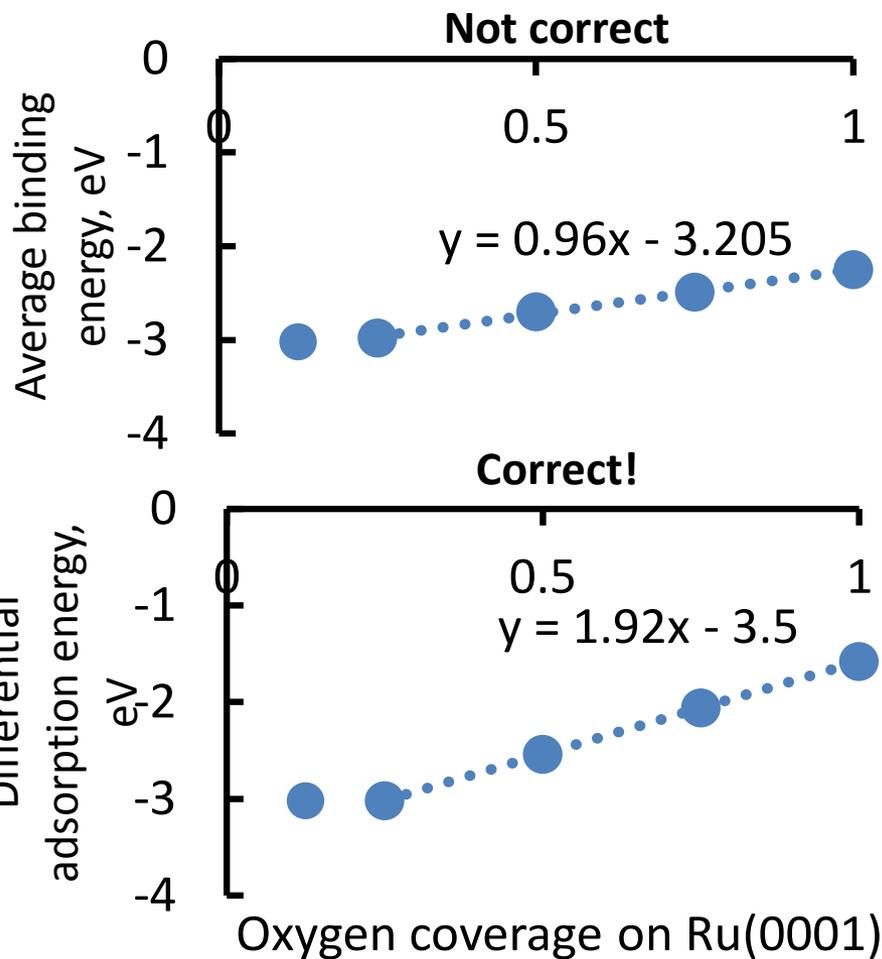
$$\Delta E_{avg} = \frac{E_{n-slab} - E_{slab} - n \times E_{gas}}{n}$$

$$\Delta E_{avg} = a\theta + b$$

$$\Delta E_{int} = \theta \times \Delta E_{avg} = a\theta^2 + b\theta$$

$$\Delta E_{diff} = \frac{\partial \Delta E_{int}}{\partial \theta} = 2a\theta + b$$

$$\Delta H_{diff} = 2a\theta + b + ZPE + H_{corr}(T)$$

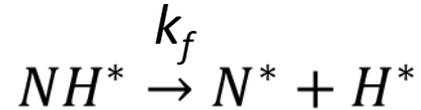


Lateral interaction can be approximated by linear model

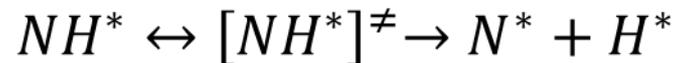
¹Guo, Wei, and Dionisios G. Vlachos. *The Journal of chemical physics* 138 (2013): 174702.

²Grabow, Lars C., Britt Hvolbæk, and Jens K. Nørskov. *Topics in Catalysis* 53.5-6 (2010): 298-310.

Rate Constants for Surface Reactions



Transition state theory



$$k_f = \frac{k_B T}{h} \exp\left(\frac{S_{NH^*}^\ddagger - S_{NH^*}}{R}\right) \exp\left(-\frac{H_{NH^*}^\ddagger - H_{NH^*}}{RT}\right)$$

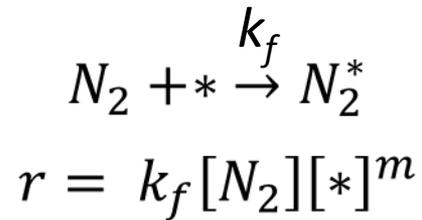
Rate constants can be calculated from DFT energies and vibrational frequencies of initial and transition states

In the first approximation:

$$k_f = \frac{k_B T}{h} \exp\left(-\frac{E_{NH^*}^\ddagger - E_{NH^*}}{RT}\right)$$

Useful for first-pass MKM models

Rate of Adsorption



From collision theory:

Sticking coefficient

$$k_f = \frac{S}{(\Gamma_{tot})^m} \sqrt{\frac{RT}{2\pi M}}$$

Site density

Mean thermal velocity

The model is applicable to both gases and liquids¹

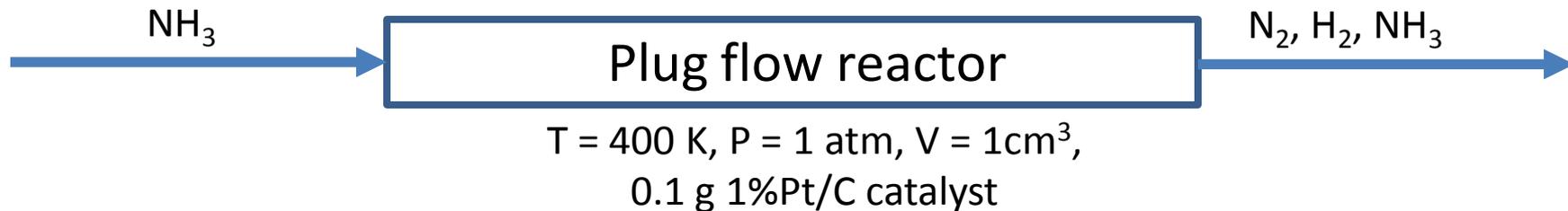
$S = 0.1-1$: non-activated adsorption

$S < 10^{-6}$: activated adsorption

$S = 10^{-8} - 10^{-6}$: liquids¹

¹Jung and Campbell. Physical Review Letters 84: 5164 (2000)

Number of Catalytic Sites



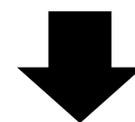
CO Chemisorption:

$2.2 \cdot 10^{-4} \text{ mol CO/g of catalyst}$



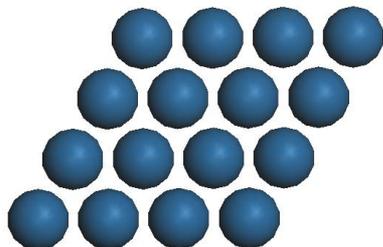
$2.2 \cdot 10^{-4} \text{ mol Pt/g of catalyst}$

$8.3 \cdot 10^3 \text{ cm}^2 \text{ of Pt surface}$
in the reactor



Area-to-volume ratio
 $A/V = 83 \text{ cm}^{-1}$

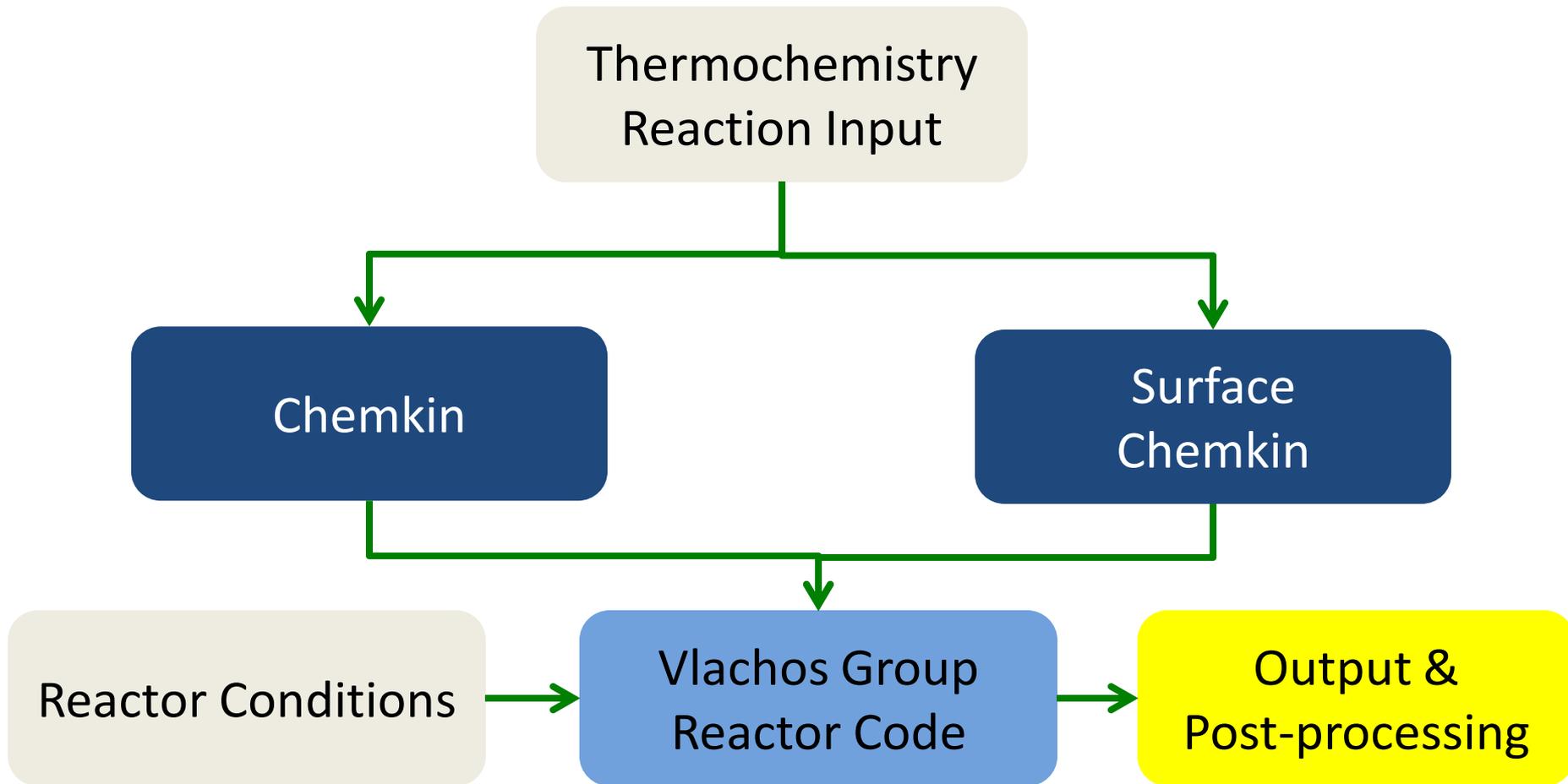
$2.6 \cdot 10^{-9} \text{ mol Pt sites/cm}^2$



A/V can be calculated from CO chemisorption data

Chemkin-II is the Foundation of the Reactor

Code



Chemkin/ Chemkin II libraries from Sandia laboratories facilitate model development

Defining the Thermochemistry

- Properties are usually defined in one file *thermdat*
- Data is stored as NASA polynomial coefficients

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

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

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

```

thermdat
File Edit Search Options Help
THERMO
    300      5000      1000
CH3CH2OH      C      2H      60      1      G200      6000      1E+03      1
6.56243650E+00 1.52042220E-02 -5.38967950E-06 8.62250110E-10 -5.12897870E-14 2
-3.15256210E+04 -9.47302020E+00 4.85869570E+00 -3.74017260E-03 6.95553780E-05 3
-8.86547960E-08 3.51688350E-11 -2.99961320E+04 4.80185450E+00 4
    
```

High T $a_1 - a_7$ followed by low T $a_1 - a_7$ in 15 character wide fields

Defining the System Chemistry

Gas.inp (gas phase)

surf.inp (surface phase)

```

fort.15
File Edit Search Options Help
ELEMENTS
O
H
C
HE
PT
END

SPECIES
CH3CH2OH
CH3CHO
CH3CH3
CH2CH2
CHCH
CH3OH
CH2O
CH4
H2
O2
CO
CO2
H2O
HE
END

!THERMO
! Insert GRI-M
!END
REACTIONS
!O+H2<=>H+OH          3.870E+04    2.700    6260.00
END
    
```

Elements go here (required)
key word – ELEMENTS

Species go here (required)
key word – SPECIES

Reactions go here (optional)
key word – REACTIONS

```

surf.inp
File Edit Search Options Help
!Surface species
!=====
!Format is Label(S)/number of sites occupied/

SITE/SURFACE/          SDEN/2.49081E-9/

H2O(S)/1/
OH(S)/1/
O(S)/1/
H(S)/1/
PT(S)

BULK PT(B)/21.4/
END

!Reactions
!=====

REACTIONS MWOFF KCAL/MOLE
!Adsorption/Desorption *****

H2 + 2PT(S) = 2H(S) + 2PT(B)      0.5  0.00  0.00
STICK
O2 + 2PT(S) = 2O(S) + 2PT(B)      0.5  0.00  0.00
STICK
H2O + PT(S) = H2O(S) + PT(B)      0.5  0.00  0.00
STICK

!Surface Reactions *****

H2O(S) + PT(S) = OH(S) + H(S) + PT(B)  8.37E+18  1.00  15.91
OH(S) + PT(S) = O(S) + H(S) + PT(B)    8.37E+18  1.00  18.72
2OH(S) = H2O(S) + O(S)                 8.37E+18  1.00  1.49

END
    
```

All fields start with a key word and end with 'END'
Anything after an exclamation point (!) is a comment

Defining the System Chemistry

Gas.inp (gas phase)

surf.inp (surface phase)

```

fort.15
File Edit Search Options Help
ELEMENTS
O
H
C
HE
PT
END

SPECIES
CH3CH2OH
CH3CHO
CH3CH3
CH2CH2
CHCH
CH3OH
CH2O
CH4
H2
O2
CO
CO2
H2O
HE
END

!THERMO
! Insert GRI-Mech thermodynamics here or use in default file
!END
REACTIONS
!O+H2<=>H+OH          3.870E+04    2.700    6260.00

END
    
```

```

surf.inp
File Edit Search Options Help
!Surface species
!=====
!Format is Label(S)/number of sites occupied
SITE/SURFACE/          SDEN/2.49081E-9/

  H2O(S)/1/
  OH(S)/1/
  O(S)/1/
  H(S)/1/
  PT(S)

BULK PT(B)/21.4/
END

!Reactions
!=====

REACTIONS MWOFF KCAL/MOLE
!Adsorption/Desorption *****

  H2 + 2PT(S) = 2H(S) + 2PT(B)      0.5  0.00  0.00
  STICK
  O2 + 2PT(S) = 2O(S) + 2PT(B)      0.5  0.00  0.00
  STICK
  H2O + PT(S) = H2O(S) + PT(B)      0.5  0.00  0.00
  STICK

!Surface Reactions *****

  H2O(S) + PT(S) = OH(S) + H(S) + PT(B) 8.37E+18 1.00 15.91
  OH(S) + PT(S) = O(S) + H(S) + PT(B)  8.37E+18 1.00 18.72
  2OH(S) = H2O(S) + O(S)                8.37E+18 1.00 1.49

END
    
```

Define surface/bulk species and number of sites occupied

Defining the System Chemistry

Gas.inp (gas phase)

surf.inp (surface phase)

```

fort.15
File Edit Search Options Help
ELEMENTS
O
H
C
HE
PT
END

SPECIES
CH3CH2OH
CH3CHO
CH3CH3
CH2CH2
CHCH
CH3OH
CH2O
CH4
H2
O2
CO
CO2
H2O
HE
END

!THERMO
! Insert GRI-Mech thermodynamics here or use in default file
!END
REACTIONS
!O+H2<=>H+OH          3.870E+04    2.700    6260.00

END
    
```

Adsorption reactions need the STICK key word

$$r = a \times T^b \times e^{-c/RT}$$

$$a = \frac{k}{h} \times \frac{1}{\sigma^{m-1}}$$

```

surf.inp
File Edit Search Options Help
!Surface species
!=====
!Format is Label(S)/number of sites occupied/

SITE/SURFACE/      SDEN/2.49081E-9/

H2O(S)/1/
OH(S)/1/
O(S)/1/
H(S)/1/
PT(S)

BULK PT(B)/21.4/
END
    
```

Reaction key words and units

```

REACTIONS MWOFF KCAL/MOLE
!Adsorption/Desorption *****
H2 + 2PT(S) = 2H(S) + 2PT(B) 0.5 0.00 0.00
STICK
O2 + 2PT(S) = 2O(S) + 2PT(B) 0.5 0.00 0.00
STICK
H2O + PT(S) = H2O(S) + PT(B) 0.5 0.00 0.00
STICK

!Surface Reactions *****
H2O(S) + PT(S) = OH(S) + H(S) + PT(B) 8.37E+18 1.00 15.91
    
```

Sticking coefficients

Balanced equation followed by pre-exponential or sticking coefficient, temperature exponent, and activation energy

Defining Adsorbate Interactions via tube_COV.inp

```

1 !Thi:
2 15 Total number of species affected
3 !Additional options
4 !BE -- adjusted for binding energy (only important if scaling relations used)
5 !Model -- 1 for old-style (simple linear), 2 for new-style (two parameter
6 ! piecewise with threshold coverage)
7 !BE Model
8 T 2
9 !Each species block has the following format:
10 ! 'Species/Phase/' n
11 ! where n is the number of lines that follow the format
12 ! 'Species/Phase/' val1 val2
13 !The first line is the species that is affected by the species on the
14 !following lines. Subsequent lines have up to two values: the interaction
15 !parameter val1 (both model types) and possibly a coverage threshold val2
16 !(model type 2 only). The Species (This line should be in quotes)
17 !-----
18 'TOL(S)/SURFACE/' 1
19 'TOL(S)/SURFACE/' -76.0 0.38
20 !--
21 'POY(S)/SURFACE/' 1
22 'TOL(S)/SURFACE/' -35 0
23 !--
24 'HPL(S)/SURFACE/' 1
25 'TOL(S)/SURFACE/' -35.0 0

```

“TOL interacts with TOL”

“When going from zero coverage limit to 1 monolayer (ML), binding energy of TOL decreases by 76 kcal/mol”

“No lateral interactions below 0.38 ML TOL coverage”

Controlling the Code via tube.inp

tube.inp

Reactor type
Number of runs

```
1 !irxtr (0=UHV/mol. beam, 1=batch, 2=cstr, 3=pfr) nruns MultiInput
2 1 1 T
```

```
3 !lstp t[K] p[atm] velo[cm3/s] abyv[cm-1] trise[K]
4 T 423.0 1.0E+0 0.066 9.00E4 0.0
```

Temperature, pressure, flow rate,
A/V ratio, T ramp

```
5 !liso(yes=T,no=F) itpd (0=no, 1=UHV, 2=High Pressure) (:
6 T 0
7 !text aextbyv htc ramp [K/s]
8 923.0 3.571 0.0 2.0
```

Reactant and MARI species to keep track of

```
9 !MARI Reactant
10 'FCH3-3/GAS/' 'FCH3-3/GAS/'
```

```
11 !rlen[cm3] nnodes ttout [s] rtime [s] ntdec ltra (F=only SS saved, T=transient saved)
12 1.0E02 10 1.00E-2 1.80E04 10 F
13 !ltol abstol reltol NonNeg(F/T: constraints off/on) restart_max (<=0 means no limit)
14 F 1.E-10 1.E-8 T 0
15 !iSolver (0/1: iterative solver off/on) mu ml (upper/lower bandwidths for Krylov solver)
16 0 0 0
17 !lcov lStatpQ lBEP iScale lEA lomega omega Tref_beta (0: Tref=300K; 1: Tref=1K)
18 T F F 0 F F 0.5 1
19 !mrpa verbose_rpa trpa lsen lDOE
20 1 F 900.0 F F
21 EOF
22
```

Controlling the Code via tube.inp

```

tube.inp x
1 !irxtr (0=UHV/mol. beam, 1=batch, 2=cstr, 3=pfr) nruns MultiInput
2 1 1 T
3 !lstp t[K] p[atm] velo[cm3/s] abyv[cm-1] trise[K]
4 T 423.0 1.0E+0 0.066 9.00E4 0.0
5 !liso(yes=T,no=F) itpd (0=no, 1=UHV, 2=High Pressure) (itpd overrides liso)
6 T 0
7 !text aextbyv htc ramp [K/s]
8 923.0 3.571 0.0 2.0
9 reactant
10 Reactant
11 rlen[cm3] nnodes ttout [s] rtime [s] ndec itra (s=only SS saved, T=transient saved)
12 1.0E02 10 1.00E-2 1.80E04 10 F
13 !itol abstol reltol NonNeg(F/T: constraints off/on) restart_max (<=0 means no limit)
14 F 1.E-10 1.E-8 T 0
15 Coverage effects on/off
16 mu ml (upper/lower bandwidths for Krylov solver)
17 0 0
18 !lcv lStatpQ lBEP iScale lEA lomega omega Tref_beta (0: Tref=300K; 1: Tref=1K)
19 T F F 0 F F 0.5 1
20 !mrpa verbose_rpa trpa lsen lDOE
21 1 F 900.0 F F
22 EOF

```

Reactor volume

Running time

Coverage effects on/off

Sensitivity Analysis on/off (to determine a rate-determining step)

List of Important Output Files

Output Type

File(s)

Kinetic parameters	Beta_out.out, Ea_over_RT.out, Preex_out.out, stoich_matrix.out
Thermochemistry	EQKC_out.out, [HGS]rxn_out.out, [HS]form_out.out
Conversion	tube_conv.out
Surface coverages	tube_cov_tra.out, tube_cov_ss.out
Gas composition	tube_gasmole.out, tube_gasmass.out (mole/mass fractions)
Species production rates	tube_gas_sdot.out (in mol/cm ² /s)
Reaction Path Analysis	tube_rpa.out, rpa_vis_output.txt
Sensitivity Analysis	tube_sen.out

- Most output files/types are self-explanatory
- Further examine **green** highlighted output types

Overview of Reaction Path Analysis

- Reaction path analysis involves following the production/consumption of each species
- Partial equilibrium ratio shows the degree of reversibility of an elementary step (PEI~0.45-0.55 denotes partial equil.)

$$PEI = \frac{|r_{fwd}|}{|r_{fwd}| + |r_{rev}|}$$

- Can be used to understand the fluxes, i.e., which reactions contribute to products and to construct reduced mechanisms

Overview of Reaction Path Analysis

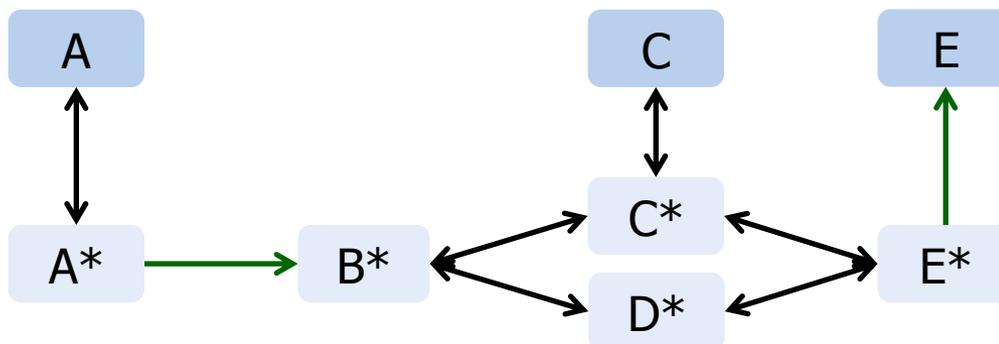
- Format of tube_rpa.out

$$PEI = \frac{|r_{fwd}|}{|r_{fwd}| + |r_{rev}|}$$

```

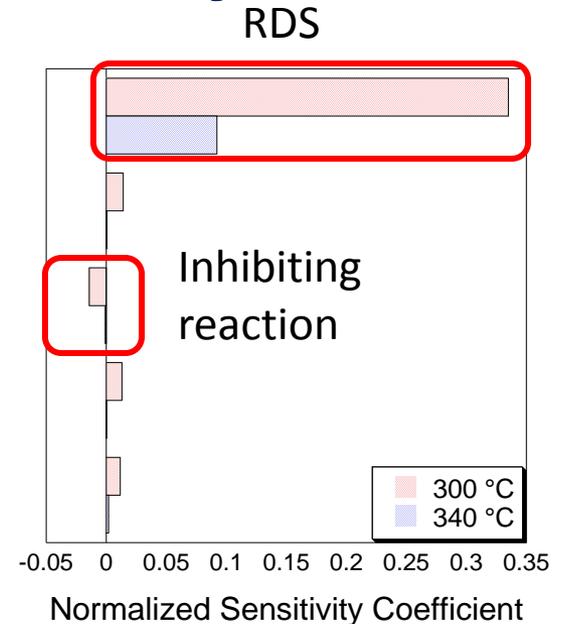
tube_rpa.out
File Edit Search Options Help
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going to species number:      15  and name: CH3CH2OH(S)
Rxn #   % Prod/Cons   Net Rate   Fwd Rate   PE Ratio
  1      1.00000E+02   4.10835E-09 1.23745E-03 5.00001E-01  CH3CH2OH+PT(S)=CH3CH2OH(S)+PT(B)
 14     -9.99287E+01   4.10728E-09 4.12797E-09 9.95013E-01  CH3CH2OH(S)+PT(S)=CH3CHO(H(S)+H(S)+PT(B)
 36     -1.56066E-02   6.41465E-13 6.45029E-13 9.94505E-01  CH3CH2OH(S)+2PT(S)=CH2CH2OH(S)+H(S)+2PT(B)
 68     -5.56966E-02   2.28925E-12 3.69797E-09 5.00155E-01  CH3CH2OH(S)+PT(S)=CH3CH2O(S)+H(S)+PT(B)
 84     -1.76760E-16   7.26521E-27 7.26521E-27 1.00000E+00  CH3CH2OH(S)+PT(S)=CH2OH(S)+CH3(S)+PT(B)
117     -4.13143E-09   1.69810E-19 1.69810E-19 1.00000E+00  CH3CH2OH(S)+PT(S)=CH3CH2(S)+OH(S)+PT(B)
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```



Overview of Sensitivity Analysis

- Sensitivity analysis measures the effect of perturbing a parameter (e.g. a pre-exponential) on a response (e.g., the conversion)
- Sensitivity analysis is useful for
 - Determining a rate-controlling step
 - Subsequent parameter refinement



Determining the sensitive reactions in ethanol SR

$$NSC_i = \frac{d \ln X}{d \ln k_i}$$

Running chemkin

- Copy input files to your machine
 - `cp -r ./software/Workshop14/Tutorials/Tutorial4/chemkin_toy .`
- Type `chmod +x chemkin.sh`
- Launch chemkin by typing `./chemkin.sh`

Output Files to Look For

OUT.d directory

1. *tube_conv.out*: conversion and reaction rate
2. *tube_gasmole_ss.out*: gas composition along the reactor
3. *tube_cov_ss.out*: surface coverages along the reactor
4. *tube_rpa.out*: Reaction path analysis output

Running Sensitivity Analysis

1. */INP.d/tube.inp*: set $l_{sen} = T$
2. *../chemkin.sh*: run the model
3. */OUT.d/tube_sen.out*: output file
4. Find the reactant; the highest absolute value corresponds to the rate-controlling step

Things to Play With

1. Vary temperature, pressure, reactor volume and see what effect it has on conversion, rates, and coverages
2. Turn off lateral interactions, reduce the $N_2 \rightarrow 2N$ barrier, and increase the pressure. What effect it has on coverages?
3. Change the feed composition; flow rate and see what effect it has on the output.
4. Run the sensitivity analysis and explore the changes in a rate-controlling step, when elementary barriers are perturbed

Advanced Exercises

1. In a first approximation, energy barriers can be linearly related to reaction energies via BEP relationships. The relationships are given in INP.d/BEP.inp.
 - Set $IBEP = T$ in tube.inp file, and see how different the results are compared to fully ab initio, DFT-based case.
2. All reaction energetics can be related to C, H, O, N atomic binding energies, so that reactant conversion can be plotted as a function of only 2 descriptors. In this way, optimal catalyst properties can be predicted. Alter Scaling.inp file following instructions in it, assuming that binding energies of NH_x species are linearly related to the N binding energy with the slope $(3-x)/3$.