

1 Lecture 0: Intro to Reaction Engineering

1. Reaction engineering

Understanding, modeling, designing, using, controlling, analyzing, improving anything in which chemical reactions happen.

1. Reaction engineering applications

(a) Traditional

- i. Industrial chemical/petroleum processes
- ii. Fine chemical/pharmaceutical processes
- iii. Emerging, eg biorefinery, shale gas, <http://cistar.us>

(b) Energy storage, batteries, fuel cells

(c) Environmental systems

- i. Atmosphere, lake, bioreactor (water purification), catalytic convertor

(d) Biological systems

- i. Cell, organ, body

(e) Laboratory reactors - interrogate, quantify

(f) Research - improved materials (catalysts), improved processes, understand limitations

- i. Sabatier plot, <https://doi.org/10.1038/nchem.121>

2. Course structure

(a) Quantifying chemical reactions

- i. Stoichiometry
- ii. Thermodynamics - heat flow, direction, equilibrium
- iii. Kinetics - rates, mechanisms

(b) Physical/chemical interactions

- i. Transport, mixing, diffusion resistance, ...

(c) Chemical reactors

- i. Ideal 0 and 1-dimensional
- ii. Non-ideal
- iii. Non-isothermal
- iv. Non-steady state
- v. Multiphase

(d) Chemical processes (beyond us)

(e) Markets (beyond us)

2 Stoichiometry and reactions

1. Substances
2. Amounts
 - (a) mass, moles, volumes
 - (b) flow rates
3. compositions
 - (a) amount/total amount
4. Reactions and stoichiometric coefficients
 - (a) Advancements $n_j = \sum_i \nu_{ij} \xi_i$
 - (b) Limiting reagents

3 Chemical thermodynamics and equilibria

1. Chemical reactions $\sum_j \nu_j A_j = 0$
2. Thermodynamic potential differences
 - (a) Standard states
 - (b) Formation reactions
 - (c) Reaction enthalpy $\Delta H^\circ(T) = \sum_j \nu_j H_j^\circ(T) = \sum_j \nu_j H_{f,j}^\circ(T)$
 - (d) Reaction entropy $\Delta S^\circ(T) = \sum_j \nu_j S_j^\circ(T)$
3. Equilibrium-closed system
 - (a) Free energy vs reaction advancement, $G(\xi, T) = \sum_j n_j \mu_j = \sum_j (n_{j0} + \nu_j \xi) (\mu_j^\circ(T) + RT \ln a(\xi, T))$
 - (b) Equilibrium $(\partial G / \partial \xi)_{T,P} = 0$
 - (c) Equilibrium constants and algebraic solutions
 - (d) Multiple reactions
4. Le'Chatlier principle - system at equilibrium responds to oppose any perturbation
 - (a) Pressure, composition
 - (b) Temperature: Gibbs-Helmholtz and van't Hoff
5. Equilibrium-open system
 - (a) Reaction phase diagrams, see <http://pubs.acs.org/doi/abs/10.1021/jacs.6b02651> for an example
 - (b) Electrochemical reactions
6. The molecular interpretation
7. Non-ideal activities
8. Surface adsorption
 - (a) Langmuir

4 Empirical kinetics

1. rates: number per unit time per unit something
2. reactor mass balance
3. rate expressions, Functions of T , P , composition C_i
4. rate orders
5. apparent orders
6. integrated rate expressions
7. temperature and Arrhenius expression, $k = Ae^{-E_a/k_B T}$
 - (a) Arrhenius plot, $\ln k$ vs $1/T$

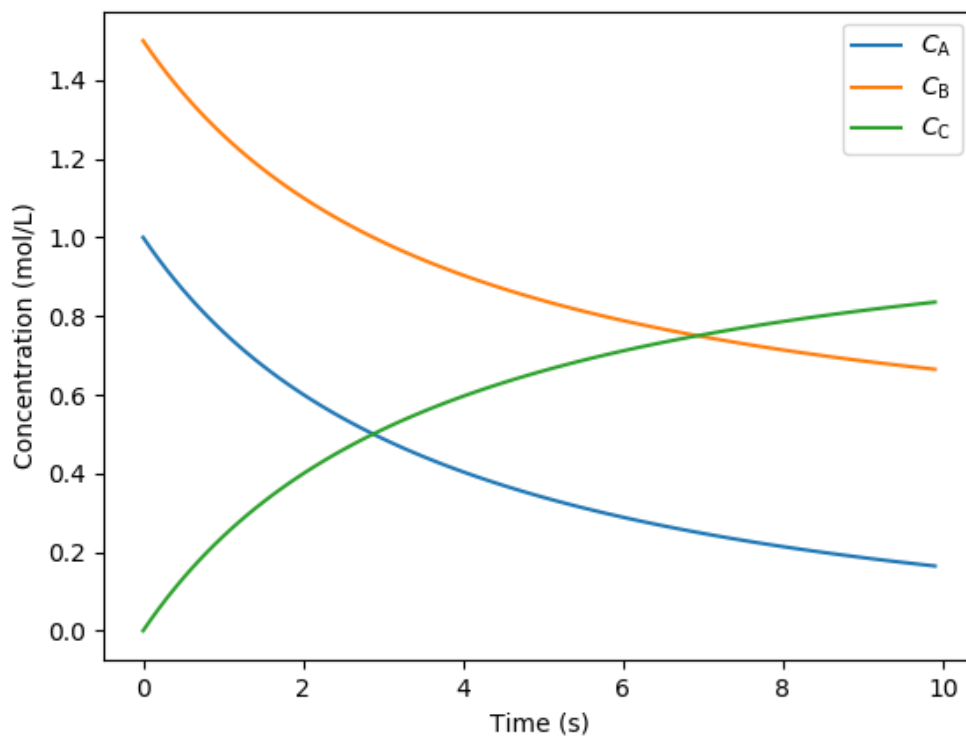
Table 1: Basic kinetic rate laws

	differential rate	integrated rate	half-life
First order	$r = kC_A$	$C_A = C_{A0}e^{-k\tau}$	$\ln 2/k$
Second order	$r = kC_A^2$	$1/C_A = 1/C_{A0} + k\tau$	$1/kC_{A0}$

```

1 import numpy as np           #this lets up handles arrays of data
2 import matplotlib.pyplot as plt
3 from scipy.integrate import odeint, solve_ivp
4
5 def dCdt(C,t,k):
6     dC_Adt = -k*C[0]*C[1]    # A + B -> C;  r = k CA CB
7     dC_Bdt = -k*C[0]*C[1]
8     dC_Cdt =  k*C[0]*C[1]
9     dCdt = [dC_Adt,dC_Bdt,dC_Cdt]
10    return dCdt
11
12 # initialize concentrations
13 C_0 = [1., 1.5, 0.]
14
15 # initialize k's
16 k = 0.2
17
18 # Range of time to solve over
19 t = np.arange(0,10,0.1)
20 t_span = (0., 10.)
21
22 p = (k,) # turn parameters into a tuple
23 # Solve two ODEs with odeint
24 #C = solve_ivp(dCdt,t_span,C_0,p,method='LSODA')
25 C = odeint(dCdt,C_0,t,p)
26
27 C_A = C.transpose()[0] # Get C_A from C
28 C_B = C.transpose()[1] # Get C_B from C
29 C_C = C.transpose()[2]
30 plt.figure()
31 plt.plot(t,C_A,'-',label=r'$C_{\rm A}$')
32 plt.plot(t,C_B,'-',label=r'$C_{\rm B}$')
33 plt.plot(t,C_C,'-',label=r'$C_{\rm C}$')
34 plt.xlabel('Time (s)')
35 plt.ylabel('Concentration (mol/L)')
36 plt.legend()
37 plt.savefig('./conc.png')

```



5 Analyzing reactor data

1. Differential methods
 - (a) Measuring rates
2. Integral methods
3. Half-lives

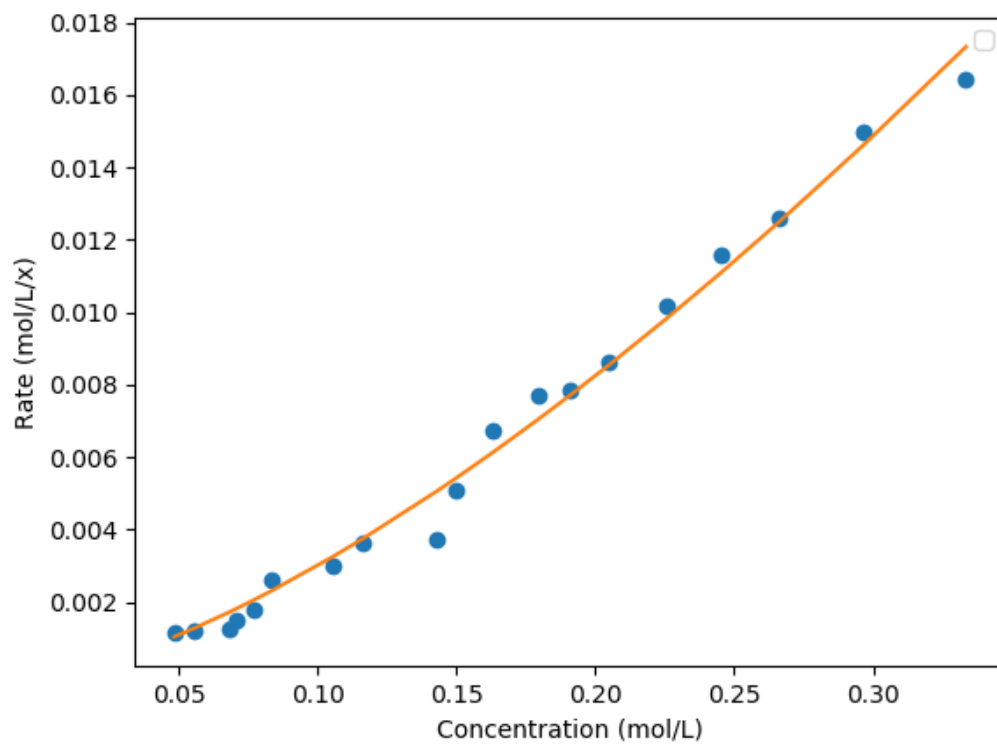
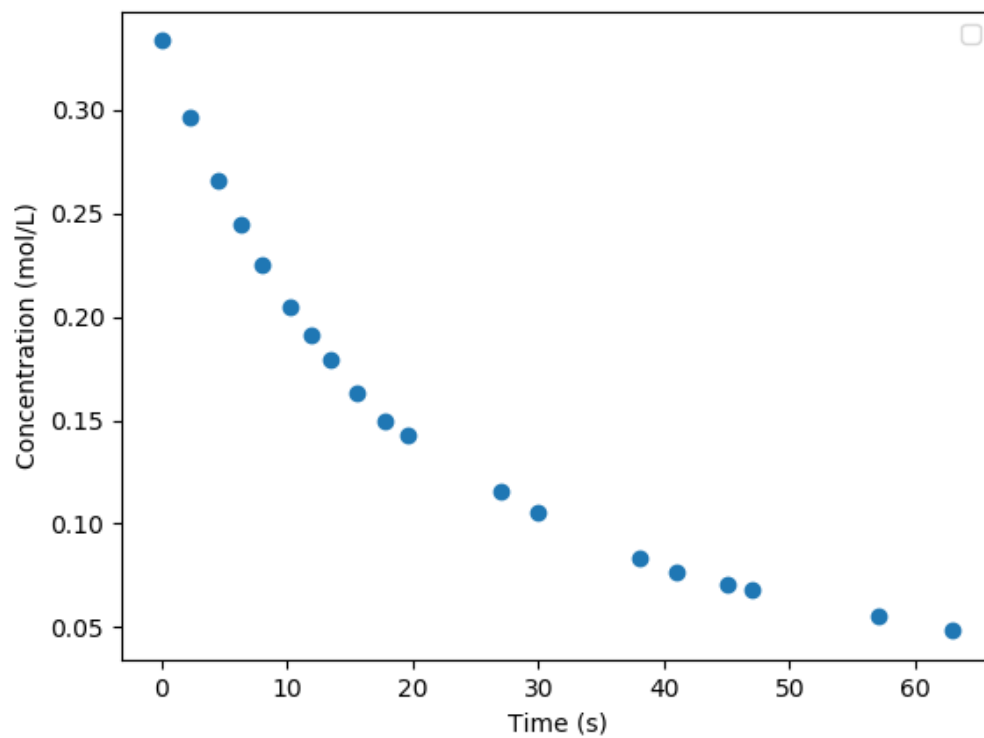
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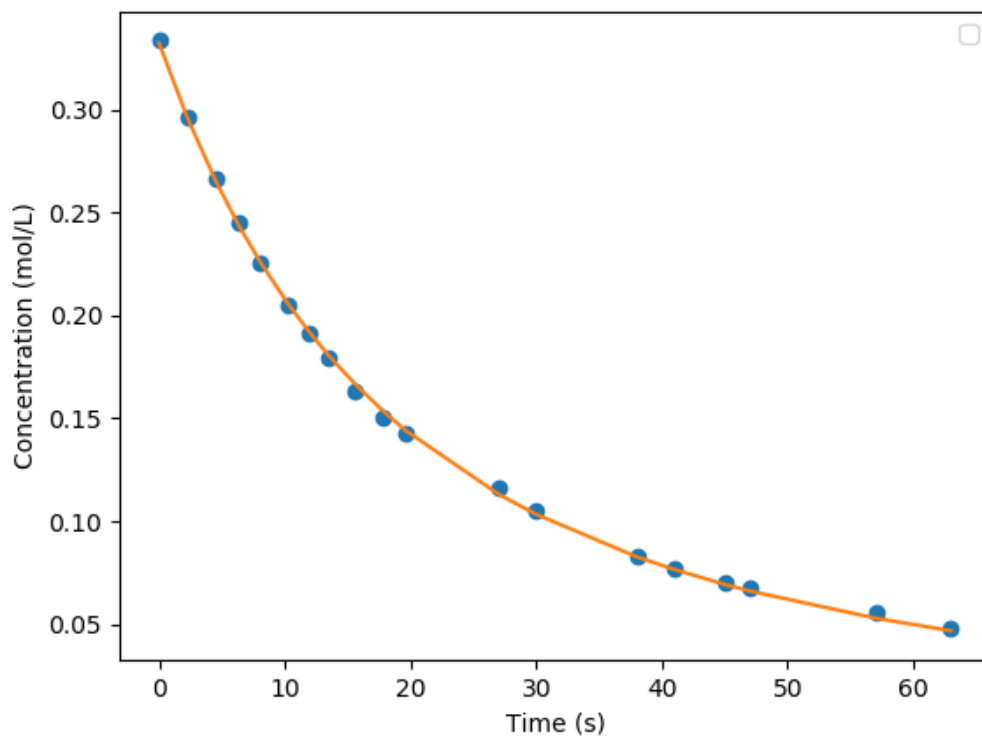
1  import numpy as np                #this lets up handles arrays of data
2  import matplotlib.pyplot as plt
3  from scipy.optimize import curve_fit
4
5  def differential(x, k, alpha):
6      return k*x**alpha
7
8  def integral(t, a, b):
9      return (2*a/(2+a*b*t))**2
10
11  t = np.array([0.00, 2.25, 4.50, 6.33, 8.00, 10.25, 12.00, 13.50, 15.60, 17.85, 19.60, 27.00, 30.00, 38.00, 41.00, 45.00, 47.00,
12
13  C_Br2 = np.array([0.3335, 0.2965, 0.2660, 0.2450, 0.2255, 0.2050, 0.1910, 0.1794, 0.1632, 0.1500, 0.1429, 0.1160, 0.1053, 0.0830,
14
15  plt.figure()
16  plt.plot(t, C_Br2, 'o')
17  plt.xlabel('Time (s)')
18  plt.ylabel('Concentration (mol/L)')
19  plt.legend()
20  plt.savefig('./xylene-conc.png')

```

```
21
22 delta_t = np.ediff1d(t)          # finite difference between adjacent points
23 delta_C = np.ediff1d(C_Br2)
24
25 grad_t = np.gradient(t)          # second order approximation to gradient, allowing for unequal step size
26 grad_C = np.gradient(C_Br2)
27 rate = -np.divide(grad_C, grad_t)
28
29 plt.figure()
30 plt.plot(C_Br2, rate, 'o')
31 plt.xlabel('Concentration (mol/L)')
32 plt.ylabel('Rate (mol/L/x)')
33 plt.legend()
34
35 popt, pcov = curve_fit(differential, C_Br2, rate )
36
37 print('k = {0:f}, alpha={1:f}'.format(popt[0], popt[1]))
38
39 model = differential(C_Br2, popt[0], popt[1])
40 plt.plot(C_Br2, model, '-')
41
42 plt.savefig('./xylene-rate.png')
43
44 difference_array = np. subtract(rate, model)
45 squared_array = np. square(difference_array)
46 mse = squared_array. mean()
47 print(mse)
48
49 # Suggests order of 1.5
50 popt1, pcov1 = curve_fit(integral, t, C_Br2)
51 print('k = {0:f}'.format(popt[1]))
52
53 model1 = integral(t, popt1[0], popt1[1])
54
55 plt.figure()
56 plt.plot(t, C_Br2, 'o')
57 plt.plot(t, model1, '-')
58 plt.xlabel('Time (s)')
59 plt.ylabel('Concentration (mol/L)')
60 plt.legend()
61 plt.savefig('./xylene-int-model.png')
```

```
k = 0.085277, alpha=1.450860
2.4942019231742367e-07
k = 1.450860
```





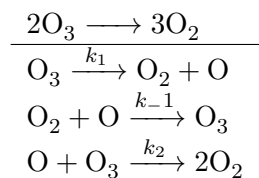
6 Molecular basis

1. reaction pathway, detailed balance
2. bimolecular, collision theory, TST
3. unimolecular reactions

7 Chemical kinetics

7.0.1 Reaction mechanisms

1. Elementary steps and molecularity
2. Ozone decomposition, rate second-order at high P_{O_2} , first-order at low P_{O_2}



3. Detailed balance and microscopic reversibility
4. Equilibrium requirement $K_{eq}(T) = k_f(T)/k_r(T)$

5. Reversibility $r_{\text{net}} = r_f(1 - \beta)$, $\beta = Q/K_c = \exp(-\Delta G(T, c_j)/RT)$

6. Collision theory

(a) $A + B \rightarrow \text{products}$

(b) rate proportional to A/B collision frequency z_{AB} weighted by fraction of collisions with energy $> E_a$

$$r = kC_A C_B, k = \left(\frac{8k_B T}{\pi \mu} \right)^{1/2} \sigma_{AB} N_{av} e^{-E_a/k_B T}$$

(c) upper bound on real rates

7.0.2 Transition state theory (TST)

1. Assumptions

(a) Existence of reaction coordinate (PES)

(b) Existence of dividing surface

(c) Equilibrium between reactants and “transition state”

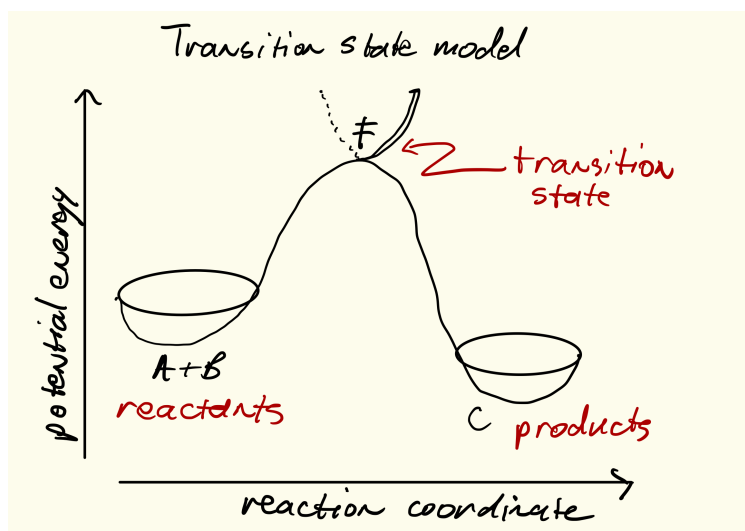
(d) Harmonic approximation for transition state

2. rate proportional to concentration of “activated complex” over reactants times crossing frequency

$$\begin{aligned} r &= kC_A C_B \\ &= k^\ddagger C_{AB}^\ddagger \\ &= \nu^\ddagger K^\ddagger C_A C_B \\ &= \nu^\ddagger \frac{k_B T}{h \nu^\ddagger} \bar{K}^\ddagger(T) C_A C_B \\ &= \frac{k_B T}{h} \frac{q^\ddagger(T)}{q_A(T) q_B(T)} e^{-\Delta E(0)/k_B T} C_A C_B \end{aligned}$$

3. application to atom - atom collision

4. application to two molecules - vinyl alcohol to acetaldehyde



7.0.3 Locating transition states computationally

7.0.4 Thermodynamic connection

1. Relate activated complex equilibrium constant to activation free energy

$$\bar{K}^\ddagger(T) = e^{-\Delta G^{\circ\ddagger}(T)/kT} = e^{-\Delta H^{\circ\ddagger}(T)/k_B T} e^{\Delta S^{\circ\ddagger}(T)/k_B}$$

2. Compare to Arrhenius expression

$$E_a = \Delta H^{\circ\ddagger}(T) + kT, A = \frac{k_B T}{h} e^1 e^{\Delta S^{\circ\ddagger}(T)/k_B}$$

Vinyl alcohol to TS 216 kJ/mol

7.0.5 Application: gas-phase reactions

1. Ethane pyrolysis, $\text{C}_2\text{H}_6 \longrightarrow \text{C}_2\text{H}_4 + \text{H}_2$, [doi:10.1021/jp206503d](https://doi.org/10.1021/jp206503d)

7.0.6 Heterogeneous reactions and catalysis

1. molecule-surface collisions
2. surface reactions
3. Ammonia oxidation, $\text{NH}_3 + \text{O}_2 \longrightarrow \text{NON}_2$, [doi:10.1021/acscatal.8b04251](https://doi.org/10.1021/acscatal.8b04251)
[./Images/TS-Ethylene.gif](#)

7.0.7 Diffusion-controlled reactions

1. Intermediate complex
2. Steady-state approximation
3. Diffusion-controlled limit ($k_D = 4\pi(r_A + r_B)D_{AB}$)
4. Reaction-controlled limit ($k_{app} = (k_D/k_{-D})k_r$)

8 Mechanisms

1. simple reaction network
2. free energy surface
3. QSSA
4. Pre-equilibrium
5. Selectivity
6. Rate control

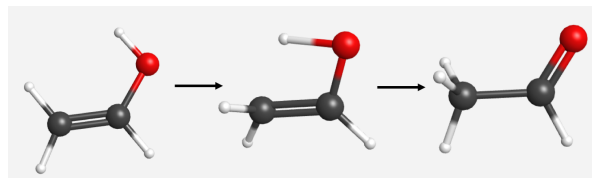
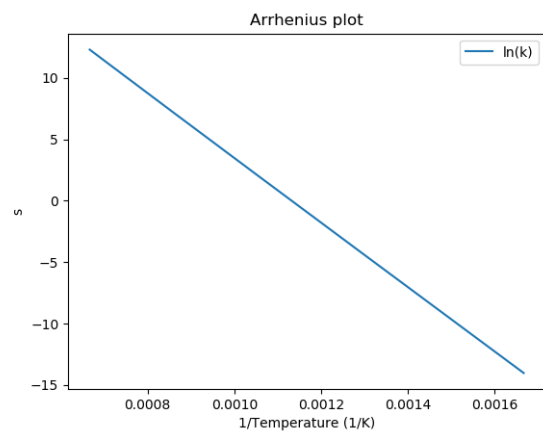
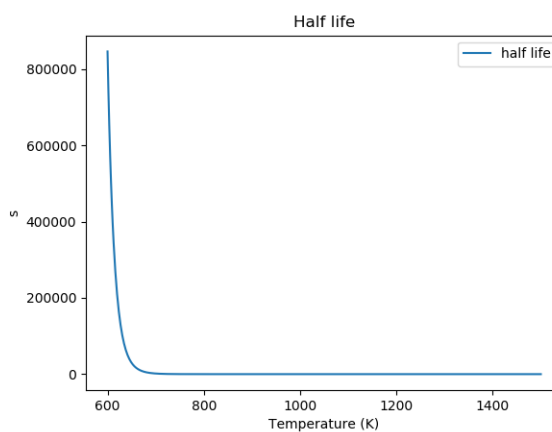
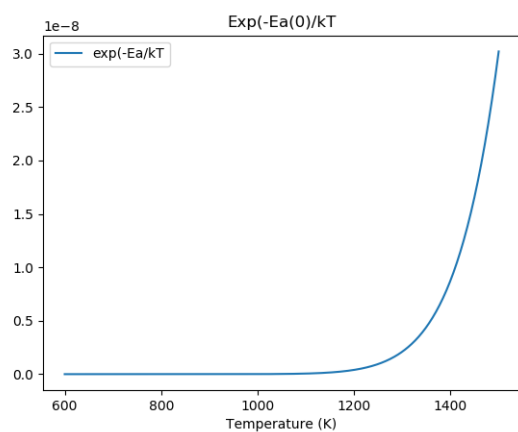
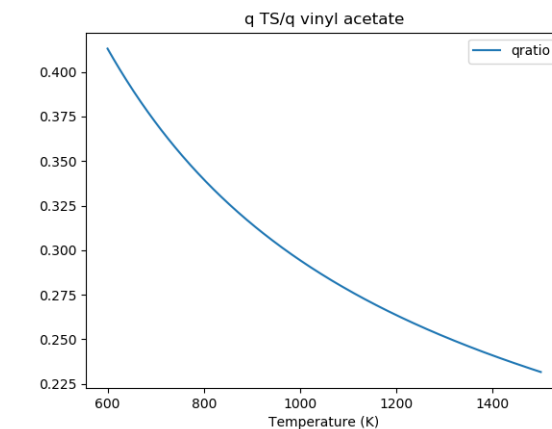
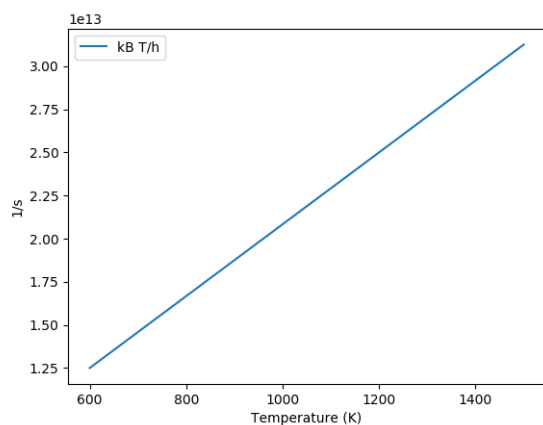
Table 2: Vinyl alcohol to acetaldehyde

Table 3: DFT PES for ethylene dissociation on Ni2P







					
./Images/ethylene-001.png	./Images/ethylene-002.png	./Images/ethylene-003.png	./Images/ethylene-004.png	./Images/ethylene-005.png	./Images/ethylene-pes-animation.png

Table 4: Equilibrium and Rate Constants**Equilibrium Constants** $a A + b B \rightleftharpoons c C + d D$

$$K_{eq}(T) = e^{\Delta S^\circ(T)/k_B} e^{-\Delta H^\circ(T)/k_B T}$$

$$K_c(T) = \left(\frac{1}{c^\circ}\right)^{\nu_c + \nu_d - \nu_a - \nu_b} \frac{(q_c/V)^{\nu_c} (q_d/V)^{\nu_d}}{(q_a/V)^{\nu_a} (q_b/V)^{\nu_b}} e^{-\Delta E(0)\beta}$$

$$K_p(T) = \left(\frac{k_B T}{P^\circ}\right)^{\nu_c + \nu_d - \nu_a - \nu_b} \frac{(q_c/V)^{\nu_c} (q_d/V)^{\nu_d}}{(q_a/V)^{\nu_a} (q_b/V)^{\nu_b}} e^{-\Delta E(0)\beta}$$

Unimolecular Reaction $[A] \rightleftharpoons [A]^\ddagger \rightarrow C$

$$k(T) = \nu^\ddagger \bar{K}^\ddagger = \frac{k_B T}{h} \frac{\bar{q}^\ddagger(T)/V}{q_A(T)/V} e^{-\Delta E^\ddagger(0)\beta}$$

$$E_a = \Delta H^{\circ\ddagger} + k_B T \quad A = e^1 \frac{k_B T}{h} e^{\Delta S^{\circ\ddagger}}$$

Bimolecular Reaction $A + B \rightleftharpoons [AB]^\ddagger \rightarrow C$

$$k(T) = \nu^\ddagger \bar{K}^\ddagger = \frac{k_B T}{h} \frac{q^\ddagger(T)/V}{(q_A(T)/V)(q_B(T)/V)} \left(\frac{1}{c^\circ}\right)^{-1} e^{-\Delta E^\ddagger(0)\beta}$$

$$E_a = \Delta H^{\circ\ddagger} + 2k_B T \quad A = e^2 \frac{k_B T}{h} e^{\Delta S^{\circ\ddagger}}$$

9 Heterogeneous reactions

1. adsorption, L-H
2. TPD
3. catalysis
4. Sabatier analysis

10 Liquid-phase reactions