

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 $1/T$

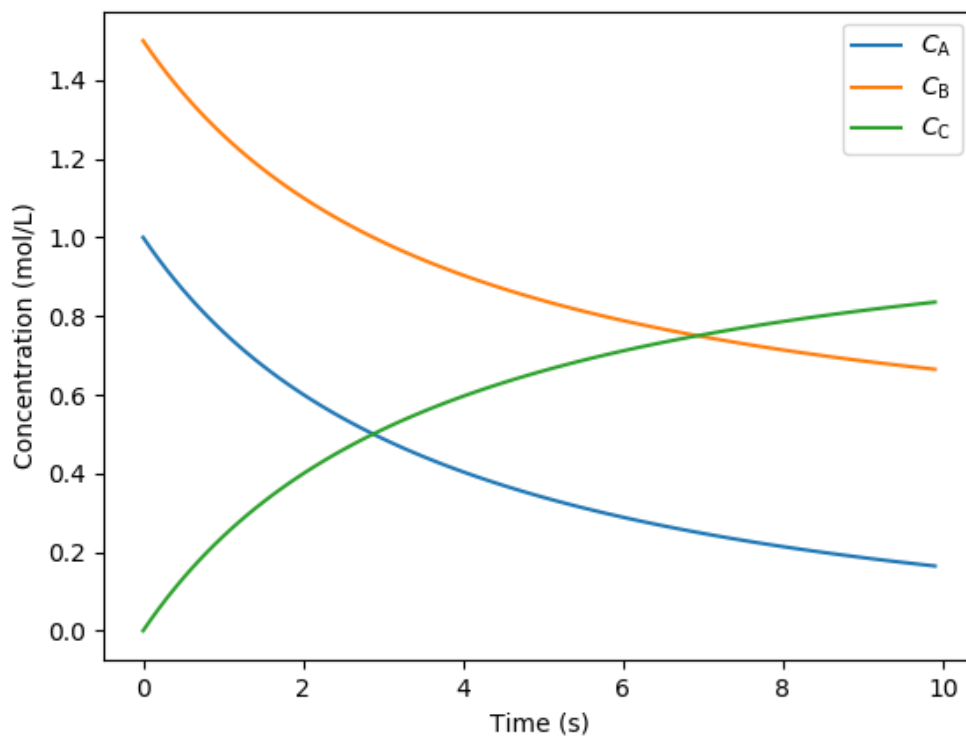
Table 1: Basic kinetic rate laws

	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

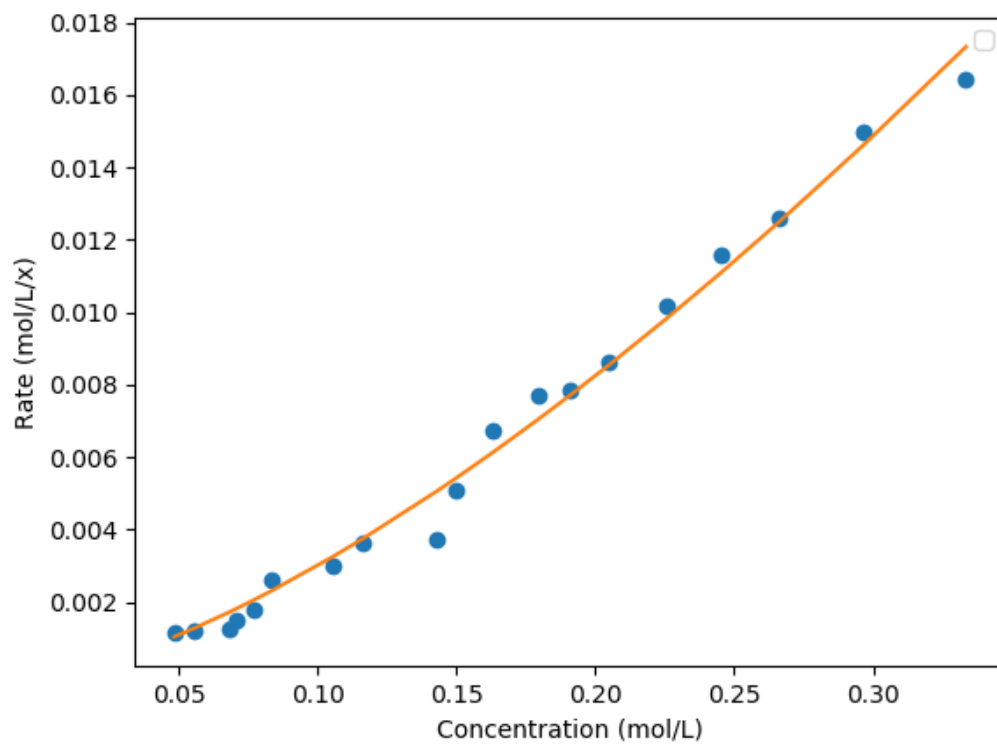
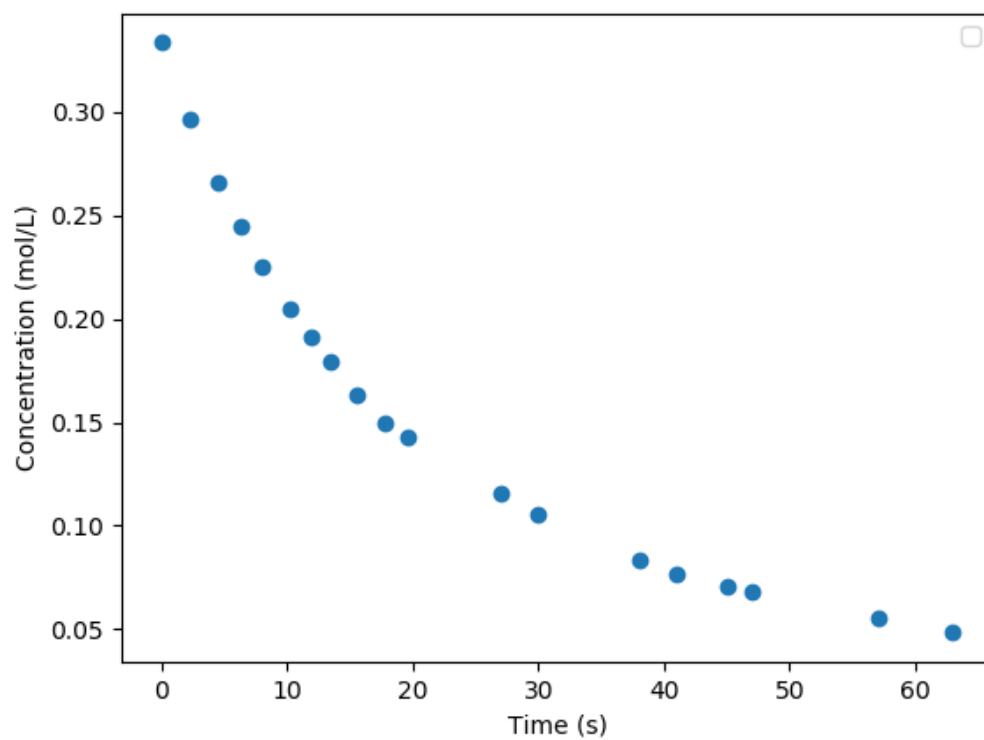
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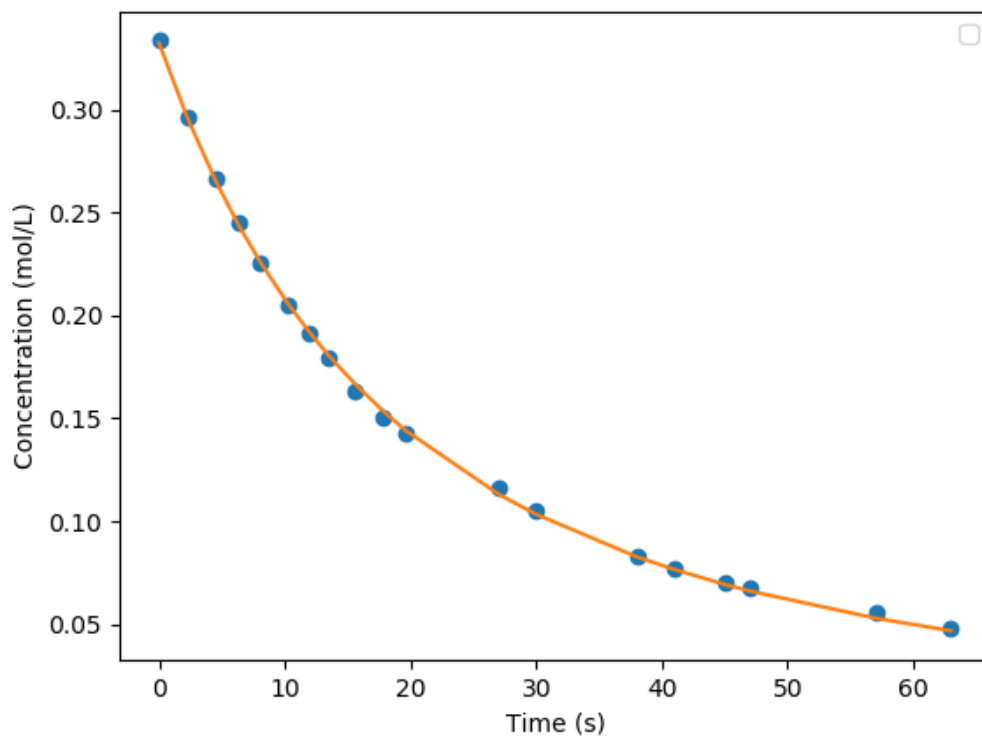
1  import numpy as np                #this lets up handles arrays of data
2  import matplotlib.pyplot as plt
3  from scipy.optimize import curve_fit
4
5  def differential(x, k, alpha):
6      return k*x**alpha
7
8  def integral(t, a, b):
9      return (2*a/(2+a*b*t))**2
10
11  t = np.array([0.00, 2.25, 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
```





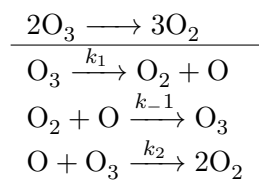
6 Molecular basis

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. Detailed balance and reversibility
3. Ozone decomposition, rate second-order at high P_{O_2} , first-order at low P_{O_2}



4. 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)

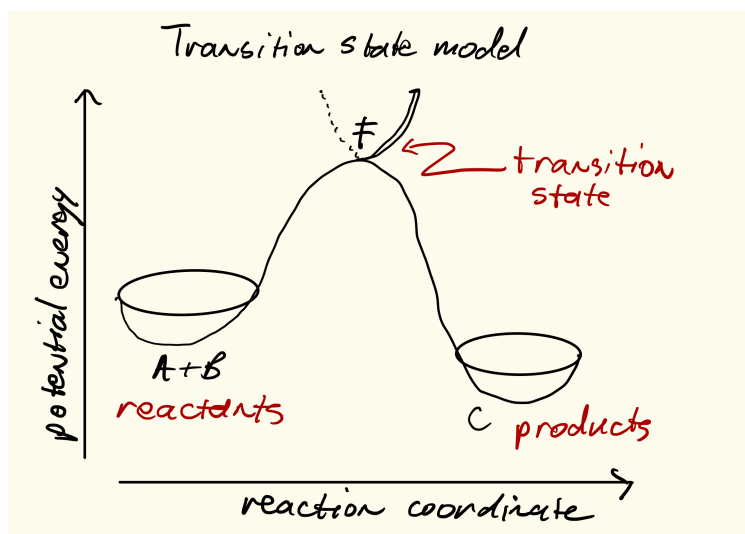
1. Assumptions

- (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
- 5. microscopic reversibility
- 6. equilibrium requirement $K_{eq}(T) = k_f(T)/k_r(T)$



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

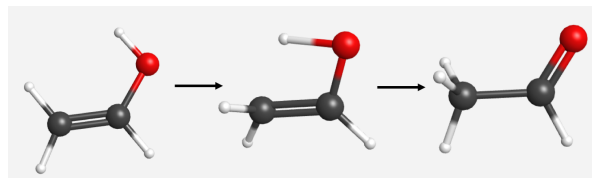
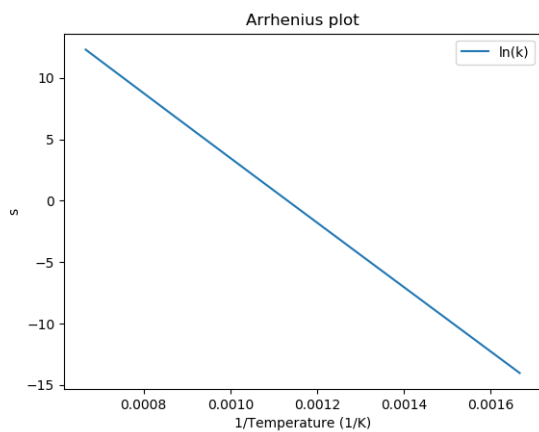
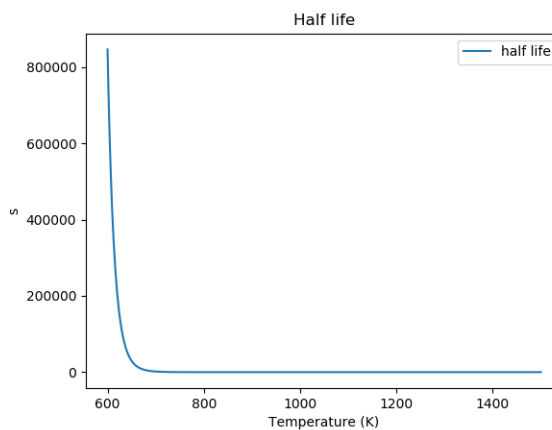
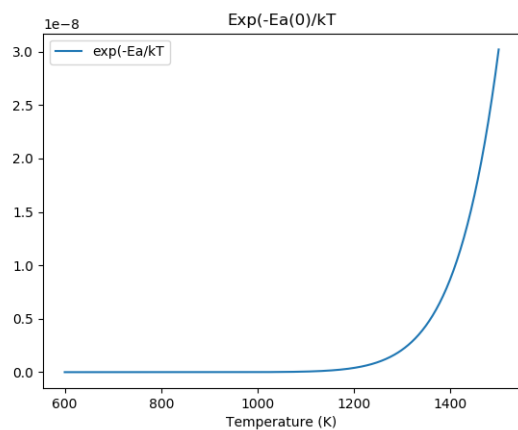
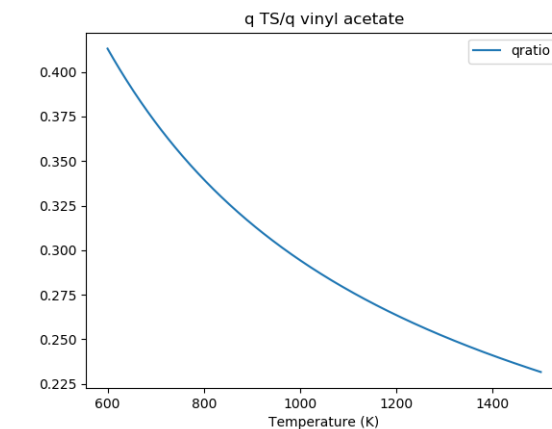
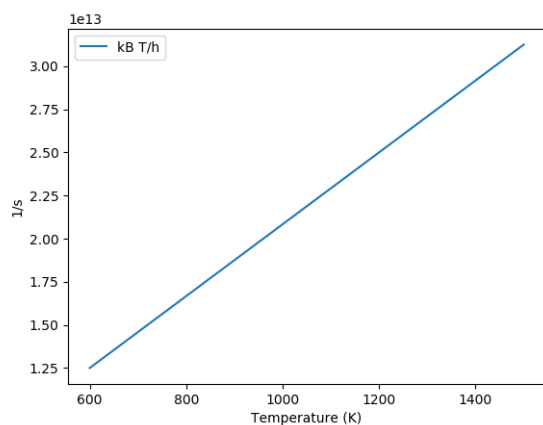
Table 2: Vinyl alcohol to acetaldehyde

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