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 biorefinergy, 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 $\Delta H^\circ(T) = \sum_j {}_j H_j^\circ(T) = \sum_j \nu_j H_{f,j}^\circ(T)$
   (d) Reaction entropy $\Delta S^\circ(T) = \sum_j {}_j S_j^\circ(T)$
3. Equilibrium-closed system
   (a) Free energy vs reaction advancement, $G(\xi, T) = \sum_j n_j\mu_j = \sum_j (n_{j0} + \nu_j\xi)\left(\mu_j^\circ(T) + RT\ln a(\xi, T)\right)$
   (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

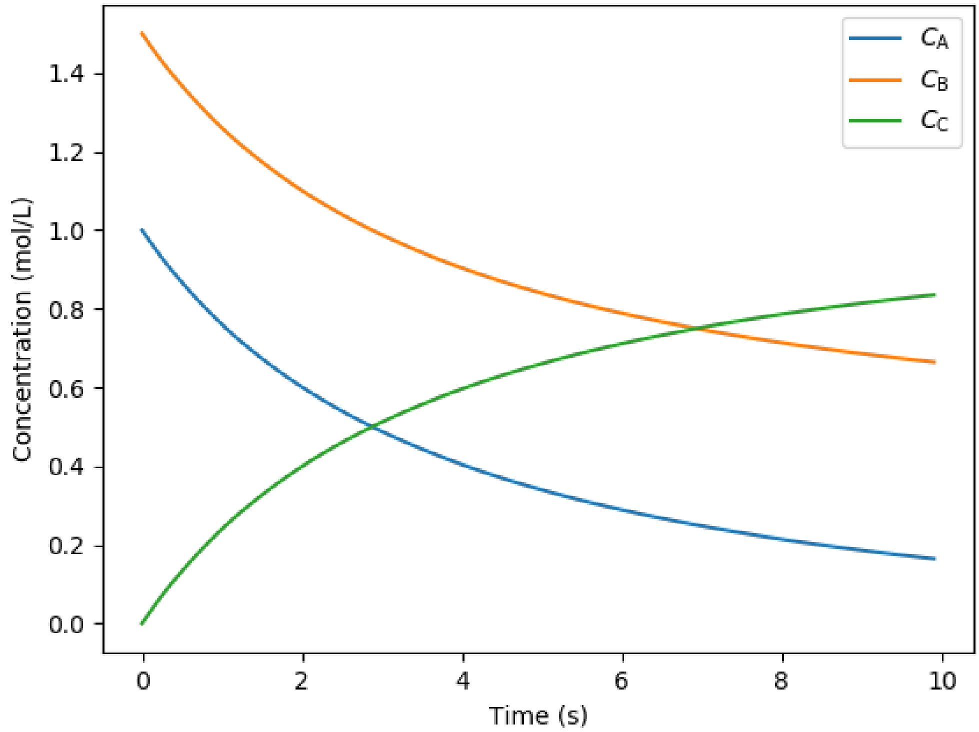
4 Empirical kinetics

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, $k = Ae^{-E_a/k_BT}$
   (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	$r = kC_A^2$	$1/C_A = 1/C_{A0} + k\tau$	$1/kC_{A0}$

```python
import numpy as np                #this lets up handles arrays of data
import matplotlib.pyplot as plt
from scipy.integrate import odeint, solve_ivp

def dCdt(C,t,k):
    dC_Adt = -k*C[0]*C[1]       # A + B -> C;  r = k CA CB
    dC_Bdt = -k*C[0]*C[1]
    dC_Cdt =  k*C[0]*C[1]
    dCdt = [dC_Adt,dC_Bdt,dC_Cdt]
    return dCdt

# initialize concentrations
C_0 = [1., 1.5, 0.]

# initialize k's
k = 0.2

# Range of time to solve over
t = np.arange(0,10,0.1)
t_span = (0., 10.)

p = (k,) # turn parameters into a tuple
# Solve two ODEs with odeint
#C = solve_ivp(dCdt,t_span,C_0,p,method='LSODA')
C = odeint(dCdt,C_0,t,p)

C_A = C.transpose()[0] # Get C_A from C
C_B = C.transpose()[1] # Get C_B from C
C_C = C.transpose()[2]
plt.figure()
plt.plot(t,C_A,'-',label=r'$C_{\rm A}$')
plt.plot(t,C_B,'-',label=r'$C_{\rm B}$')
plt.plot(t,C_C,'-',label=r'$C_{\rm C}$')
plt.xlabel('Time (s)')
plt.ylabel('Concentration (mol/L)')
plt.legend()
plt.savefig('./conc.png')
```

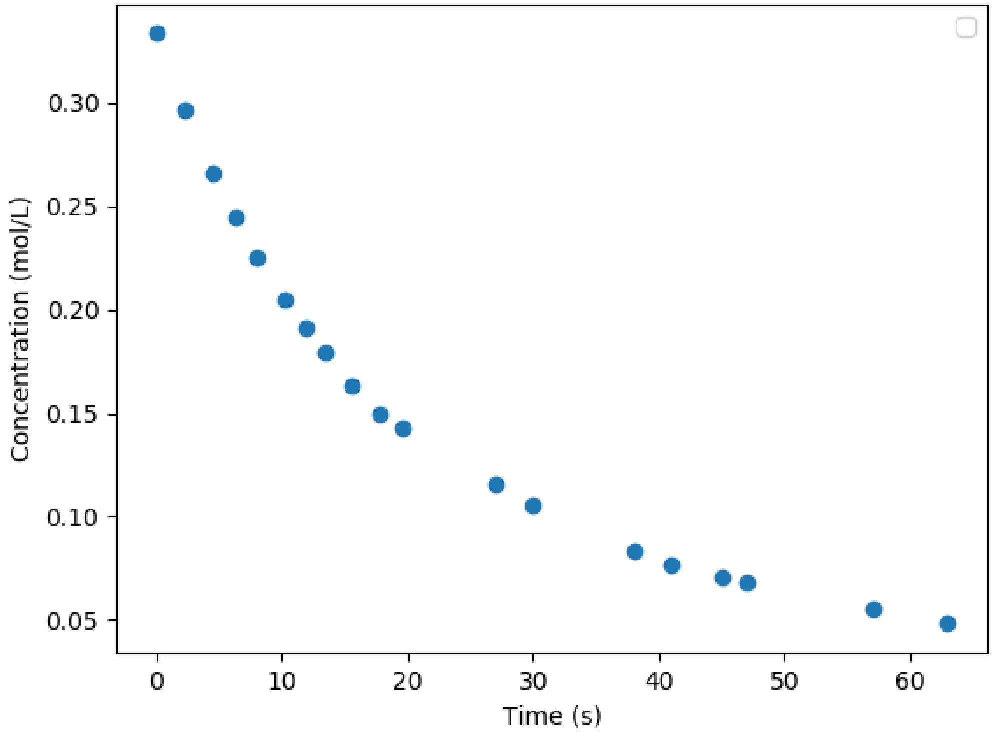
5 Analyzing reactor data

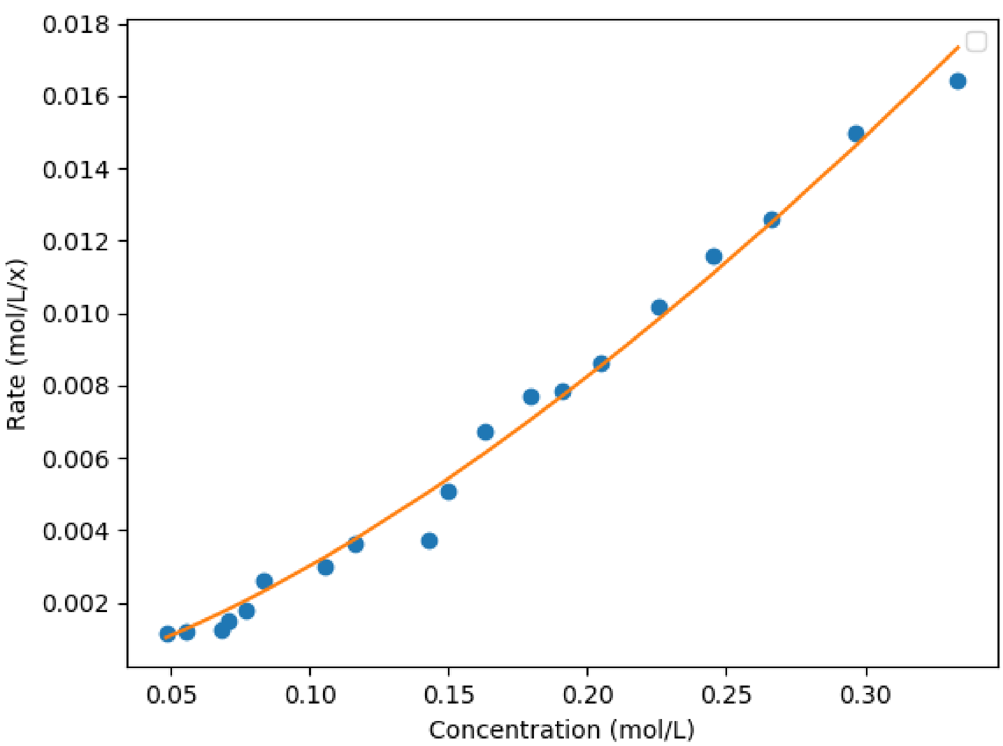
1. Differential methods
   (a) Measuring rates
2. Integral methods
3. Half-lives

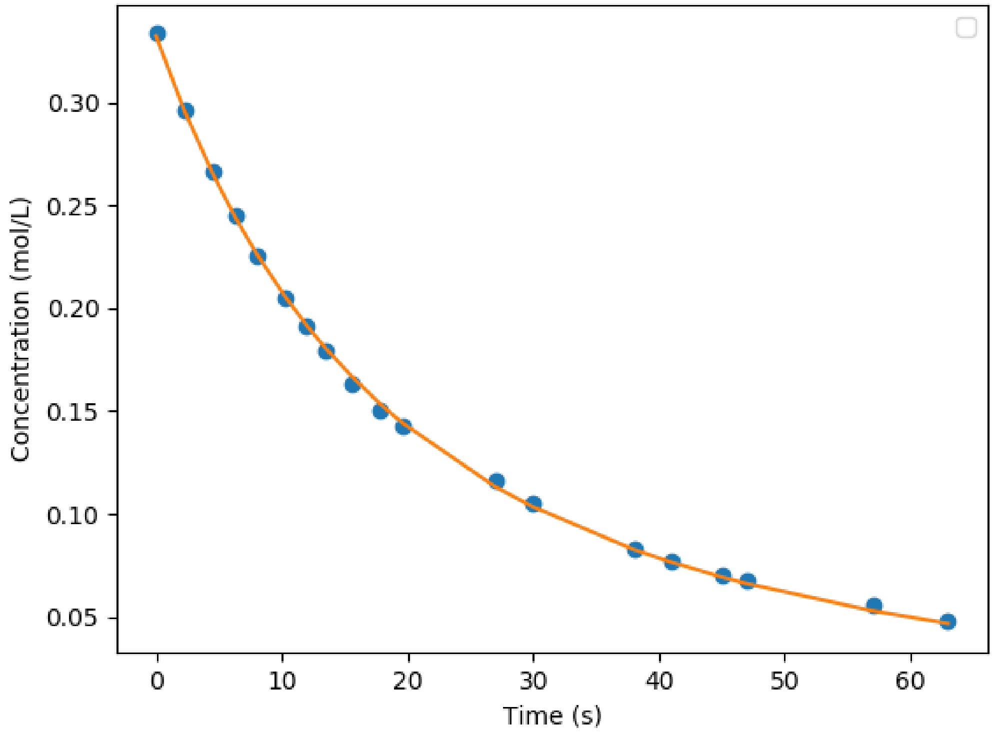
```python
import numpy as np              #this lets up handles arrays of data
import matplotlib.pyplot as plt
from scipy.optimize import curve_fit

def differential(x, k, alpha):
    return k*x**alpha

def integral(t, a, b):
    return (2*a/(2+a*b*t))**2

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,

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

plt.figure()
plt.plot(t,C_Br2,'o')
plt.xlabel('Time (s)')
plt.ylabel('Concentration (mol/L)')
plt.legend()
plt.savefig('./xylene-conc.png')
```

```python

delta_t = np.ediff1d(t)        # finite difference between adjacent points
delta_C = np.ediff1d(C_Br2)

grad_t = np.gradient(t)            # second order approximation to gradient, allowing for unequal step size
grad_C = np.gradient(C_Br2)
rate = -np.divide(grad_C,grad_t)

plt.figure()
plt.plot(C_Br2,rate,'o')
plt.xlabel('Concentration (mol/L)')
plt.ylabel('Rate (mol/L/x)')
plt.legend()

popt, pcov = curve_fit(differential, C_Br2, rate )

print('k = {0:f}, alpha={1:f}'.format(popt[0],popt[1]))

model = differential(C_Br2,popt[0],popt[1])
plt.plot(C_Br2,model,'-')

plt.savefig('./xylene-rate.png')

difference_array = np. subtract(rate, model)
squared_array = np. square(difference_array)
mse = squared_array. mean()
print(mse)

# Suggests order of 1.5
popt1, pcov1 = curve_fit(integral, t, C_Br2)
print('k = {0:f}'.format(popt[1]))

model1 = integral(t, popt1[0], popt1[1])

plt.figure()
plt.plot(t,C_Br2,'o')
plt.plot(t,model1,'-')
plt.xlabel('Time (s)')
plt.ylabel('Concentration (mol/L)')
plt.legend()
plt.savefig('./xylene-int-model.png')
```

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


Concentration (mol/L)
0.30
0.25
0.20
0.15
0.10
0.05
0
10
20
30
40
50
60
Time (s)


Rate (mol/L/x)
0.018
0.016
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.05
0.10
0.15
0.20
0.25
0.30
Concentration (mol/L)



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}

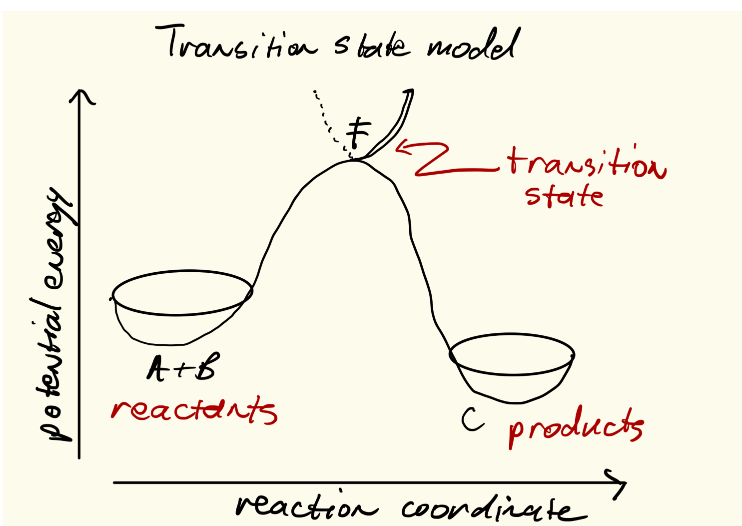
$$\begin{array}{l} 2O_3 \longrightarrow 3O_2 \\ \hline O_3 \xrightarrow{k_1} O_2 + O \\ O_2 + O \xrightarrow{k_{-1}} O_3 \\ O + O_3 \xrightarrow{k_2} 2O_2 \end{array}$$

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 → products
   (b) rate proportional to A/B collision frequency z_{AB} weighted by fraction of collisions with energy $> E_a$
   $$r = kC_AC_B, k = \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} \sigma_{AB}N_{av}e^{-E_a/k_BT}$$
   (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
   $$\begin{aligned} r &= kC_AC_B \\ &= k^{\ddagger}C^{\ddagger}_{AB} \\ &= \nu^{\ddagger}K^{\ddagger}C_AC_B \\ &= \nu^{\ddagger}\frac{k_BT}{h\nu^{\ddagger}}\bar{K}^{\ddagger}(T)C_AC_B \\ &= \frac{k_BT}{h}\frac{q^{\ddagger}(T)}{q_A(T)q_B(T)}e^{-\Delta E(0)/k_BT}C_AC_B \end{aligned}$$
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

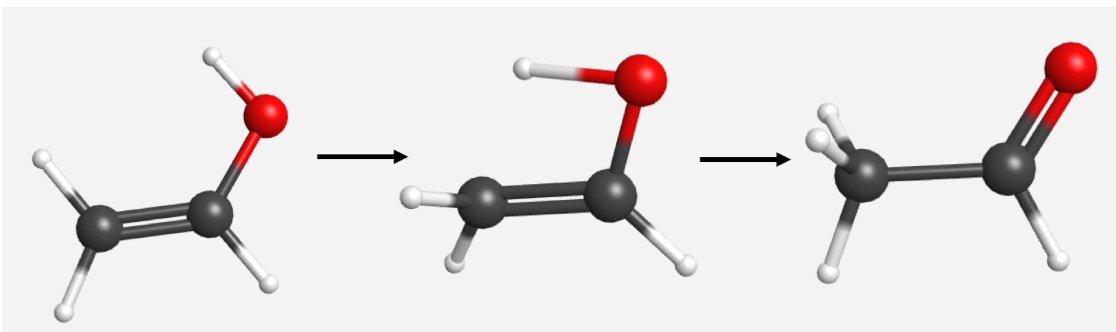
1. Relate activated complex equilibrium constant to activation free energy

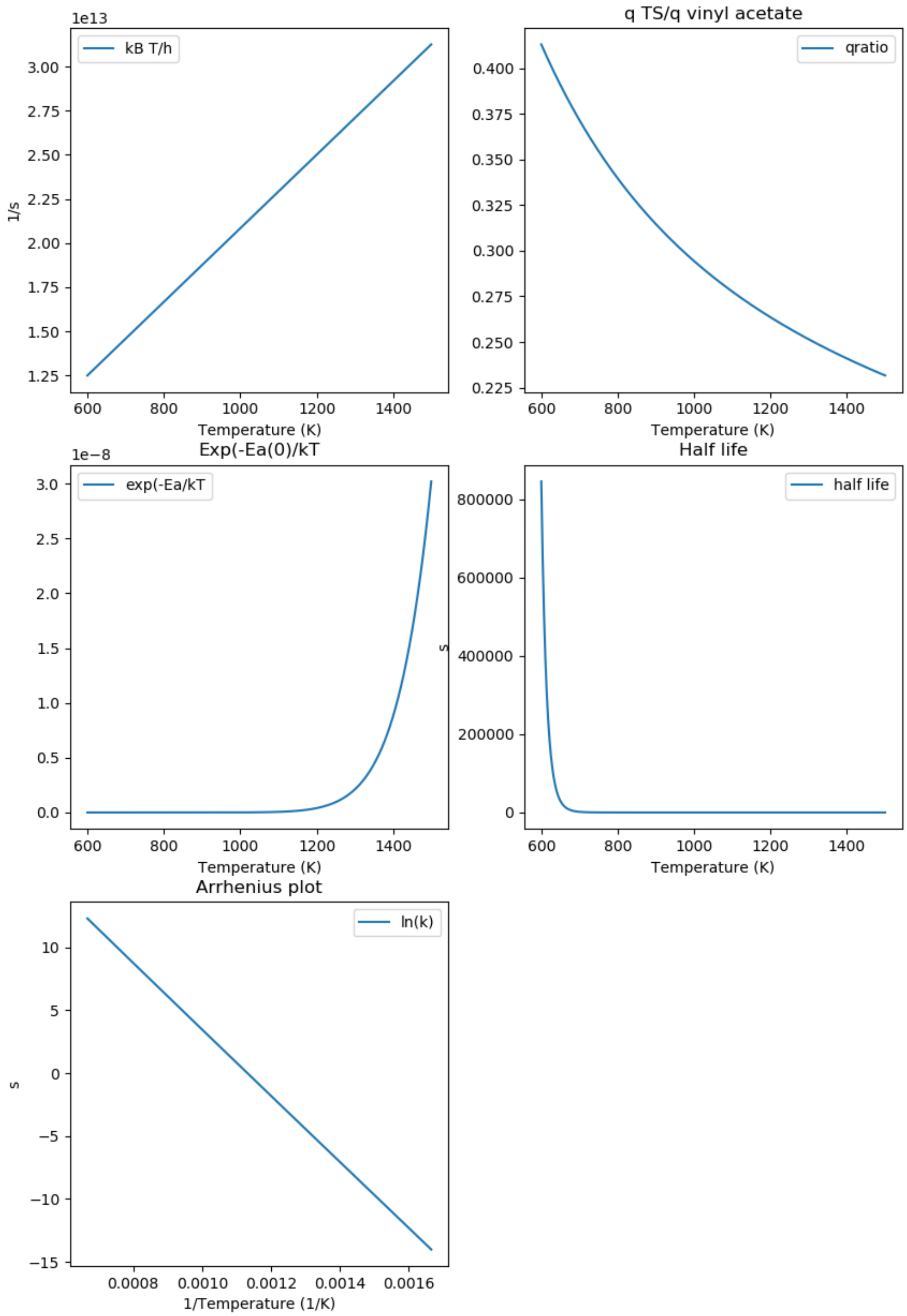
$$\bar{K}^{\ddagger}(T) = e^{-\Delta G^{\circ\ddagger}(T)/kT} = e^{-\Delta H^{\circ\ddagger}(T)/k_BT} e^{\Delta S^{\circ\ddagger}(T)/k_B}$$

2. Compare to Arrhenius expression

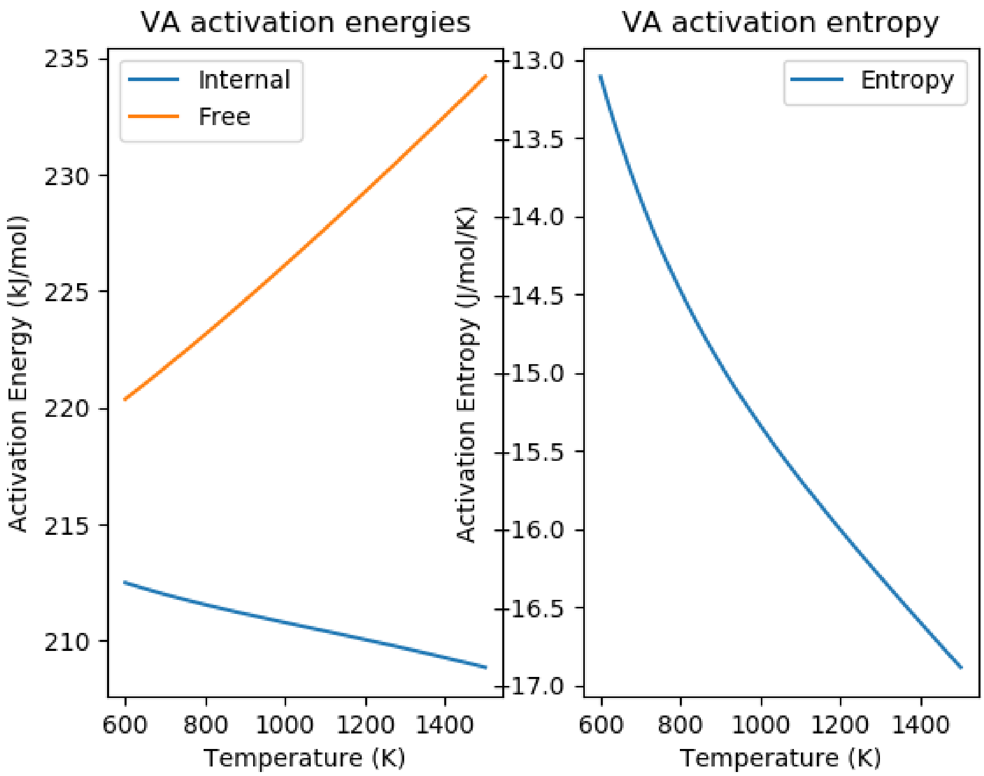
$$E_a = \Delta H^{\circ\ddagger}(T) + kT, A = \frac{k_BT}{h} e^1 e^{\Delta S^{\circ\ddagger}(T)/k_B}$$

```
Vinyl alcohol to TS  216 kJ/mol
Delta Uddagger (1000 K) =  211 kJ/mol
Delta Addagger (1000 K) =  226 kJ/mol
Delta Sddagger (1000 K) = -1480 J/mol K
```





1e13
kB T/h
1/s
Temperature (K)
q TS/q vinyl acetate
qratio
Temperature (K)
1e−8
Exp(-Ea(0)/kT
exp(-Ea/kT
Temperature (K)
Half life
half life
s
Temperature (K)
Arrhenius plot
ln(k)
s
1/Temperature (1/K)



7.0.5 Application: gas-phase reactions

1. Ethane pyrolysis, $C_2H_6 \longrightarrow C_2H_4 + H_2$, doi:10.1021/jp206503d

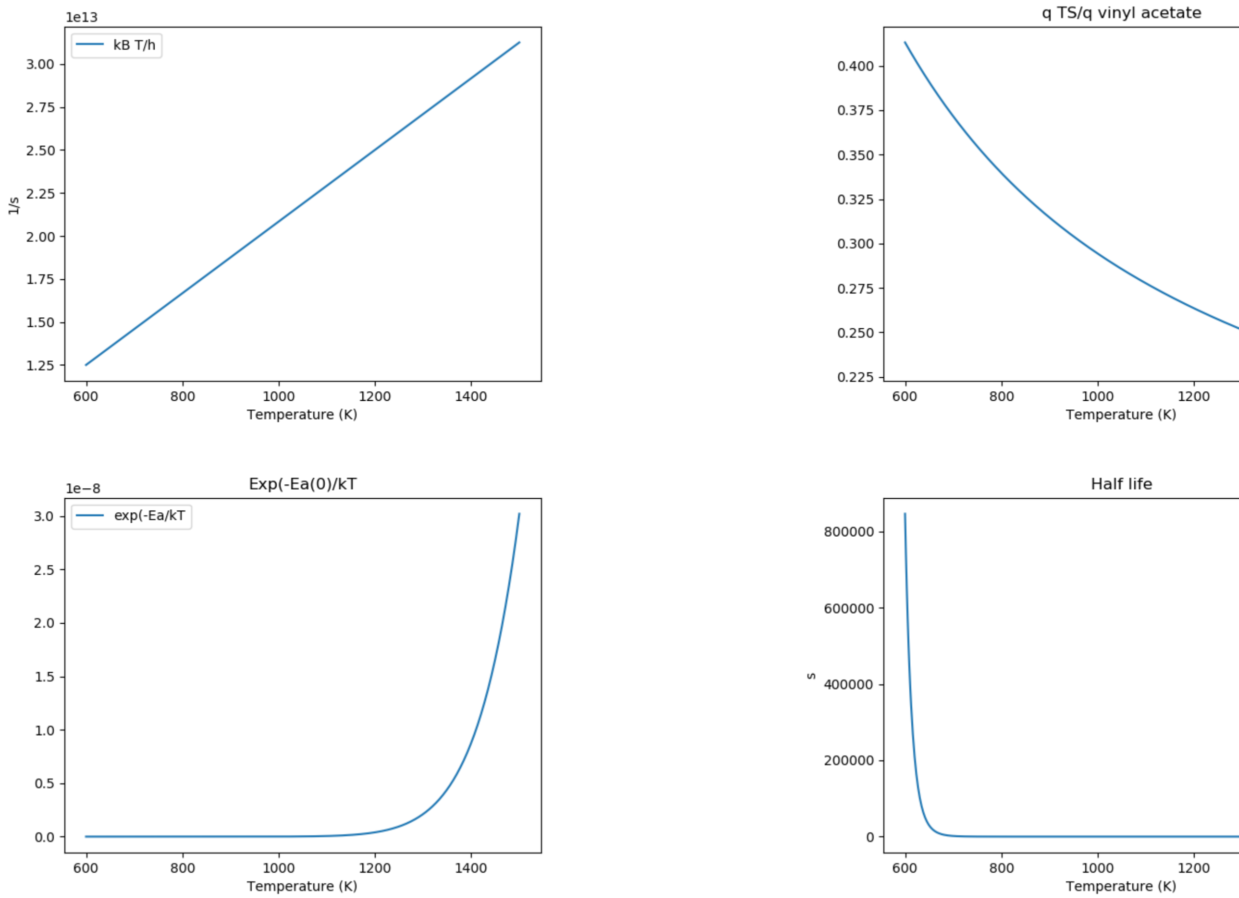
8 Mechanisms

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

9 Heterogeneous reactions

1. adsorption, L-H
2. TPD
3. catalysis

Table 2: Vinyl alcohol to acetaldehyde



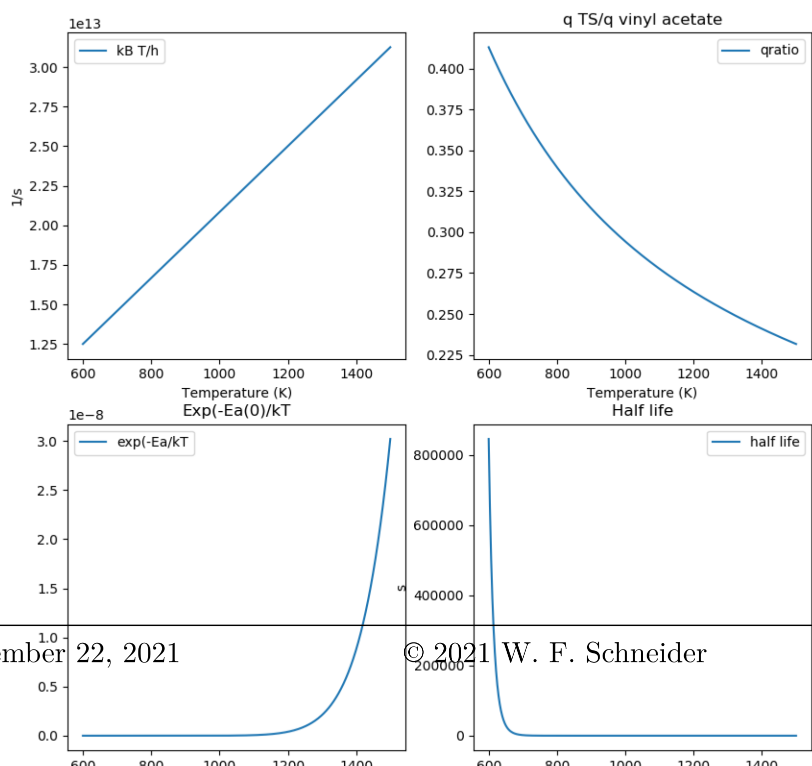


Table 3: DFT PES for ethylene dissociation on Ni2P

./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

4. Sabatier analysis

9.0.1 Heterogeneous reactions and catalysis

1. molecule-surface collisions
2. surface reactions
3. Ammonia oxidation, $NH_3 + O_2 \longrightarrow NON_2$, doi:10.1021/acscatal.8b04251

./Images/TS-Ethylene.gif

10 Liquid-phase reactions

10.0.1 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 ($k_{app} = (k_D/k_{-D})k_r$)

Table 4: Equilibrium and Rate Constants

Equilibrium Constants $a\ \mathrm{A} + b\ \mathrm{B} \rightleftharpoons c\ \mathrm{C} + d\ \mathrm{D}$

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

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

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

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

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

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

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

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

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

