

▼ Advanced Chemical Reaction Engineering (CBE 60546)

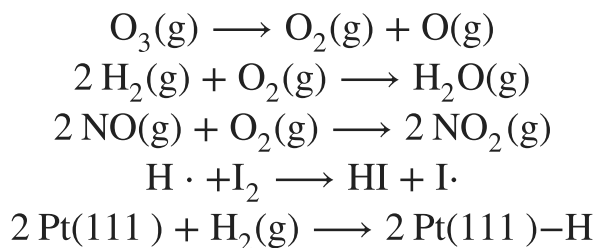
Homework 4

Due October 1, 2021

Carefully and neatly document your answers. You may use a mathematical solver like Jupyter/iPython. Use plotting software for all plots.

▼ 1 Its elementary, really ...

- ▼ 1.1 Which of the following reactions can be assumed to be elementary? If it is elementary, indicate the molecularity. Briefly Justify your answers.



In the last example, Pt(111) indicates the surface of a Pt particle.

Answer Here

(1) $\text{O}_3(\text{g}) \longrightarrow \text{O}_2(\text{g}) + \text{O}(\text{g})$ - This **is** an elementary reaction that is unimolecular. O atom is not a stable specie and will be used in another step.

(2) $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{H}_2\text{O}(\text{g})$ - This **is not** an elementary reaction. This reaction would require several steps to break and reform bonds of reactants and intermediates.

(3) $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \longrightarrow 2 \text{NO}_2(\text{g})$ - This **is probably not** an elementary reaction as this too would seem to require several steps to break and reform bonds. Experimental evidence is inconclusive.

(4) $\text{H} \cdot + \text{I}_2 \longrightarrow \text{HI} + \text{I} \cdot$ - This **is** an elementary step that is bimolecular. This step describes the propagation of a radical from one species to another which is completed in a single step.

(5) $2 \text{Pt}(111) + \text{H}_2(\text{g}) \longrightarrow 2 \text{Pt}(111)\text{--H}$ - Assuming the dissociation occurs as the molecule adsorbs, this **is** a bimolecular elementary reaction. If the H_2 molecule dissociates after adsorption,

▼ 2 The Path less traveled

Chlorine monoxide, ClO , exhibits three different self-reaction channels:

	$A \text{ (L mol}^{-1}\text{s}^{-1}\text{)}$	$E_a \text{ (kJ mol}^{-1}\text{)}$
$\text{ClO} \cdot + \text{ClO} \cdot \longrightarrow \text{Cl}_2 + \text{O}_2$	6.08×10^8	13.2
$\text{ClO} \cdot + \text{ClO} \cdot \longrightarrow \text{Cl} \cdot + \text{ClOO}$	1.79×10^{10}	20.4
$\text{ClO} \cdot + \text{ClO} \cdot \longrightarrow \text{Cl} \cdot + \text{OCIO}$	2.11×10^8	11.4

2.1 Make Arrhenius plots of the three reactions from 150 to 500K. Which reaction dominates at low temperature? At high temperature?

```
# Arrhenius equation is: k = A*exp(Ea/R*T) (you can replace R for kb just make units r
# Solve for k for a set of T based on the table above
```

```
import numpy as np
from scipy import constants # easy way to get physical constants
import matplotlib.pyplot as plt
```

```
# get constants
R = constants.physical_constants['molar gas constant'][0]/1000 # units are kJ mol-1 K-1
```

```
Temp = np.linspace(150,500,100) # temperature range in K
A = [6.08e8, 1.79e10,2.11e8] # Pre-exponential factor from table
Ea = [13.2,20.4,11.4] # Activation energy from table above
```

```
k0=[] # rate constants corresponding to the first reaction
k1=[] # second reaction
k2=[] # third reaction
```

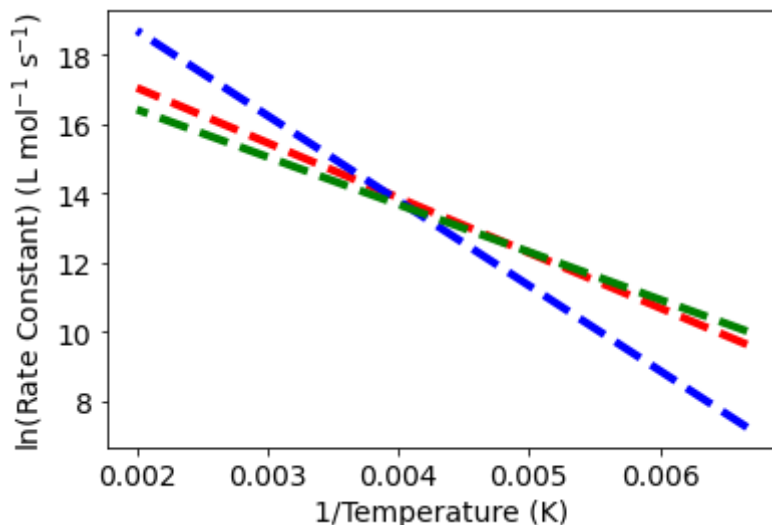
```
for t in Temp:
    k0.append(A[0]*np.exp((-1*Ea[0])/(R*t))) # evaluate the Arrhenius equation and save
    k1.append(A[1]*np.exp((-1*Ea[1])/(R*t)))
    k2.append(A[2]*np.exp((-1*Ea[2])/(R*t)))
```

```
# Arrhenius plots are present in log form
```

```
# Make one plot showing the entire range
plt.plot(1/Temp,np.log(k0),linestyle='dashed',linewidth=4,label='Reaction 1',color='red')
plt.plot(1/Temp,np.log(k1),linestyle='dashed',linewidth=4,label='Reaction 2',color='blue')
```

```
plt.plot(1/Temp,np.log(k2),linestyle='dashed',linewidth=4,label='Reaction 3',color='g')

plt.xticks(size=14)
plt.yticks(size=14)
plt.xlabel('1/Temperature (K)',size=14)
plt.ylabel(r'ln(Rate Constant) (L mol$^{-1}$ s$^{-1}$)',size=14)
plt.show()
```



2.2 Can Collision theory account for the variations in rate constants amongst the three reactions? Why or Why not?

Answer Here

Not really. Collision theory relates rates to rates of collision; it has no way to account for the same colliding species to give different products.

2.3 The rate constant for a gas-phase bimolecular reaction can be written within transition state theory (using an isobaric standard state) as shown below. Use

- the definition of E_a to derive relationships between the Arrhenius parameters and the standard activation enthalpy, ΔH^{\ddagger} and standard activation entropy, ΔS^{\ddagger} , at 1 bar standard state.

$$k = \frac{k_b T}{h} \left(\frac{RT}{P^\circ} \right) \exp\left(\frac{-\Delta G^{\ddagger}(T)}{RT} \right)$$

Answer here

Using the equation above we can do the following:

- (1) assuming equilibrium $\Delta G^{\circ\ddagger}(T) = \Delta H^{\circ\ddagger} - T\Delta S^{\circ\ddagger}$
- (2) evaluate the derivate of the function with respect to T

$$\begin{aligned}
 k &= \frac{k_b T}{h} \left(\frac{RT}{P^\circ} \right) \exp\left(\frac{-\Delta G^{\circ\ddagger}(T)}{k_b T} \right) \\
 \ln(k) &= \ln\left(\frac{k_b RT^2}{h P^\circ} \right) + \frac{-\Delta G^{\circ\ddagger}(T)}{k_b T} \\
 \ln(k) &= \ln\left(\frac{k_b RT^2}{h P^\circ} \right) + \frac{-\Delta H^{\circ\ddagger}}{k_b T} + \frac{\Delta S^{\circ\ddagger}}{k_b} \\
 \frac{\partial}{\partial T} \ln(k) &= \frac{\partial}{\partial T} \left(\ln\left(\frac{k_b RT^2}{h P^\circ} \right) + \frac{-\Delta H^{\circ\ddagger}}{k_b T} + \frac{\Delta S^{\circ\ddagger}}{k_b} \right) \\
 \frac{\partial}{\partial T} \ln(k) &= \left(\frac{h P^\circ}{k_b RT^2} \frac{2k_b RT}{h P^\circ} + \frac{\Delta H^{\circ\ddagger}}{k_b T^2} + 0 \right)
 \end{aligned}$$

Some units cancel, and we get the relationship:

$$\frac{\partial}{\partial T} \ln(k) = \left(\frac{2}{T} + \frac{\Delta H^{\circ\ddagger}}{k_b T^2} \right)$$

We can follow the same procedures for the Arrhenius equation (but it is much simpler)

$$\begin{aligned}
 k &= A \exp\left(\frac{-E_a}{k_b T} \right) \\
 \ln(k) &= \ln(A) + \frac{-E_a}{k_b T} \\
 \frac{\partial}{\partial T} \ln(k) &= \frac{\partial}{\partial T} \left(\ln(A) + \frac{-E_a}{k_b T} \right) \\
 \frac{\partial}{\partial T} \ln(k) &= \left(0 + \frac{E_a}{k_b T^2} \right)
 \end{aligned}$$

By setting the two equations equal to each other, we get:

$$\frac{2}{T} + \frac{\Delta H^{\circ\ddagger}}{k_b T^2} = \frac{E_a}{k_b T^2}$$

and by some simple manipulation, we get:

$$\begin{aligned}
 \frac{2k_b T}{k_b T^2} + \frac{\Delta H^{\circ\ddagger}}{k_b T^2} &= \frac{E_a}{k_b T^2} \\
 2k_b T + \Delta H^{\circ\ddagger} &= E_a
 \end{aligned}$$

And thus, $E_a = 2k_bT + \Delta H$ or $E_a = 2RT + \Delta H$ the entropy of activation can be evaluated by back solving into one of the equations above

2.4 Calculate ΔH° (transition state) and ΔS° (transition state) of the three reactions.

```
# Evaluate H using the relationship from above
H0 = Ea[0] - (2*R*Temp) # Enthalpy for reaction 1
H1 = Ea[1] - (2*R*Temp) # reation 2
H2 = Ea[2] - (2*R*Temp) # reaction 3

print('Reaction 1 has an enthalpy of {0:.2f} kJ/mol at 298K'.format(H0[42])) # value 1
print('Reaction 2 has an enthalpy of {0:.2f} kJ/mol at 298K'.format(H1[42]))
print('Reaction 3 has an enthalpy of {0:.2f} kJ/mol at 298K'.format(H2[42]))

Reaction 1 has an enthalpy of 8.24 kJ/mol at 298K
Reaction 2 has an enthalpy of 15.44 kJ/mol at 298K
Reaction 3 has an enthalpy of 6.44 kJ/mol at 298K
```

To evaluate ΔS° , we need to rearrange

$$\ln(k) = \ln\left(\frac{k_b RT^2}{hP^\circ}\right) + \frac{-\Delta H^{\ddagger}}{k_b T} + \frac{\Delta S^{\ddagger}}{k_b}$$

$$\Delta S^{\ddagger} = (\ln(k) - \ln\left(\frac{k_b RT^2}{hP^\circ}\right))k_b + \frac{\Delta H^{\ddagger}}{T}$$

$$\Delta S^{\ddagger} = \left(\ln\left(\frac{k}{\frac{k_b RT^2}{hP^\circ}}\right)\right)k_b + \frac{\Delta H^{\ddagger}}{T}$$

Be careful with units

```
kb = constants.physical_constants['Boltzmann constant'][0] # J K^-1
h = constants.physical_constants['Planck constant'][0] # J sec
bar_pas = constants.bar # conversion between bar and pascall
liter_m3 = constants.liter # conversion between liter and m^3
Na = constants.physical_constants['Avogadro constant'][0] #avogadro constant (mol^-1)

# Evaluate the three components separatley

# ln(k)
logk0 = np.array(k0)*liter_m3 # reaction 1 units m^3 mol^-1 sec^-1
logk1 = np.array(k1)*liter_m3 # reaction 2
```

```

logk2 = np.array(k2)*liter_m3 # reaction 3

# ln(constants)
logCon = (kb*(R*1000)*(Temp**2))/(h*bar_pas) # units m^3 mol^-1 sec^-1

# enthalpy term
H_T0 = H0*1000/Temp
H_T1 = H1*1000/Temp
H_T2 = H2*1000/Temp

S0 = np.log(logk0/logCon)*kb*Na + H_T0 # units are in J mol^-1 K^-1
S1 = np.log(logk1/logCon)*kb*Na + H_T1
S2 = np.log(logk2/logCon)*kb*Na + H_T2

print('Reaction 1 has an entropy of {0:.2f} J/mol K at 298K'.format(S0[42]))
print('Reaction 2 has an entropy of {0:.2f} J/mol K at 298K'.format(S1[42]))
print('Reaction 3 has an entropy of {0:.2f} J/mol K at 298K'.format(S2[42]))

    Reaction 1 has an entropy of -120.10 J/mol K at 298K
    Reaction 2 has an entropy of -91.98 J/mol K at 298K
    Reaction 3 has an entropy of -128.90 J/mol K at 298K

```

2.5 Using chemical intuition and the calculated ΔS° (transition state) as

- ▼ guides, draw candidate transition state structures for each of the three reactions. Include arrows to show motion along the reaction coordinates.

see the attached pdf document

2.6 following is some thermodynamic data. Use it to sketch/dra/plot a potential

- ▼ enthalpy surface for the three reactions and a potential free energy surface for the three reactions at 298 K.

	$\Delta H_f^\circ(298K) \text{ (kJ mol}^{-1}\text{)}$	$\Delta S_f^\circ(298K) \text{ (J mol}^{-1}\text{)}$
ClO·	101.22	226.65
OCLO·	104.60	257.22
ClO ₂	98.0	269.32
Cl	121.3	165.19
Cl ₂	0	223.08
O ₂	0	205.15

```

# Enthalpy PES
H_ClO = 101.22

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H_OC10 = 104.60
H_ClO2 = 98.0
H_Cl = 121.3
H_Cl2 = 0
H_O2 = 0

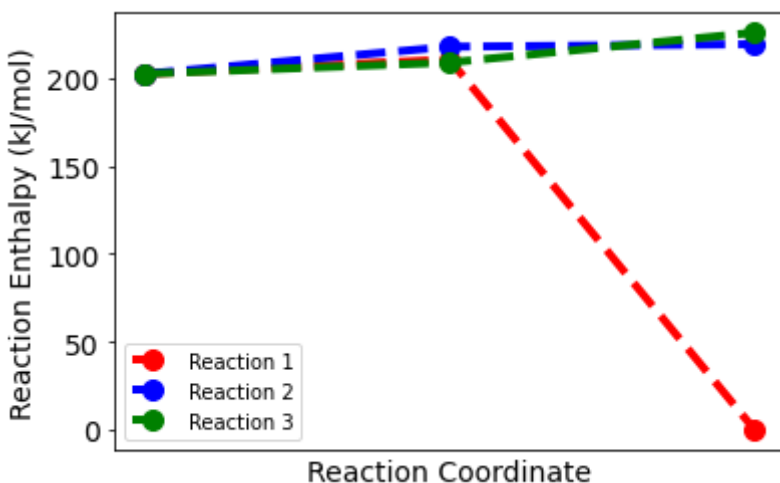
H0_react = H_ClO * 2 # location of the reactants
H0_react_trans = H0_react + H0[42] # from question 2.3 (How does the TS change)
H0_prod = H_Cl2 + H_O2

H1_react = H_ClO * 2
H1_react_trans = H1_react + H1[42]
H1_prod = H_Cl + H_ClO2

H2_react = H_ClO * 2
H2_react_trans = H2_react + H2[42]
H2_prod = H_Cl + H_OC10

plt.plot([0,1,2],[H0_react,H0_react_trans,H0_prod],color='red',marker='o',
         markersize=10,linestyle='dashed',linewidth=4,label = 'Reaction 1')
plt.plot([0,1,2],[H1_react,H1_react_trans,H1_prod],color='blue',marker='o',
         markersize=10,linestyle='dashed',linewidth=4,label = 'Reaction 2')
plt.plot([0,1,2],[H2_react,H2_react_trans,H2_prod],color='green',marker='o',
         markersize=10,linestyle='dashed',linewidth=4,label = 'Reaction 3')
plt.legend()
plt.ylabel('Reaction Enthalpy (kJ/mol)',size=14)
plt.xlabel('Reaction Coordinate',size=14)
plt.xticks([])
plt.yticks(size=14)
plt.show()

```



```

# Free Energy PES
G_ClO = H_ClO - (298*.22665) #kJ/mol
G_OC10 = H_OC10 - (298*.25722)
G_ClO2 = H_ClO2 - (298*.26932)

```

```

G_C1 = H_C1 - (298*.16519)
G_C12 = H_C12 - (298*.22308)
G_O2 = H_O2 - (298*.20515)

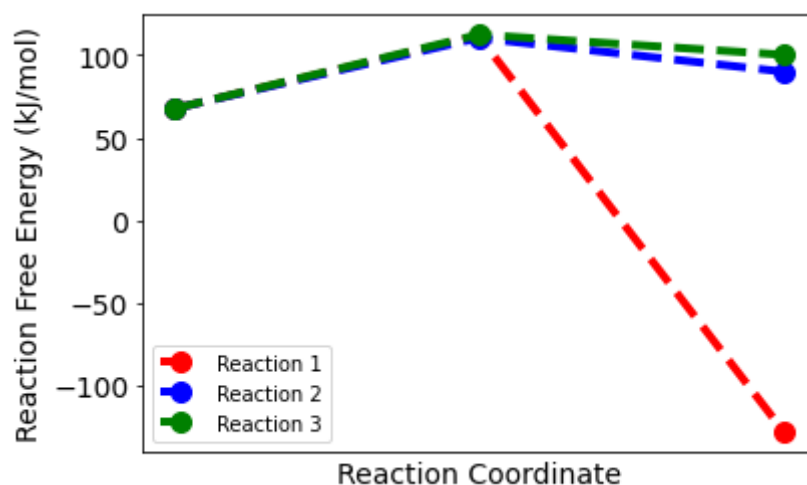
G0_react = (G_C10*2)

G0 = H0[42] - (298*S0[42]/1000) + (G_C10*2)
G1 = H1[42] - (298*S1[42]/1000) + (G_C10*2)
G2 = H2[42] - (298*S2[42]/1000) + (G_C10*2)

G0_prod = G_C12 + G_O2
G1_prod = G_C1 + G_C102
G2_prod = G_C1 + G_OC10

plt.plot([0,1,2],[G0_react,G0,G0_prod],color='red',marker='o',
          markersize=10,linestyle='dashed',linewidth=4,label = 'Reaction 1')
plt.plot([0,1,2],[G0_react,G1,G1_prod],color='blue',marker='o',
          markersize=10,linestyle='dashed',linewidth=4,label = 'Reaction 2')
plt.plot([0,1,2],[G0_react,G2,G2_prod],color='green',marker='o',
          markersize=10,linestyle='dashed',linewidth=4,label = 'Reaction 3')
plt.legend()
plt.ylabel('Reaction Free Energy (kJ/mol)',size=14)
plt.xlabel('Reaction Coordinate',size=14)
plt.xticks([])
plt.yticks(size=14)
plt.show()

```



▼ What do I get in compensation?

Following are some observed data for the dehydrogenation of *iso*-propanol,



$A \text{ (s}^{-1}\text{)}$	$E_a \text{ (kJ mol}^{-1}\text{)}$
-----------------------------	------------------------------------

$A \text{ (s}^{-1}\text{)}$	$E_a \text{ (kJ mol}^{-1}\text{)}$
4.3×10^{12}	172
2.3×10^{11}	159
2.2×10^{10}	146
1.6×10^9	134

3.1 What can you say about the relationship between ΔH^\ddagger (transition state) and ΔS^\ddagger (transition state)

```
# Customize the figure to plot; just to make things pretty. Not mandatory.
from matplotlib.ticker import FormatStrFormatter
from matplotlib.pyplot import *

font = {'family' : 'DejaVu Sans',
        'weight' : 'normal',
        'size'    : 15}
rcParams['axes.linewidth'] = 2
rcParams['lines.linewidth'] = 2
rcParams['lines.markersize'] = 8
rcParams['xtick.major.width'] = 2
rcParams['ytick.major.width'] = 2
matplotlib.rc('font', **font)
rcParams['figure.figsize'] = (4, 4)

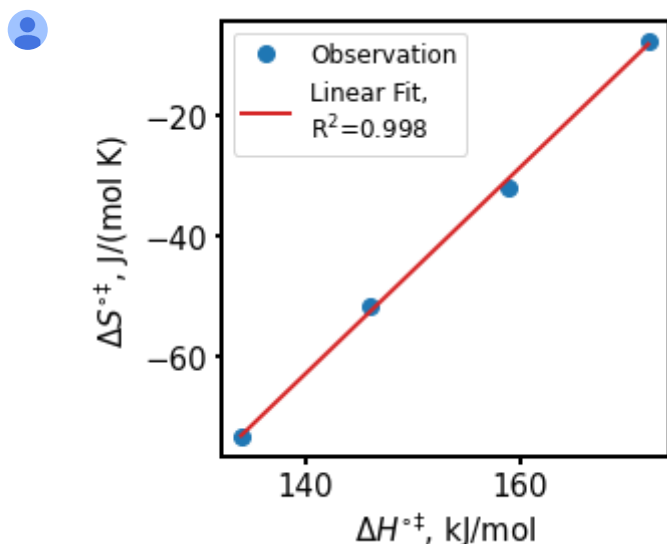
from sklearn.metrics import r2_score

A = np.array([4.3* 10**12,2.3* 10**11,2.2* 10**10,1.6* 10**9])
Ea = np.array([172,159,146,134])

# k = A exp(-Ea/RT) = kB*T/h exp(delta S ddagger/R) exp(-delta H ddagger/RT)
# Ea is approximately equal to delta H ddagger. ln A = ln(kB*T/h)+delta S ddagger/R.
# ln(kB*T/h) is approximately 30. delta S ddagger = (lnA-30)*R
# Plot lnA vs Ea since k = A exp(-Ea/RT)
lnA = np.log(A)
deltaH = Ea
deltaS = (lnA-30)*8.314
plt.plot(deltaH,deltaS, 'o', label = 'Observation')

# Fit the observations with a linear line
linear_model=np.polyfit(deltaH,deltaS,1)
linear_model_fn=np.polyld(linear_model)
# x_s=np.arange(20,31)
# Plot and add R2 in the label
R2 = r2_score(linear_model_fn(deltaH),deltaS)
plt.plot(deltaH,linear_model_fn(deltaH),c='tab:red',label='Linear Fit, \nR$^2$={:.3f}')
```

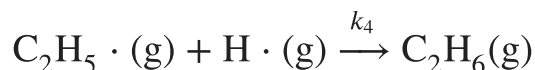
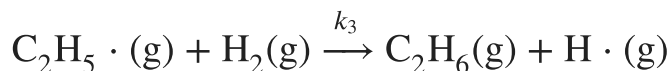
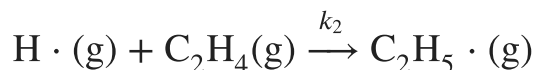
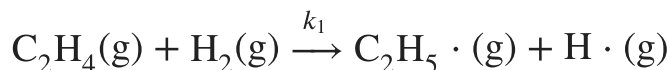
```
plt.legend(fontsize=12)
plt.ylabel('$\Delta S^{\ddagger}$, J/(mol K)')
plt.xlabel('$\Delta H^{\ddagger}$, kJ/mol')
plt.show()
```



We can say there is a compensation relationship between the apparent pre-exponential factor and apparent activation energy. There is likely a compensation relationship between ΔH_p^{\ddagger} (transition state) and ΔS^{\ddagger} (transition state) of the rate-controlling step.

▼ 4 The Radical Path

At high temperature, ethylene can be hydrogenated to ethane. The proposed mechanism has four steps, all of which are presumed to be elementary and essentially irreversible under realistic conditions.



At quasi-steady-state, concentrations of intermediates are constants.

$$\frac{dC_{C_2H_5\cdot}}{dt} = 0$$

$$\frac{dC_{H\cdot}}{dt} = 0$$

Solve the two algebraic equations with two unknowns.

$$C_{H\cdot} = \sqrt{\frac{k_1 k_3}{k_2 k_4}} C_{H_2}$$

$$C_{C_2H_5\cdot} = \sqrt{\frac{k_1 k_2}{k_3 k_4}} C_{C_2H_4}$$

- 4.5 Combine your answers to obtain an expression for the rate of disappearance of ethylene that involves only reactants and products. What is the apparent reaction order with respect to H_2 ? To C_2H_4 ?

$$\frac{dC_{C_2H_4}}{dt} = -k_1 C_{C_2H_4} C_{H_2} - k_2 C_{C_2H_4} C_{H\cdot} = -k_1 C_{C_2H_4} C_{H_2} - k_2 C_{C_2H_4} \sqrt{\frac{k_1 k_3}{k_2 k_4}} C_{H_2}$$

$$\frac{dC_{C_2H_4}}{dt} = \left(-k_1 - \sqrt{\frac{k_1 k_2 k_3}{k_4}} \right) C_{C_2H_4} C_{H_2}$$

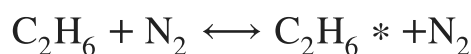
Apparent orders with H_2 and C_2H_4 are both 1.

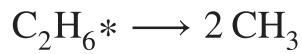
- 4.6 What is the apparent rate constant? Do you expect it to exhibit Arrhenius behavior in general?

$$\text{Apparent rate constant is } k_1 + \sqrt{\frac{k_1 k_2 k_3}{k_4}}.$$

Even if each k is Arrhenius, the combination is not.

- 4.7 Ethane dissociation $C_2H_6 \longrightarrow 2 CH_3$ is a key step in the initiation of gas-phase ethane reactions. If the reaction is observed in a diluent, say N_2 , the rate is found to be a function of total pressure and to reach a limiting value at high pressure. Why? Can you propose a simple model for this behavior?





$$\frac{dC_{\text{C}_2\text{H}_6^*}}{dt} = k_1 C_{\text{C}_2\text{H}_6} C_{\text{N}_2} - k_{-1} C_{\text{C}_2\text{H}_6^*} C_{\text{N}_2} - k_2 C_{\text{C}_2\text{H}_6^*}$$

At steady state, $\frac{dC_{\text{C}_2\text{H}_6^*}}{dt} = 0$

$$C_{\text{C}_2\text{H}_6^*} = \frac{k_1 C_{\text{C}_2\text{H}_6} C_{\text{N}_2}}{k_{-1} C_{\text{N}_2} + k_2}$$

$$\frac{dC_{\text{CH}_3}}{dt} = 2 \frac{k_2 k_1 C_{\text{C}_2\text{H}_6} C_{\text{N}_2}}{k_{-1} C_{\text{N}_2} + k_2}$$

When C_{N_2} is small, total pressure impacts the rate of CH_3 generation.

When C_{N_2} is large but $C_{\text{C}_2\text{H}_6}$ is a constant, $\frac{dC_{\text{CH}_3}}{dt} = 2 \frac{k_2 k_1 C_{\text{C}_2\text{H}_6}}{k_{-1}}$. The rate will reach a limiting value.