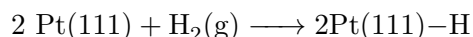
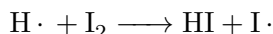
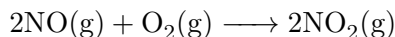
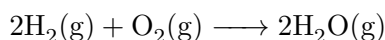
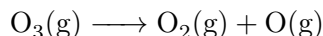


Carefully and neatly document your answers. You may use a mathematical solver like Jupyter/iPython. Use plotting software for all plots.

## 1 It's 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.

## 2 The path less traveled

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

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

- 2.1 Make Arrhenius plots of the three reactions from 150 to 500 K. Which reaction dominates at low temperature? At high temperature?
- 2.2 Can collision theory account for the variations in rate constants amongst the three reactions? Why or why not?
- 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,  $\Delta H^{\circ\dagger}$  and standard activation entropy,  $\Delta S^{\circ\dagger}$ , at 1 bar standard state.

$$k = \frac{k_B T}{h} \left( \frac{RT}{P^\circ} \right) e^{-\Delta G^\circ(T)/k_B T}$$

- 2.4 Calculate  $\Delta H^{\circ\dagger}$  and  $\Delta S^{\circ\dagger}$  for each of the three reactions.
- 2.5 Using chemical intuition and the calculated  $\Delta S^{\circ\dagger}$  as guides, draw candidate transition state structures for each of the three reactions. Include arrows to show motion along the reaction coordinates.
- 2.6 Following is some thermodynamic data. Use it to sketch/draw/plot a potential enthalpy surface for the three reactions and a potential free energy surface for the three reactions at 298 K.

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

### 3 What do I get in compensation?

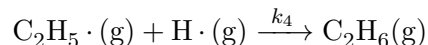
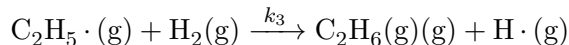
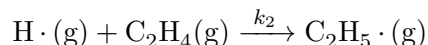
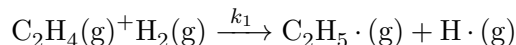
Following are some observed data for the dehydrogenation of *iso*-propanol,  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3 \longrightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{H}_2$ , over a series of catalysts:

$A$ (s <sup>-1</sup> )	$E_a$ (kJ mol <sup>-1</sup> )
$4.3 \times 10^{12}$	172
$2.3 \times 10^{11}$	159
$2.2 \times 10^{10}$	146
$1.6 \times 10^9$	134

- 3.1 What can you say about the relationship between  $\Delta S^{\circ\dagger}$  and  $\Delta H_p^{\circ\dagger}$ ?

### 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.



- 4.1 Identify the reactants, products, and intermediates, and state whether the mechanism is open or closed.
- 4.2 Why is it reasonable to assume that the first reaction is irreversible (that is, that the forward reaction rate is much greater than the reverse)? What about the second reaction?
- 4.3 Based on the mechanism above, write an expression for the rate of disappearance of ethylene.
- 4.4 Apply the quasi-steady-state approximation separately to H atoms and ethyl radicals. Use the results to derive expressions for the concentrations of each in terms of only reactants and products.
- 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  $\text{H}_2$ ? To  $\text{C}_2\text{H}_4$ ?
- 4.6 What is the apparent rate constant? Do you expect it to exhibit Arrhenius behavior in general?
- 4.7 The opposite of ethylene hydrogenation is ethane dehydrogenation,  $\text{C}_2\text{H}_6 \longrightarrow 2\text{CH}_3$ . If the reaction is run in a diluent, say  $\text{N}_2$ , the rate is observed 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?