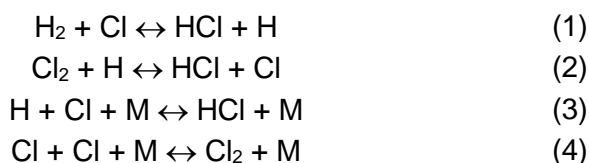


## Homework #1: Chemical Kinetics and Simple Mechanisms

- Homework solutions should be neat and logically presented, see format requirements at <http://seitzman.gatech.edu/classes/ae6766/homeworkformat.html>.

### 1. H<sub>2</sub>/Cl<sub>2</sub> Kinetic Mechanism and Reaction Rates

The combustion of hydrogen gas (H<sub>2</sub>) and chlorine gas (Cl<sub>2</sub>) to form their stable combustion product, hydrogen chloride (HCl), can be modeled using a mechanism involving four reactions:



The table below provides the heats of reaction, Gibbs free energy of reaction and modified Arrhenius parameters for the *forward* reaction rate constants of each of the four steps.

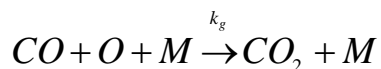
Reaction	$\Delta H_R @ 500K$ (kcal/mol)	$\Delta G_R @ 500K$ (kcal/mol)	A (see note)	b	$E_a/R$ (K)
1	0.97	0.374	$9.5 \times 10^7$	1.7	1540
2	-45.4	-46.82	$8.6 \times 10^{13}$	0	590
3	-104	-91.87	$2.0 \times 10^{23}$	-2.5	0
4	-58.4	-45.04	$2.3 \times 10^{19}$	-1.5	0

(Note: A values are in appropriate combination of *cm*, *s* and *mol* units.)

- Based on this mechanism, would you expect H<sub>2</sub>/Cl<sub>2</sub> mixtures to exhibit induction periods with a slow build-up of radicals followed by a sudden, drastic increase in the production rate of HCl, i.e., typical chain-branching behavior?
- Determine the values of the reaction rate constants for the forward ( $k_{if}$ ) and reverse ( $k_{ir}$ ) reactions of each of the 4 steps, at a temperature of 500 K.
- Estimate the chemical times ( $\tau_{\text{chem}}$ ) for the forward reactions (1) and (2) at early times for a mixture initially at 500. K and 0.50 bar with mole fractions of 1% H<sub>2</sub>, 1% Cl<sub>2</sub> and 98% Ar. (In Turn's wording, use the limit for bimolecular reactions where one of the reactants is in "much greater abundance.")
- Which of the following reactions has the highest reaction rate at the conditions listed in part c), and assuming a Cl radical mole fraction of at least 1 ppb: forward reaction 1f, forward reaction 4f, or reverse reaction 4r?

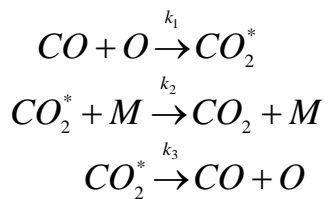
## 2. Apparent Termolecular Reactions – Pressure Dependence

Consider the apparent termolecular reaction that is a major heat release step in the “dry” CO mechanism described in the class lectures,



This termolecular reaction describing how CO can be oxidized to form CO<sub>2</sub> via reaction with O radicals can also be important in oxidation of intermediate CO formed in hydrocarbon flames.

This termolecular reaction can be described by the following detailed reaction mechanism:

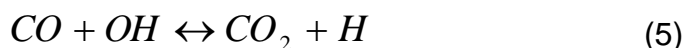
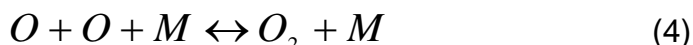


where CO<sub>2</sub>\* represents a short-lived activated complex.

- Find an expression for the rate constant of the overall reaction ( $k_g$ ) in terms of the detailed rate constants ( $k_1$ ,  $k_2$  and  $k_3$ ), the pressure, and any other necessary variables. In finding this expression, you can use the steady-state assumption for the concentration of the activated complex CO<sub>2</sub>\*.
- For the production rate of CO<sub>2</sub> at high pressures, what is the overall order of the apparent reaction with respect only to the major species? In answering this question, assume we are examining combustion of a “dry” CO-air reactant mixture.
- Sketch how  $k_g / k_0$  ( $k_0$  is the value of  $k_g$  as the pressure **approaches** zero) would vary with pressure (for fixed temperature).

### 3. CO Burnout – Reduced Mechanism (based on former midterm problem)

As noted in class, CO<sub>2</sub> is primarily formed in hydrocarbon-air mixtures by the reaction of CO with OH. The following detailed chemical mechanism for the **burnout of CO** in lean hydrocarbon-air flames has been suggested:



Consider CO burnout in **lean propane-air** combustion, at a late point in the combustion process where the oxyhydrogen species (molecules that contain only O and/or H atoms) are equilibrated, i.e., the partial equilibrium assumption can be considered valid for reactions involving only these species.

- a) Develop an expression for the concentration of OH, i.e.,  $[OH]$ , as a function of the concentrations of **major species** (and **only** major species) involved in the **oxyhydrogen** reactions and any temperature dependent properties, e.g., reaction rate constants,  $k_{fi}$  and  $k_{ri}$ , for the reactions listed above, and/or any equilibrium constants,  $K_p$ , you find necessary to define.
- b) Assuming that the CO+OH reaction can proceed **ONLY** in the forward direction, write a global **reaction rate** expression for the production rate of CO<sub>2</sub>,  $d[CO_2]/dt$ , in terms of the concentrations of CO and any necessary **major species** that exist in the CO burnout region (no minor species except CO should appear in your global reaction rate expression). Your expression can also include any elementary reaction rate constants from the reactions listed above and any equilibrium constants you find necessary to include (just make sure you have defined them).
- c) Based on your global reaction rate expression, how much would the relative rate of CO destruction, i.e.,  $d[CO]/dt / [CO]$ , change if we doubled the pressure without changing the temperature or mole fractions of the major species.

#### 4. Thermal NO<sub>x</sub> in an IC Engine

We are interested in examining NO reaction time scales and NO levels in an IC (e.g., piston-cylinder) engine. Consider constant volume combustion, which is a simple model of what happens in an IC engine. Essentially, we assume the piston does not move (much) from the time ignition occurs to when most of the heat release has occurred. For this problem, consider a mixture of iso-octane and air that has been compressed at the end of the compression stroke to 390 K, 2.9 atm, with an equivalence ratio of  $\phi=0.85$ .

For this problem, assume that the NO kinetics are described by the unmodified Zeldovich mechanism, that the N atom population can be assumed to be in (quasi) steady-state and that the O concentration remains in equilibrium with the O<sub>2</sub> population. In other words, you can use the analytic model derived (for  $\alpha$ ) in the class notes.

You may also assume that the cylinder walls are adiabatic and the combustion reactions occur much more rapidly than the (slow) NO formation reactions. So you can start by assuming that the major species concentrations (and temperature and pressure) remain approximately constant after the fuel is burned, which is when the thermal NO chemistry is occurring.

- a) What is the equilibrium NO mole fraction in the combustion products (before expansion) for this system? You may use whatever method or tool is convenient to determine this value?
- b) Estimate the time required for the NO concentration to **reach 1/3<sup>rd</sup>** of this equilibrium value.
- c) For an IC engine operating at 3300 rpm, the time required for the expansion stroke is ~9 msec. Would it be likely that the level of NO in the gas leaving the cylinder's exhaust valve operating at this rpm would be as much as 1/3<sup>rd</sup> of the equilibrium value calculated in part (a)?