| AME 513	Assigned: Tuesday 10/2/2012
Problem Set #2	• **Due Monday 10/15/2012 at 4:30 pm in the drop box in OHE 430N (Xerox room)** • **Email to the grader (Thada Suksila) at ame513_fall2012@yahoo.com or fax to 213-740-8071 if you're off campus** • **DEN students submit through the usual channels**

Textbook problems:

4.20 (Partial equilibrium)
5.6 (Beta scission)
5.7 (Butane oxidation)
5.8 (Reduced mechanisms)

Other problems:

PDR1. In a well-stirred reactor with a volume of 1 liter, burning a stoichiometric methane-air mixture at 1 atm, the reactor extinguished at a mass flow rate of 0.4 kg/s and a temperature of 0.85 T_{ad}.

(a) From this information, estimate the pre-exponential factor Z and activation energy E_a.
(b) Assuming this Z and E_a are correct, what would the extinction mass flow rate and extinction temperature be at equivalence ratio 0.8?
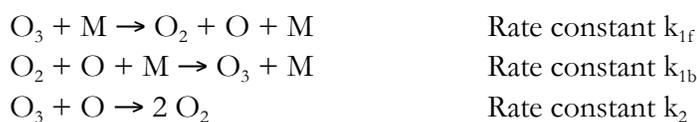
PDR2. Consider the decomposition of ozone (O_3) to O_2, i.e.

$$O_3 \rightarrow 1.5\ O_2$$
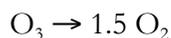
When the concentrations of O_3 and O_2 were comparable (i.e. O_3 was not a minor species in a bath of O_2), the overall reaction rate has been observed to have the form
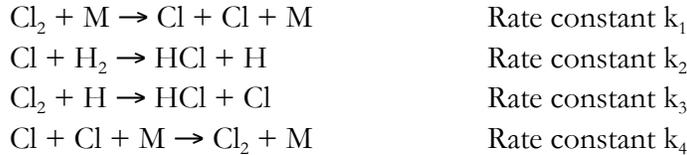
$$\frac{d[O_3]}{dt} = -k_{effective} \frac{[O_3]^2}{[O_2]}$$

In other words, ozone decomposition was inhibited by oxygen, its own combustion product! Assume the important steps in ozone decomposition are as follows:

$$O_3 + M \rightarrow O_2 + O + M \qquad \text{Rate constant } k_{1f}$$
$$O_2 + O + M \rightarrow O_3 + M \qquad \text{Rate constant } k_{1b}$$
$$O_3 + O \rightarrow 2\ O_2 \qquad \text{Rate constant } k_2$$

(a) Assuming steady-state for O atoms, derive an expression for the O atom concentration
(b) Using the result of (a), determine the rate of decomposition of O_3
(c) Using the result of (b), in order to observe the overall reaction rate given above, what assumptions about the rate constants must be made (e.g. $k_{1f} >> k_2$)?
(d) If the assumptions made in part (c) are true, what is k_{eff} in terms of k_{1f}, k_{1b} and k_2?
(e) In the limit where $[O_3]$ is extremely small, what is expression for $d[O_3]/dt$?

PDR3. Assume the important steps in the reaction between hydrogen (H_2) and chlorine (Cl_2) are as follows:

$Cl_2 + M \rightarrow Cl + Cl + M$	Rate constant k_1
$Cl + H_2 \rightarrow HCl + H$	Rate constant k_2
$Cl_2 + H \rightarrow HCl + Cl$	Rate constant k_3
$Cl + Cl + M \rightarrow Cl_2 + M$	Rate constant k_4

(d) Assuming steady-state for H atoms, derive an expression for the H atom concentration
(e) Using the result of (a), assuming steady-state for Cl atoms, derive an expression for the Cl atom concentration
(f) Find the rate of formation of HCl in terms of $[H_2]$, $[Cl_2]$, k_1, k_2, k_3 and k_4. You should find that, oddly enough, $d[HCl]/dt \sim [H_2]^1[Cl_2]^{1/2}$.

PDR4. Consider a reaction vessel whose characteristic time for radical loss is 1 second at atmospheric pressure and scales linearly with pressure, e.g. at 10 atm it's 10 seconds and at 0.1 atm it's 0.1 second. For a stoichiometric $H_2 - O_2$ mixture at 600°C, using the online chemical kinetics calculator:

http://navier.engr.colostate.edu/~dandy/code/code-5/index.html

(a) Determine the lowest pressure at which the reaction time scale is shorter than the loss time scale (i.e. determine the first explosion limit). At 600°C I get around 0.013 atm, that is at 0.013 atm, the time scale for 50% completion of reaction is about 0.013 second.
(b) Repeat for the second and third limits.
(c) Repeat parts (a) and (b) for 550°C and 650°C. Do the trends you observe agree or disagree with the experimental data shown in Fig. 5.1 in the text?