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

\[ \frac{d[O_3]}{dt} = -k_{\text{effective}} \frac{[O_3]^2}{[O_2]} \]

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

- \[ O_3 + M \rightarrow O_2 + O + M \] Rate constant k_{1f}
- \[ O_2 + O + M \rightarrow O_3 + M \] Rate constant k_{1b}
- \[ O_3 + O \rightarrow 2 O_2 \] 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 O₃
(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. \( k_{1f} \gg k_2 \))?
(d) If the assumptions made in part (c) are true, what is \( k_{\text{eff}} \) in terms of \( k_{1f}, k_{ib} \), and \( k_2 \)?
(e) In the limit where \([\text{O}_3]\) is extremely small, what is an expression for \( d[\text{O}_3]/dt \)?

**PDR3.** Assume the important steps in the reaction between hydrogen (H₂) and chlorine (Cl₂) are as follows:

\[
\begin{align*}
\text{Cl}_2 + M &\rightarrow \text{Cl} + \text{Cl} + M & \text{Rate constant} \ k_1 \\
\text{Cl} + \text{H}_2 &\rightarrow \text{HCl} + \text{H} & \text{Rate constant} \ k_2 \\
\text{Cl}_2 + \text{H} &\rightarrow \text{HCl} + \text{Cl} & \text{Rate constant} \ k_3 \\
\text{Cl} + \text{Cl} + M &\rightarrow \text{Cl}_2 + M & \text{Rate constant} \ k_4
\end{align*}
\]

(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 \([\text{H}_2], [\text{Cl}_2], k_1, k_2, k_3\), and \( k_4 \). You should find that, oddly enough, \( d[\text{HCl}]/dt \sim [\text{H}_2]^{1/2}[\text{Cl}_2]^{1/2} \).

**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 H₂ – O₂ 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?