Chem350 Assignment 4: Chemical Kinetics.

   A. **Reid and Engel problems.**
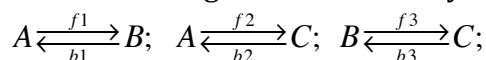
    1. **18.7 (Determine rate law empirically)**
    2. **18.13 (First order rate constant)**
    3. **18.38 (Arrhenius, from 2 data points)**
    4. **18.49 (Arrhenius, from multiple data points, use excel)**
    5. **19.4 (rate law radical reaction)**
    6. **19.7 (analysis Br_2 reaction, see lecture notes. See also Matlab section)**
    7. **19.19 (enzyme catalysis and inhibition)**

   B. **Matlab problems.**

    8. **Skip Bromine question.**

    9. **Consistency relation between rate constants (same as before).**
    Consider the following set of elementary reactions, and code in Matlab

$$A \underset{b1}{\overset{f1}{\rightleftarrows}} B; \quad A \underset{b2}{\overset{f2}{\rightleftarrows}} C; \quad B \underset{b3}{\overset{f3}{\rightleftarrows}} C;$$

   Use the following values for the forward and back ward rates:

$$f = [1.0, 1.0, 1.0]; \quad b = [0.5, 0.2, 2.0]$$

    Run the simulation starting from initially compound A only, with $[A_0] = 1$.
    At chemical equilibrum we usually expect that the rate of each elementary
    reaction goes to zero. This does not happen in this case. Print the rates (r1,
    r2, r3) in your matlab model_file and examine the asymptotic long time
    behavior. If you plot the concentration profiles you will see that they do
    reach a plateau, but the rates for the elementary reactions themselves are
    non-zero. The reason the individual rates do not vanish at long time is that
    our forward and backward rates are not thermodynamically consistent:
    They should satisfy $K_{eq} = f / b$: If A is in equilibrium with B and C, also B and
    C should be in equilibrium. *Derive an expression for a correct* b_3, in terms of
    the other rate constants, using thermodynamical equilibrium conditions, and
    rerun the simulation (after changing b3 to the correct value). Verify that now
    indeed the rate for each elementary reaction goes to zero. This is called
    detailed balance. It is a fundamental consequence of the Gibbs free energy
    being a function of state (or an exact differential). It shows we cannot just
    choose the rate constants. It would be better to define them in terms of Gibbs
    free energies and activation energies. That would always lead to a
    thermodynamically consistent set of rate constants.

10. **Investigating steady state and pre-equilibrium approximations (updated).**

Consider the reactions

$$A \underset{b_1}{\overset{f_1}{\rightleftharpoons}} I \underset{b_2}{\overset{f_2}{\rightleftharpoons}} P$$
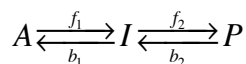
In this problem we will investigate the validity of steady state and pre-equilibrium approximations. The first step is to create the matlab file to do the exact simulations (model_AIP for example). We can best define reaction rates using the Arrhenius formula using activation energies (for reasons of consistency, see previous problem).

$$f = \exp(-1000*(E_{TS} - E_R)/(R*T))$$
$$b = \exp(-1000*(E_{TS} - E_P)/(R*T))$$

We can use the following three cases to illustrate different regimes:

Energy (kJ mol^{-1})	E_A	E_TS1	E_I	E_TS2	E_P
Case 1	-10.0	5.0	-5.0	0.0	-50.0
Case 2	-6.0	0.0	-5.0	15.0	-50.0
Case 3	-6.0	5.0	-5.0	5.0	-50.0

You can plot the energy profile for each case. I find it convenient to define the array (in Matlab):

$$Eall = [E\_A, E\_A, E\_TS1, E\_TS1, E\_I, E\_I, E\_TS2, E\_TS2, E\_P, E\_P]$$
$$xall = [1:10]$$

Then you can use plot(xall, Eall) and get a nice picture.
For each case calculate the forward and backward rate constants, and run the reactions, using an initial concentration of A_0=10.0, and a tspan = [0 1000]. In a second figure plot [A], [I] and [P] vs. time. To extract the rate constant,

we can use that in all cases $\dfrac{d[A]}{dt} = -keff[A] \rightarrow [A(t)] = [A_0]e^{-keff*t}$. Therefore if

we plot $\ln([A(t)]$ .vs. t, we expect to get a straight line, except for beginning and end pieces perhaps. To see the plot (in Matlab: plot(t,log(A), 'b'), and determine a tbegin (I used 25) and tend (I used nt-5, where nt=length(t)), so you can plot it a second time (

        plot(t(tbegin:tend), log(A(tbegin:tend), 'r')
If you determine the slope of the straight line segment (in red) you get –keff. The value for keff can be compared to the formulas derived and in the class

notes and in the text book. The steady state rate: $\dfrac{d[A]}{dt} = -\dfrac{f_2 f_1}{f_2 + b_1}[A]$ and pre-

equilibrium rate: $\frac{d[A]}{dt} = -\frac{f_2 f_1}{b_1 + f_1}[A]$. We will see that we get a straight line behavior, but the resulting slope can be different from either steady state or pre-equilibrium. You can rationalize the behavior given the energy profile.

11. **Follow-up kinetics lab II: Radical chain explosion (see R&E 19.7 explosions): updated.**

Let us investigate the following set of elementary reactions that enter the simple $2H_2 + O_2 \rightleftarrows 2H_2O$ reaction.

1. $O_2 \rightleftarrows 2 \cdot O \cdot$
2. $O_2 + \cdot O \cdot \rightleftarrows O_3$
3. $\cdot O \cdot + H_2 \rightleftarrows OH^{\cdot} + H^{\cdot}$
4. $H^{\cdot} + O_2 \rightleftarrows OH^{\cdot} + \cdot O \cdot$
5. $OH^{\cdot} + H_2 \rightleftarrows H_2O + H^{\cdot}$
6. $OH^{\cdot} + O_2 \rightleftarrows OOH^{\cdot} + \cdot O \cdot$
7. $H^{\cdot} + OH^{\cdot} \rightleftarrows H_2O$
8. $OH^{\cdot} + OH^{\cdot} \rightleftarrows HOOH$
9. $H^{\cdot} + OOH^{\cdot} \rightleftarrows HOOH$
10. $H_2 + O_2 \rightleftarrows 2OH^{\cdot}$

Reactions 1 and 2 create an equilibrium among pure O species. These reactions should be pre-equilibrated. Reactions 3-6 lead to a proliferation of radicals, while reactions 7-9 take away radicals. Reaction 10 is used in he textbook as the initial source of radicals. I rather think it is reaction 1. Moreover, I added reaction 6, generating peroxide radicals. Initially use the following set of forward and backward rate constants:

f=[1e-4, 1.0e-3, 1.0e-3, 1.0e-2 , 1.0e-2, 1.0e-2, 1.0e-1 , 1.0e-1, 1.0e-1, 1.0e-4]

b=[1e-2, 1.0e-5, 1.0e-2, 1.0e-4 , 1.0e-3, 1.0e-2, 1.0e-6 , 1.0e-6, 1.0e-6, 1.0e-1]

Use as initial #of moles: 10 for O_2 and 20 for H_2. Build a kinetic model for this reaction, and run a simulation (pre-equilibrate O_2 for say 3000 s. Check the profile go flat in the end), and run the actual reaction (propagate for 500 s). Plot the individual concentrations of radicals and stable molecules as a function of time. Also plot the *overall* concentration of radicals. It is clear that the radical concentration grows rapidly in time. To analyse more quantitatively plot 'minus the square root of -ln of the total radical concentration'. I verified that this looks more or less like a straight line.

Hence you can define sqrt_ln_rad=(-sqrt(-log(Radtot)) and plot this vs. t. Then we can take the slope of this (I used beginning and end points of 15 and 35). If the resulting slope $k_{eff} > 0$ you are in the explosive regime.

Optional investigation (will not be graded):

   Somewhat surprisingly a main reaction product is HOOH, besides water. Maybe I should have put in more reactions involving peroxide radicals (with H_2 for example). To investigate switch off reaction 6 (i.e. make forward rate constant very small (10^{-6}). Do you still observe explosive growth now? Next remove reaction 10 (give it a small forward rate). How does this affect matters? I think you can observe that none of the issues are trivial, but at least we have the means to explore in detail.

C. **Additional practice problems to consider for exam (*not for this assignment*)**

12. **Problem 19.10 (derivation rate law.**
13. **Problem 19.13 (Lindemann).**
14. **Problem 19.25, 19.26 (rate laws radical reaction)**