

CE 561 Homework 1: Assigned 08/31/09, due 09/09/09

- 1) Send an email to me at swihart@buffalo.edu. In your message let me know (a) whether you plan to pursue an M.Eng., M.S., or Ph.D. degree; (b) at what colleges or Universities you previously studied, and (c) about how many semesters of undergraduate chemical kinetics and reaction engineering courses you took. If you wish, you may describe other things that you would like me to know about you, or any concerns you may have about this course.
- 2) Print, read and sign the [Policy on Academic Honesty and Integrity](#). Submit it with your homework solutions.
- 3) What are the units of the rate constants of first-, second-, and third-order reactions if the concentrations are expressed in (moles per liter) and time is expressed in hours? What are the conversion functions that must be used to convert to concentration units of (molecules cm⁻³) in each case?

In all cases, the reaction rate has units of (moles liter⁻¹ hr⁻¹). The rate constant has whatever units are required to make that the case.

$$1^{\text{st}} \text{ order} - r \text{ (moles liter}^{-1} \text{ hr}^{-1}) = k \text{ (hr}^{-1}) C_A \text{ moles liter}^{-1}$$

$$2^{\text{nd}} \text{ order} - r \text{ (moles liter}^{-1} \text{ hr}^{-1}) = k \text{ (moles}^{-1} \text{ liter hr}^{-1}) (C_A \text{ (moles liter}^{-1}))^2$$

$$3^{\text{rd}} \text{ order} - r \text{ (moles liter}^{-1} \text{ hr}^{-1}) = k \text{ (moles}^{-2} \text{ liter}^2 \text{ hr}^{-1}) (C_A \text{ (moles liter}^{-1}))^3$$

If we use concentrations units of (molecules cm⁻³) then

1st order – no change in rate constant

2nd order – divide by Avagadro's number ($N_A=6.022 \times 10^{23}$ molecules/mole) and multiply by 1000 cm³ per liter

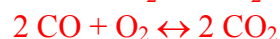
$$k \text{ (molecules}^{-1} \text{ cm}^3 \text{ hr}^{-1}) = k \text{ (moles}^{-1} \text{ liter hr}^{-1}) * 1000 \text{ cm}^3 \text{ liter}^{-1} / 6.022 \times 10^{23} \text{ (molecules/mole)}$$

3rd order – divide by Avagadro's number squared and multiply by 10⁶ cm⁶ liter⁻²

$$k \text{ (molecules}^{-2} \text{ cm}^6 \text{ hr}^{-1}) = k \text{ (moles}^{-2} \text{ liter}^2 \text{ hr}^{-1}) * 10^6 \text{ cm}^6 \text{ liter}^{-2} / (6.022 \times 10^{23} \text{ (molecules/mole)})^2 =$$

- 4) Define the following: reaction rate, stoichiometric coefficient, reaction order, elementary reaction, overall reaction, molecularity, equilibrium constant, law of microscopic reversibility, Arrhenius plot, reaction mechanism, pseudo-steady-state approximation. Please put the definition in your own words. That is, do not simply copy the definition from the lecture notes, a textbook, or (especially) Wikipedia.

Stoichiometric coefficient: the number of moles of a species produced or consumed in a reactant per mole of reaction that occurs. These are defined by convention to be negative for reactants (consumed) and positive for products (produced) of the reaction. They can only be defined relative to a particular written version of a reaction. Take, for example, the three reactions:



The stoichiometric coefficients are different in each case, even though all three represent the same process.

Reaction order: for a reaction whose rate exhibits a power-law dependence on the

reactant concentrations $\left(r = k \prod_{j=1}^N C_{A_j}^{\nu_j} \right)$ the overall reaction order is the sum of the

exponents $\sum_{j=1}^N \nu_j$. The order with respect to reactant j is its exponent ν_j .

Elementary Reaction: an elementary reaction is one that obeys the law of mass action and that physically occurs as written.

Overall Reaction: the chemical process observed on macroscopic timescales – often occurring via a sequence of elementary reactions. This is also called the stoichiometric reaction.

Molecularity: the molecularity of an elementary reaction is the number of reactant molecules participating in the reaction. It is almost always 1 or 2, rarely 3, and never anything else. (A reaction with a molecularity of one is called unimolecular, and a reaction with a molecularity of two is called bimolecular).

Equilibrium constant: the constant of proportionality relating the concentrations of reactants and products, each raised to the power corresponding to its stoichiometric coefficient, at equilibrium. That is, the equilibrium constant K_i for reaction i is given

by $K_i = \prod_{j=1}^N C_{A_j,eq}^{\nu_{ij}}$. In thermodynamic terms, K_i can be written as $K_i = \exp(-$

$\Delta G_i / (RT))$, where ΔG_i is the change in free energy in going from reactants to products (expressed relative to some standard state consistent with the concentration units used for the species). The equilibrium constant relates the forward and reverse rate constants for a reaction through the relationship $K_i = k_{i,f} / k_{i,r}$.

Law of Microscopic reversibility: this is the principle that all elementary reactions must occur by the same mechanism in both the forward and reverse directions. It follows from the time reversibility of the laws of quantum mechanics. It can be used to prove that the ratio of the forward and reverse rate constants must equal the equilibrium constant, although there are more intuitive, phenomenological ways of proving that as well.

Arrhenius plot: A plot of the logarithm of a rate constant vs. the inverse temperature. If the rate constant obeys the Arrhenius temperature dependence, this plot is a straight line whose slope is equal to $-E_a/R$, where E_a is the activation energy for the reaction and R is the universal gas constant.

Reaction mechanism: the sequence of elementary reactions that makes up an observed overall reaction.

Pseudo-steady-state approximation (or just the steady-state approximation): This is the approximation that the rate of change of concentration for reactive intermediates whose concentrations are expected to be relatively small relative to other concentrations in the system is zero. It also allows us to replace a differential equation (the rate equation for the reactive intermediate) with an algebraic equation (the same equation, with the derivative of concentration with respect to time set equal to zero).

- 5) For the sequential reactions $A \rightarrow B$ with reaction rate $k_1 C_A$ and $B \rightarrow C$ with reaction rate $k_2 C_B$, derive expressions for the concentrations of A, B, and C as functions of time, starting with $C_A(t=0) = C_{A0}$, $C_B(t=0) = C_C(t=0) = 0$. Investigate limiting cases for $k_1 \gg k_2$ and $k_2 \gg k_1$.

$A \rightarrow B$ with $r_1 = k_1 C_A$, $B \rightarrow C$ with $r_2 = k_2 C_B$, so the rate equations are

$$\begin{aligned}\frac{dC_A}{dt} &= -k_1 C_A \\ \frac{dC_B}{dt} &= k_1 C_A - k_2 C_B \\ \frac{dC_C}{dt} &= k_2 C_B\end{aligned}$$

Just for fun, we'll do this one in matrix form:

$$\frac{d}{dt} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix} = \begin{bmatrix} -k_1 & 0 & 0 \\ k_1 & -k_2 & 0 \\ 0 & k_2 & 0 \end{bmatrix} \begin{bmatrix} C_A \\ C_B \\ C_C \end{bmatrix}$$

The eigenvalues and eigenvectors of the matrix of rate coefficients are:

$$\lambda_1 = 0, \lambda_2 = -k_1, \lambda_3 = -k_2, \underline{x}_1 = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}, \underline{x}_2 = \begin{bmatrix} \frac{k_1 - k_2}{k_2} \\ \frac{-k_1}{k_2} \\ 1 \end{bmatrix}, \underline{x}_3 = \begin{bmatrix} 0 \\ -1 \\ 1 \end{bmatrix}$$

So the matrices \underline{T} and \underline{T}^{-1} are given by

$$\underline{T} = \begin{bmatrix} 0 & \frac{k_1 - k_2}{k_2} & 0 \\ 0 & \frac{-k_1}{k_2} & -1 \\ 1 & 1 & 1 \end{bmatrix} \quad \text{and} \quad \underline{T}^{-1} = \begin{bmatrix} 1 & 1 & 1 \\ \frac{k_2}{k_1 - k_2} & 0 & 0 \\ \frac{-k_1}{k_1 - k_2} & -1 & 0 \end{bmatrix}$$

The concentrations are given by the expression we derived in class:

$$\underline{C}(t) = (\underline{T} \exp(\underline{\Lambda}t) \underline{T}^{-1}) \underline{C}_o$$

Substituting the matrices from this problem, this becomes

$$\underline{C}(t) = \begin{bmatrix} 0 & \frac{k_1 - k_2}{k_2} & 0 \\ 0 & \frac{-k_1}{k_2} & -1 \\ 1 & 1 & 1 \end{bmatrix} \begin{bmatrix} 1 & 0 & 0 \\ 0 & \exp(-k_1 t) & 0 \\ 0 & 0 & \exp(-k_2 t) \end{bmatrix} \begin{bmatrix} 1 & 1 & 1 \\ \frac{k_2}{k_1 - k_2} & 0 & 0 \\ \frac{-k_1}{k_1 - k_2} & -1 & 0 \end{bmatrix} \begin{bmatrix} C_{A,o} \\ 0 \\ 0 \end{bmatrix}$$

Carrying out the matrix multiplication gives

$$\underline{C}(t) = \begin{bmatrix} C_{A,o} \exp(-k_1 t) \\ C_{A,o} \left(\frac{k_1}{k_1 - k_2} \right) (\exp(-k_2 t) - \exp(-k_1 t)) \\ C_{A,o} \left(\frac{k_1}{k_1 - k_2} \right) \left(1 - \exp(-k_2 t) - \frac{k_2}{k_1} (1 - \exp(-k_1 t)) \right) \end{bmatrix}$$

Another (easier) way to solve this problem would be to first integrate the rate equation for A, then integrate the rate equation for B (using the known concentration vs. time of A) and finally finding the concentration of C from $C_C = C_{A0} - C_A - C_B$.

If the first reaction is much faster than the second ($k_1 \gg k_2$) then the two consecutive reactions are well separated in time, and there are distinct short and long time solutions

At short times (where $k_2 t \cong 0$), the solution is approximately

$$\underline{C}(t) = \begin{bmatrix} C_{A,o} \exp(-k_1 t) \\ C_{A,o} (1 - \exp(-k_1 t)) \\ 0 \end{bmatrix}$$

which is just the solution for $A \rightarrow B$ (since the 2nd reaction is slow, a negligible amount of C is formed on this time scale)

At long times (where $\exp(-k_1 t) \cong 0$) the solution is

$$\underline{C}(t) = \begin{bmatrix} 0 \\ C_{A,o} \exp(-k_2 t) \\ C_{A,o} (1 - \exp(-k_2 t)) \end{bmatrix}$$

All of the A has already been converted to B, and we just have the solution for $B \rightarrow C$

For the other limiting case, $k_2 \gg k_1$, the solution becomes

$$\underline{C}(t) = \begin{bmatrix} C_{A,o} \exp(-k_1 t) \\ C_{A,o} \left(\frac{k_1}{k_2} \right) (\exp(-k_1 t)) \\ C_{A,o} (1 - \exp(-k_1 t)) \end{bmatrix}$$

This is the same result that we would get if we applied the pseudo-steady-state approximation to B before solving the equations. If the second reaction is much faster than the first, then B is a reactive intermediate, present in very small quantities, and the pseudo-steady-state approximation on it is appropriate.

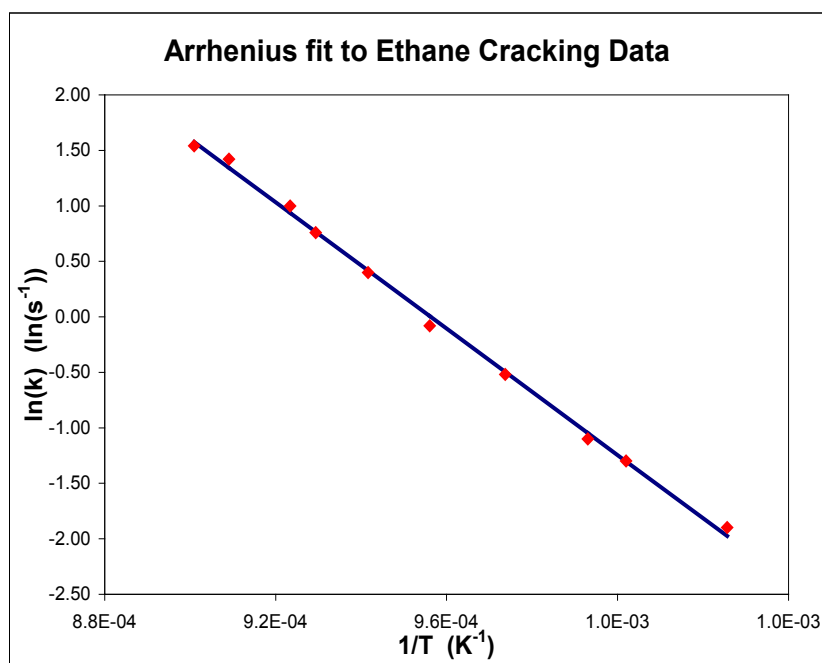
- 6) For thermal cracking of ethane in a tubular reactor, the following data were obtained for the rate coefficient vs. temperature:

| | | | | | | | | | | |
|---------------------|------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| T(°C) | 702 | 725 | 734 | 754 | 773 | 789 | 803 | 810 | 827 | 837 |
| k(s ⁻¹) | 0.15 | 0.273 | 0.333 | 0.595 | 0.923 | 1.492 | 2.138 | 2.718 | 4.137 | 4.665 |

Determine the activation energy and pre-exponential factor. Does this process obey the Arrhenius equation? Predict the rate coefficient at 1500 °C. How much does the predicted rate coefficient at 1500 °C change if the activation energy is increased or decreased by 5%?

This problem requires fitting the data to the Arrhenius form, which is readily done using a mathematical program like Mathematica, Matlab, or Maple, a plotting program with fitting routines, like Cricket Graph, SigmaPlot, or Kaleidagraph, or a spreadsheet like Excel. Below is an Excel spreadsheet for fitting the data. Note that we always use absolute temperatures (in Kelvin or Rankine) for fitting activation energies.

| T (°C) | T(K) | 1/T (K ⁻¹) | k (s ⁻¹) | ln(k) | Slope | Intercept | Fit ln(k) |
|--------|------|------------------------|----------------------|-------|----------------------------------|-----------------------------|------------|
| 702 | 975 | 1.03E-03 | 0.150 | -1.90 | -28470 | 27.2 | -1.9750514 |
| 725 | 998 | 1.00E-03 | 0.273 | -1.30 | | | -1.3020942 |
| 734 | 1007 | 9.93E-04 | 0.333 | -1.10 | <i>E_a</i> (kcal/mole) | <i>A</i> (s ⁻¹) | -1.0471312 |
| 754 | 1027 | 9.74E-04 | 0.595 | -0.52 | 56.6 | 6.7E+11 | -0.4965455 |
| 773 | 1046 | 9.56E-04 | 0.923 | -0.08 | | | 0.00700868 |
| 789 | 1062 | 9.42E-04 | 1.492 | 0.40 | | | 0.4170792 |
| 803 | 1076 | 9.29E-04 | 2.138 | 0.76 | | | 0.76588687 |
| 810 | 1083 | 9.23E-04 | 2.718 | 1.00 | | | 0.93690891 |
| 827 | 1100 | 9.09E-04 | 4.137 | 1.42 | | | 1.3431862 |
| 837 | 1110 | 9.01E-04 | 4.665 | 1.54 | | | 1.57635966 |



At 1500 °C (=1773 K) the Arrhenius expression predicts

$$k = 6.7 \times 10^{11} \exp(-56600/1.987/1773) = 70800 \text{ s}^{-1}$$

Increasing the activation energy by 5% gives $k = 31700 \text{ s}^{-1}$

Decreasing the activation energy by 5% gives $k = 158000 \text{ s}^{-1}$

For this long temperature extrapolation, a 5% change in the activation energy changes the rate constant by more than a factor of 2!

- 7) Consider the following set of elementary reactions describing the reaction of hydrogen and bromine to give hydrogen bromide:

Initiation: $\text{Br}_2 \rightarrow 2 \text{ Br}$, with rate coefficient k_1

Propagation: $\text{Br} + \text{H}_2 \rightarrow \text{HBr} + \text{H}$, with rate coefficient k_2

$\text{H} + \text{Br}_2 \rightarrow \text{HBr} + \text{Br}$, with rate coefficient k_3

Inhibition: $\text{H} + \text{HBr} \rightarrow \text{H}_2 + \text{Br}$, with rate coefficient k_4

Termination: $2 \text{ Br} \rightarrow \text{Br}_2$, with rate coefficient k_5

This is a typical *free-radical chain reaction* in which each initiation reaction starts a sequence of fast propagation reactions involving highly reactive free radical species (in

this case H and Br atoms). This sequence continues until it is ended by a termination reaction. Since these are elementary reactions, they all follow the law of mass action.

(a) Write the full set of rate equations for these reactions

The rate equations are as follows:

$$\frac{d[\text{Br}_2]}{dt} = -k_1[\text{Br}_2] - k_3[\text{H}][\text{Br}_2] + k_5[\text{Br}]^2$$

$$\frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2$$

$$\frac{d[\text{H}_2]}{dt} = -k_2[\text{Br}][\text{H}_2] + k_4[\text{H}][\text{HBr}]$$

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

$$\frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]$$

(b) simplify these rate equations by applying the pseudo-steady-state approximation to the concentrations of H and Br atoms

Applying the pseudo-steady-state approximation to [Br] gives

$$2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 = 0$$

and applying it to [H] gives

$$k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] = 0$$

Solving the second equation for [H] gives

$$[\text{H}] = \frac{k_2[\text{Br}][\text{H}_2]}{k_3[\text{Br}_2] + k_4[\text{HBr}]}$$

Substituting this into the the first equation gives

$$2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + (k_3[\text{Br}_2] + k_4[\text{HBr}]) \frac{k_2[\text{Br}][\text{H}_2]}{k_3[\text{Br}_2] + k_4[\text{HBr}]} - 2k_5[\text{Br}]^2 = 0$$

$$2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_2[\text{Br}][\text{H}_2] - 2k_5[\text{Br}]^2 = 0$$

$$2k_1[\text{Br}_2] - 2k_5[\text{Br}]^2 = 0$$

$$[\text{Br}] = \sqrt{\frac{k_1[\text{Br}_2]}{k_5}}$$

Substituting this back into the expression for [H] gives

$$[\text{H}] = k_2 \sqrt{\frac{k_1[\text{Br}_2]}{k_5}} \frac{[\text{H}_2]}{k_3[\text{Br}_2] + k_4[\text{HBr}]} = 0$$

Now, to finish simplifying the equations, we substitute the expressions for [Br] and [H] back into the rate equations for the other three species. Since the overall reaction is $\text{H}_2 + \text{Br}_2 \rightarrow 2 \text{HBr}$, we expect to find that

$$\frac{d[\text{HBr}]}{dt} = -2 \frac{d[\text{Br}_2]}{dt} = -2 \frac{d[\text{H}_2]}{dt}$$

Substituting the expressions for [H] and [Br] into the rate equation for Br_2 gives

$$\begin{aligned} \frac{d[\text{Br}_2]}{dt} &= -k_1[\text{Br}_2] - k_3 k_2 \sqrt{\frac{k_1[\text{Br}_2]}{k_5}} \frac{[\text{H}_2]}{k_3[\text{Br}_2] + k_4[\text{HBr}]} [\text{Br}_2] + k_5 \frac{k_1[\text{Br}_2]}{k_5} \\ \frac{d[\text{Br}_2]}{dt} &= -k_3 k_2 \sqrt{\frac{k_1}{k_5}} \frac{[\text{H}_2][\text{Br}_2]^{1.5}}{k_3[\text{Br}_2] + k_4[\text{HBr}]} \end{aligned}$$

Doing the same thing for the rate equation for H_2 gives

$$\begin{aligned} \frac{d[\text{H}_2]}{dt} &= -k_2 \sqrt{\frac{k_1[\text{Br}_2]}{k_5}} [\text{H}_2] + k_4 k_2 \sqrt{\frac{k_1[\text{Br}_2]}{k_5}} \frac{[\text{H}_2]}{k_3[\text{Br}_2] + k_4[\text{HBr}]} [\text{HBr}] \\ \frac{d[\text{H}_2]}{dt} &= k_2 \sqrt{\frac{k_1[\text{Br}_2]}{k_5}} \left(\frac{-[\text{H}_2](k_3[\text{Br}_2] + k_4[\text{HBr}]) + k_4[\text{H}_2][\text{HBr}]}{k_3[\text{Br}_2] + k_4[\text{HBr}]} \right) \\ \frac{d[\text{H}_2]}{dt} &= k_2 \sqrt{\frac{k_1[\text{Br}_2]}{k_5}} \left(\frac{-(k_3[\text{H}_2][\text{Br}_2])}{k_3[\text{Br}_2] + k_4[\text{HBr}]} \right) \\ \frac{d[\text{H}_2]}{dt} &= -k_2 k_3 \sqrt{\frac{k_1}{k_5}} \frac{[\text{H}_2][\text{Br}_2]^{1.5}}{k_3[\text{Br}_2] + k_4[\text{HBr}]} \end{aligned}$$

Finally, doing this for the HBr rate equation gives

$$\begin{aligned} \frac{d[\text{HBr}]}{dt} &= k_2[\text{Br}][\text{H}_2] + (k_3[\text{Br}_2] - k_4[\text{HBr}])[\text{H}] \\ \frac{d[\text{HBr}]}{dt} &= k_2\sqrt{\frac{k_1[\text{Br}_2]}{k_5}}[\text{H}_2] + (k_3[\text{Br}_2] - k_4[\text{HBr}])k_2\sqrt{\frac{k_1[\text{Br}_2]}{k_5}}\frac{[\text{H}_2]}{k_3[\text{Br}_2] + k_4[\text{HBr}]} \\ \frac{d[\text{HBr}]}{dt} &= k_2\sqrt{\frac{k_1[\text{Br}_2]}{k_5}}[\text{H}_2]\left(1 + \frac{k_3[\text{Br}_2] - k_4[\text{HBr}]}{k_3[\text{Br}_2] + k_4[\text{HBr}]}\right) \\ \frac{d[\text{HBr}]}{dt} &= k_2\sqrt{\frac{k_1[\text{Br}_2]}{k_5}}[\text{H}_2]\left(\frac{k_3[\text{Br}_2] + k_4[\text{HBr}]k_3[\text{Br}_2] - k_4[\text{HBr}]}{k_3[\text{Br}_2] + k_4[\text{HBr}]}\right) \\ \frac{d[\text{HBr}]}{dt} &= k_2\sqrt{\frac{k_1[\text{Br}_2]}{k_5}}[\text{H}_2]\left(\frac{2k_3[\text{Br}_2]}{k_3[\text{Br}_2] + k_4[\text{HBr}]}\right) \\ \frac{d[\text{HBr}]}{dt} &= 2k_2k_3\sqrt{\frac{k_1}{k_5}}\frac{[\text{H}_2][\text{Br}_2]^{1.5}}{k_3[\text{Br}_2] + k_4[\text{HBr}]} \end{aligned}$$

Reassuringly, we get the expected relationship between the three rate equations.

(c) how must the rate constants k_1 and k_5 be related to each other?

Because reaction 5 is the reverse of reaction 1, k_5 is simply the reverse rate constant for reaction 1. These are elementary reactions, so by the law of microscopic reversibility, we know that $k_1/k_5 = K$, where K is the equilibrium constant for the reaction $\text{Br}_2 \rightarrow 2 \text{Br}$. After realizing this, we might also recognize that the pseudo-steady-state concentration of Br found in part (b) is in fact also the equilibrium concentration (relative to a specified concentration of Br_2).

8) Solve the initial value problem

$$\begin{aligned} \frac{dx_1}{dt} &= 2x_2, & x_1(0) &= 1, \\ \frac{dx_2}{dt} &= -x_1 - 3x_2, & x_2(0) &= 1. \end{aligned}$$

In other words, derive explicit formulas for the functions $x_1(t)$ and $x_2(t)$ that satisfy the preceding coupled differential equations and initial conditions. Then plot the trajectory $(x_1(t), x_2(t))$ in the x_1, x_2 plane for $0 \leq t \leq 1$.

You may check your answer using Maple or a similar symbolic math package, but please work the solution out by hand, and show your work, to demonstrate that you are capable of doing so in a situation where Maple is unavailable (on an exam, for example).

Could this initial value problem represent two chemical reactions among two species? Explain why or why not.

Written in matrix form, this is:

$$\frac{d\underline{x}}{dt} = \underline{A}\underline{x}, \quad \underline{x}(0) = \underline{u}$$

with

$$\underline{A} = \begin{pmatrix} 0 & 2 \\ -1 & -3 \end{pmatrix}, \quad \underline{u} = \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

To construct the solution to this problem, we first compute the eigenvalues and eigenvectors of \underline{A} . The characteristic polynomial of \underline{A} is:

$$p(\lambda) = \det(\underline{A} - \lambda \underline{I}) = \begin{vmatrix} -\lambda & 2 \\ -1 & -3-\lambda \end{vmatrix}$$

$$p(\lambda) = \lambda^2 + 3\lambda + 2 = (\lambda + 1)(\lambda + 2) = 0$$

Thus, the eigenvalues are $\lambda_1 = -1$ and $\lambda_2 = -2$. The eigenvector corresponding to $\lambda_1 = -1$ is obtained from $(\underline{A} + \underline{I})\underline{x}_1 = \underline{0}$:

$$\underline{A} - \underline{I} = \begin{pmatrix} 1 & 2 \\ -1 & -2 \end{pmatrix} \begin{pmatrix} x_{1,1} \\ x_{1,2} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

Thus, $x_{1,1} + 2x_{1,2} = 0$, and $x_{1,1} = -2x_{1,2}$, and the value of $x_{1,2}$ can be chosen arbitrarily. Choosing $x_{1,2} = -1$ gives

$$\underline{x}_1 = \begin{pmatrix} 2 \\ -1 \end{pmatrix}$$

Similarly, we find the eigenvalue corresponding to $\lambda_2 = -2$ from

$$\underline{A} + 2\underline{I} = \begin{pmatrix} 2 & 2 \\ -1 & -1 \end{pmatrix} \begin{pmatrix} x_{2,1} \\ x_{2,2} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

From which $x_{2,1} = -x_{2,2}$. Choosing $x_{2,2} = -1$ gives

$$\underline{x}_2 = \begin{pmatrix} 1 \\ -1 \end{pmatrix}$$

Thus, we can construct the matrix of eigenvectors as:

$$\underline{T} = \begin{pmatrix} 2 & 1 \\ -1 & -1 \end{pmatrix}$$

We can find the inverse of this matrix by carrying out row operations as follows:

Start from augmented matrix: $\left(\begin{array}{cc|cc} 2 & 1 & 1 & 0 \\ -1 & -1 & 0 & 1 \end{array} \right)$

Add row 2 to row 1: $\left(\begin{array}{cc|cc} 1 & 0 & 1 & 1 \\ -1 & -1 & 0 & 1 \end{array} \right)$

Add row 1 to row 2: $\left(\begin{array}{cc|cc} 1 & 0 & 1 & 1 \\ 0 & -1 & 1 & 2 \end{array} \right)$

Multiply row 2 by -1: $\left(\begin{array}{cc|cc} 1 & 0 & 1 & 1 \\ 0 & 1 & -1 & -2 \end{array} \right)$

Thus,

$$\underline{T}^{-1} = \begin{pmatrix} 1 & 1 \\ -1 & -2 \end{pmatrix}$$

With this, we can construct the solution as:

$$\underline{x} = \underline{T} \exp(\underline{\Lambda}t) \underline{T}^{-1} \underline{u}$$

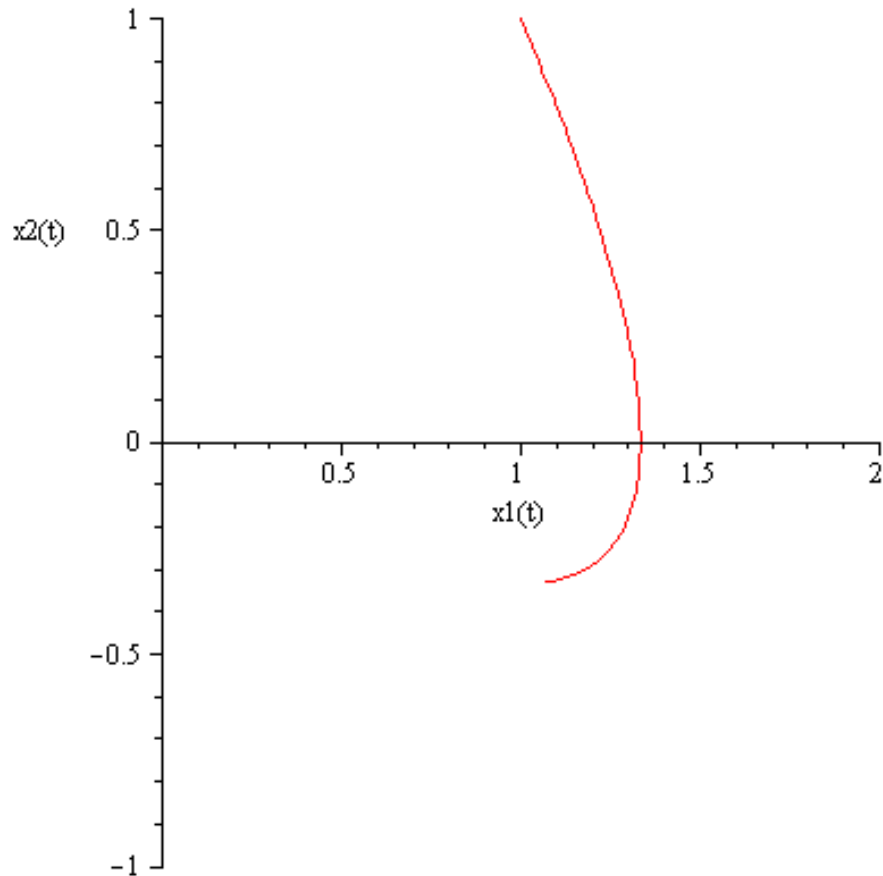
$$\underline{x} = \begin{pmatrix} 2 & 1 \\ -1 & -1 \end{pmatrix} \begin{pmatrix} \exp(-t) & 0 \\ 0 & \exp(-2t) \end{pmatrix} \begin{pmatrix} 1 & 1 \\ -1 & -2 \end{pmatrix} \begin{pmatrix} 1 \\ 1 \end{pmatrix}$$

$$\underline{x} = \begin{pmatrix} 2 & 1 \\ -1 & -1 \end{pmatrix} \begin{pmatrix} \exp(-t) & 0 \\ 0 & \exp(-2t) \end{pmatrix} \begin{pmatrix} 2 \\ -3 \end{pmatrix}$$

$$\underline{x} = \begin{pmatrix} 2 & 1 \\ -1 & -1 \end{pmatrix} \begin{pmatrix} 2 \exp(-t) \\ -3 \exp(-2t) \end{pmatrix} = \begin{pmatrix} 4 \exp(-t) - 3 \exp(-2t) \\ -2 \exp(-t) + 3 \exp(-2t) \end{pmatrix}$$

Plotted for $t = 0$ to 1 , this looks like:

```
> plot([4*exp(-t)-3*exp(-2*t), -2*exp(-t)+3*exp(-2*t), t=0..1], );
```



This set of ODE's most likely does not represent a pair of chemical reactions, at least with the variables x_1 and x_2 as species concentrations, because:

- (1) There is no stoichiometric relationship among the variables. The first term in equation 2 would represent consumption of species 2 at a rate proportional to the concentration of species 1, but there is no corresponding term in equation 1 for production of species 1 at a rate proportional to the concentration of species 1. Equation 1 would represent

production of species 1 at a rate proportional to the concentration of species 2, but independent of the concentration of species 1.

- (2) As seen in the plot above, x_2 becomes negative. Thus, it could not represent a chemical species concentration. It could represent an extent of reaction of a reversible reaction or some other concentration-related variable, but not an actual concentration.

9) Solve the initial value problem

$$\frac{d\underline{x}}{dt} = \underline{A}\underline{x}, \quad \underline{x}(0) = \underline{u}$$

with

$$\underline{A} = \begin{pmatrix} 3/2 & -7/2 & 3/2 \\ -3/2 & -1/2 & 3/2 \\ 2 & -2 & 1 \end{pmatrix}, \quad \underline{u} = \begin{pmatrix} 1 \\ 2 \\ 0 \end{pmatrix}$$

Again, you may check your answer using Maple or a similar symbolic math package, but please work the solution out by hand, and show your work, to demonstrate that you are capable of doing so in a situation where Maple is unavailable (on an exam, for example).

As usual, we start by finding the eigenvalues and eigenvectors of \underline{A} . The characteristic polynomial of \underline{A} is:

$$p(\lambda) = \det(\underline{A} - \lambda \underline{I}) = \begin{vmatrix} 3/2 - \lambda & -7/2 & 3/2 \\ -3/2 & -1/2 - \lambda & 3/2 \\ 2 & -2 & 1 - \lambda \end{vmatrix}$$

$$p(\lambda) = (3/2 - \lambda)(\lambda^2 - 1/2\lambda + 5/2) + 7/2(3/2\lambda - 9/2) + 3/2(2\lambda + 4) = 0$$

$$p(\lambda) = -\lambda^3 + 2\lambda^2 - 13/4\lambda + 15/4 + 21/4\lambda - 63/4 + 3\lambda + 6 = 0$$

$$\lambda^3 - 2\lambda^2 - 5\lambda + 6 = 0$$

$$(\lambda - 1)(\lambda + 2)(\lambda - 3) = 0$$

Thus, the eigenvalues of \underline{A} are $\lambda_1 = 1$, $\lambda_2 = -2$, and $\lambda_3 = 3$.

The eigenvector corresponding to $\lambda_1 = 1$ is obtained from $(\underline{A} - \underline{I})\underline{x}_1 = \underline{0}$:

$$\underline{A} - \underline{I} = \begin{pmatrix} 1/2 & -7/2 & 3/2 \\ -3/2 & -3/2 & 3/2 \\ 2 & -2 & 0 \end{pmatrix} \begin{pmatrix} x_{1,1} \\ x_{1,2} \\ x_{1,3} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

The third equation (last row) implies that $x_{1,1} = x_{1,2}$. Using this to eliminate $x_{1,2}$, both the first and second rows become

$$-3x_{1,1} + \frac{3}{2}x_{1,3} = 0$$

From which $x_{1,3} = 2x_{1,1} = 2x_{1,2}$. Arbitrarily selecting $x_{1,1} = 1$, we have

$$\underline{x}_1 = \begin{pmatrix} 1 \\ 1 \\ 2 \end{pmatrix}$$

The eigenvector corresponding to $\lambda_1 = -2$ is obtained from $(\underline{A} + 2\underline{I})\underline{x}_1 = \underline{0}$:

$$\underline{A} + 2\underline{I} = \begin{pmatrix} 7/2 & -7/2 & 3/2 \\ -3/2 & 3/2 & 3/2 \\ 2 & -2 & 3 \end{pmatrix} \begin{pmatrix} x_{2,1} \\ x_{2,2} \\ x_{2,3} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

Since this one leads to a full matrix, it may be worth proceeding more systematically, applying row operations to diagonalize it. First, I would scale each row to make the first element unity:

$$\begin{pmatrix} 1 & -1 & 3/7 \\ 1 & -1 & -1 \\ 1 & -1 & 3/2 \end{pmatrix} \begin{pmatrix} x_{2,1} \\ x_{2,2} \\ x_{2,3} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

Next, subtracting row 1 from row 2 and row 3:

$$\begin{pmatrix} 1 & -1 & 3/7 \\ 0 & 0 & -10/7 \\ 0 & 0 & 15/14 \end{pmatrix} \begin{pmatrix} x_{2,1} \\ x_{2,2} \\ x_{2,3} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

The second and third equations each imply that $x_{2,3} = 0$. Substituting this into the first equation shows that $x_{2,1} = x_{2,2}$. Choosing $x_{2,1} = 1$, we have

$$\underline{x}_2 = \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}$$

Finally, the third eigenvector, corresponding to $\lambda_1 = 3$ is obtained from $(\underline{A} - 3\underline{I})\underline{x}_1 = \underline{0}$:

$$\underline{A} - 3\underline{I} = \begin{pmatrix} -3/2 & -7/2 & 3/2 \\ -3/2 & -7/2 & 3/2 \\ 2 & -2 & -2 \end{pmatrix} \begin{pmatrix} x_{3,1} \\ x_{3,2} \\ x_{3,3} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

Swapping the 2nd and third rows, then subtracting the first row from the third (formerly second) row, then scaling to make the first element of each row 1 gives:

$$\begin{pmatrix} 1 & 7/3 & -1 \\ 1 & -1 & -1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x_{3,1} \\ x_{3,2} \\ x_{3,3} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

Subtracting the first row from the second then gives

$$\begin{pmatrix} 1 & 7/3 & -1 \\ 0 & -10/3 & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} x_{3,1} \\ x_{3,2} \\ x_{3,3} \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

From this we see that $x_{3,2} = 0$ and then $x_{3,1} = x_{3,3}$. Choosing $x_{3,1} = 1$ gives

$$\underline{x}_3 = \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix}$$

Thus, the matrix of eigenvectors is:

$$\underline{T} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 0 \\ 2 & 0 & 1 \end{pmatrix}$$

We can find the inverse of this matrix by carrying out row operations as follows:

Start from augmented matrix:
$$\left(\begin{array}{ccc|ccc} 1 & 1 & 1 & 1 & 0 & 0 \\ 1 & 1 & 0 & 0 & 1 & 0 \\ 2 & 0 & 1 & 0 & 0 & 1 \end{array} \right)$$

Subtract row 1 from row 2 and subtract twice row 1 from row 3:

$$\left(\begin{array}{ccc|ccc} 1 & 1 & 1 & 1 & 0 & 0 \\ 0 & 0 & -1 & -1 & 1 & 0 \\ 0 & -2 & -1 & -2 & 0 & 1 \end{array} \right)$$

Swap rows 2 and 3, then divide them by -1 and -2, respectively

$$\left(\begin{array}{ccc|ccc} 1 & 1 & 1 & 1 & 0 & 0 \\ 0 & 1 & 1/2 & 1 & 0 & -1/2 \\ 0 & 0 & 1 & 1 & -1 & 0 \end{array} \right)$$

Subtract row 3 from row 1, and subtract $1/2$ row 3 from row 2:

$$\left(\begin{array}{ccc|ccc} 1 & 1 & 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 1/2 & 1/2 & -1/2 \\ 0 & 0 & 1 & 1 & -1 & 0 \end{array} \right)$$

Finally, subtract row 2 from row 1:

$$\left(\begin{array}{ccc|ccc} 1 & 0 & 0 & -1/2 & 1/2 & 1/2 \\ 0 & 1 & 0 & 1/2 & 1/2 & -1/2 \\ 0 & 0 & 1 & 1 & -1 & 0 \end{array} \right)$$

Finally, we obtain:

$$\underline{T}^{-1} = \begin{pmatrix} -1/2 & 1/2 & 1/2 \\ 1/2 & 1/2 & -1/2 \\ 1 & -1 & 0 \end{pmatrix}$$

Using this, we can construct the solution as:

$$\underline{x} = \underline{T} \exp(\underline{\Lambda}t) \underline{T}^{-1} \underline{u}$$

$$\underline{x} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 0 \\ 2 & 0 & 1 \end{pmatrix} \begin{pmatrix} \exp(t) & 0 & 0 \\ 0 & \exp(-2t) & 0 \\ 0 & 0 & \exp(3t) \end{pmatrix} \begin{pmatrix} -1/2 & 1/2 & 1/2 \\ 1/2 & 1/2 & -1/2 \\ 1 & -1 & 0 \end{pmatrix} \begin{pmatrix} 1 \\ 2 \\ 0 \end{pmatrix}$$

$$\underline{x} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 0 \\ 2 & 0 & 1 \end{pmatrix} \begin{pmatrix} \exp(t) & 0 & 0 \\ 0 & \exp(-2t) & 0 \\ 0 & 0 & \exp(3t) \end{pmatrix} \begin{pmatrix} 1/2 \\ 3/2 \\ -1 \end{pmatrix}$$

$$\underline{x} = \begin{pmatrix} 1 & 1 & 1 \\ 1 & 1 & 0 \\ 2 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1/2 \exp(t) \\ 3/2 \exp(-2t) \\ -\exp(3t) \end{pmatrix} = \begin{pmatrix} 1/2 \exp(t) + 3/2 \exp(-2t) - \exp(3t) \\ 1/2 \exp(t) + 3/2 \exp(-2t) \\ \exp(t) - \exp(3t) \end{pmatrix}$$

We also would not expect this ODE to represent a set of chemical reactions, because two of the eigenvalues are positive. This means that those solution components (the e^t and e^{3t} terms) grow without bound. We expect problems arising from a network of chemical reactions to have all negative (or zero) eigenvalues so that all terms approach zero (or a constant) at long times.