1. (15 points) *Method of initial rates.* I am studying the reaction $2A + B \rightarrow A_2B$. In the course of my studies I obtain the following data:

<table>
<thead>
<tr>
<th>[A]₀ (M)</th>
<th>[B]₀ (M)</th>
<th>Rate (mol/L·min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>.06</td>
<td>.06</td>
<td>.000123</td>
</tr>
<tr>
<td>.06</td>
<td>.10</td>
<td>.000251</td>
</tr>
<tr>
<td>.10</td>
<td>.10</td>
<td>.000697</td>
</tr>
</tbody>
</table>

What are the order parameters for A and B in this reaction?

\[
\frac{.000251}{.000123} = \frac{k[A_2]^x[B_2]^y}{k[A_1]^x[B_1]^y} = \frac{.1^y}{.06^y} = \left(\frac{.1}{.06}\right)^y
\]

\[2.04 = 1.67^y; \ln(2.04) = y \ln(1.67)\]
\[.713 = y, .513\]
\[y = .713/.513 = 1.39\]

\[
\frac{.000697}{.000251} = \frac{k[A_2]^x[B_2]^{1.39}}{k[A_2]^x[B_2]^{1.39}} = \frac{.1^y}{.06^x} = \left(\frac{.1}{.06}\right)^x
\]

\[2.78 = 1.67^x; \ln(2.78) = x \ln(1.67)\]
\[1.02 = x, .513\]
\[x = 1.02/ .513 = 1.99 = 2\]

What is the rate constant for this reaction?

\[
.000697 = k(.1)^2(.1)^{1.39}
\]
\[
.000697/[(.1)^2(.1)^{1.39}] = k
\]
\[k = .000697/.0004074 = 1.71\]

Write the rate law for this reaction?

\[
\text{Rate} = 1.71 [A]^2[B]^{1.39}
\]
2. (15 points) Integral rate laws. I am studying the reaction $C + D \rightarrow E$
When the concentration of $D$ is 1.0 M and the concentration of $C$ is .01 M I get the following
plots for the disappearance of $C$.

A. Is this a 0, 1st, or 2nd order reaction?
Graph of $1/X$ vs time is linear so this is second order

B. What is the $k$ of this reaction

$$k = \text{slope} = \frac{\Delta y}{\Delta x} = \frac{195 - 100}{60 - 0} = 1.58$$

C. What is the half-life of this reaction when $[C]$ is .008

$$t_{1/2} = \frac{1}{k[A_0]} = \frac{1}{(1.58 \times .008)} = 79.1 \text{ min}$$

D. In this experiment the concentration of $D$ was 100X larger than $C$. Is there some reason
for doing the experiment in this manner?

By keeping the concentration of $D$ high compared to $C$, you can assume that the
concentration of $D$ doesn’t change during the reaction, so you can find the order of the
reaction with respect to $C$ without worrying about $D$. The rate you get from this analysis is
called a pseudo rate constant, because it has the $D$ concentration incorporated into it as a constant.
3. (10 points) The activation energy for the reaction
\[ \text{NO}_2(g) + \text{CO}(g) \rightarrow \text{NO}(g) + \text{CO}_2(g) \]
is 125 kJ/mol, and the \( \Delta E \) for the reaction is -216 kJ/mol. What is the activation energy for the reverse reaction? Will the reverse reaction be slower or faster than the forward reaction?

If you think about the reaction diagram, you have to go ‘up’ by the 125 kJ of activation \( E \) to get the reaction started. Once the reaction goes, you get -216 kJ of \( E \) out of the reaction as reactants go to products. In the reverse reaction we have to add +216 kJ of \( E \) to get from products to reactants, and then another 125 to get over the activation hump. So you need a total of 125+216, or 341 kJ or \( E \) to go in the reverse direction.

A higher activation energy means that you will have a slower rate.

4. (10 points) Why is the rate of a reaction affected by each of the following

a. Frequency of collisions
Molecules must collide for a reaction to occur, so the more often you have a collision, the more likely you are to have a reaction.

b. Kinetic energy of collisions
Not all collisions result in a reaction. The molecules must collide with enough energy to have a reaction occur. This minimum energy is called the activation energy and is sometimes associated with breaking the bonds that already exist in the molecule.

c. Orientation of collisions
Even when a collision has enough energy it may not react because the molecules are colliding in the wrong orientation, that is, the proper atoms may not be facing each other when the collision occurs.

d. Temperature
As the temperature rises, molecules move faster, and this gives them increased kinetic energy. Thus by increasing the temperature you increase both the number of collisions that occur and the energy of the collision, so you increase both factor a and b above.
5. (10 points) Write an equilibrium expression for each of the following reactions:

\[
2\text{CO}(g) + \text{O}_2(g) \rightleftharpoons 2\text{CO}_2(g)
\]

\[
K = \frac{[\text{CO}_2]^2}{[\text{CO}]^2[\text{O}_2]}
\]

\[
5 \text{Fe}^{2+}(\text{aq}) + \text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) \rightleftharpoons 5 \text{Fe}^{3+}(\text{aq}) + \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\ell)
\]

\[
K = \frac{[\text{Fe}^{3+}][\text{Mn}^{2+}]}{[\text{Fe}^{2+}][\text{MnO}_4^-][\text{H}^+]^8}
\]

\[
\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq})
\]

\[
K = [\text{Ag}^+][\text{Cl}^-]
\]

6. (10 points) At 200K, \(K_{\text{concentration}} = 1.3 \times 10^{-2}\) for the reaction

\[
\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)
\]

Calculate \(K\) for the following reactions at this temperature

a. \(2 \text{ N}_2(g) + 6\text{H}_2(g) \rightleftharpoons 4\text{NH}_3(g)\)

\[
2 \text{N}_2(g) + 6\text{H}_2(g) \rightleftharpoons 4\text{NH}_3(g) = 2 \times (\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g))
\]

So \(K = (K_{\text{org}})^2\)

\[
= (1.3 \times 10^{-2})^2
\]

\[
= 1.69 \times 10^{-4}
\]

b. \(\text{NH}_3(g) \rightleftharpoons \frac{1}{2} \text{N}_2(g) + 3/2 \text{H}_2(g)\)

\[
\text{NH}_3(g) \rightleftharpoons \frac{1}{2} \text{N}_2(g) + 3/2 \text{H}_2(g) = \frac{1}{2}(\text{reverse reaction})
\]

So \(K = (1/K_{\text{org}})^{1/2}\)

\[
= (1/1.3 \times 10^{-2})^{1/2}
\]

\[
= 8.77
\]

c. \(\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)\) (Give \(K\) in terms of partial pressures of gases)

\[
\Delta n = 2-4 = -2
\]

\[
K_p = K_c(RT)^{\Delta n}
\]

\[
= 1.3 \times 10^{-2} \times (0.08206 \times 200)^{-2}
\]

\[
= 4.83 \times 10^{-5}
\]
7. (15 points) I am going to mix 33.3 mls of .00005M H\(^+\) with 33.3 mls of 0.1M CH\(_3\)COO\(^-\), and 33.3 mls of 0.1 M CH\(_3\)COOH

A. What are the concentrations of the three species before any additional chemical equilibria take place?

\[
\begin{align*}
M_1V_1 &= M_2V_2; M_1V_1/V_2 &= M_2 \\
[H^+] &= 33.3(0.00005)/99.9 = 1.67\times10^{-5} M \\
[CH_3COO^-] &= 33.3(0.1)/99.9 = 0.033 M \\
[CH_3COOH] &= 33.3(0.1)/99.9 = 0.033 M
\end{align*}
\]

B. These three ions are involved in the following equilibrium:

\[
\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}^+ \quad K_{eq} = 1.8\times10^{-5}
\]

Is this a favorable reaction?

(No calculation - Does \(K\) favor reactants or products)

\(K << 1\)

\(K\) strongly favors reactants

This is an unfavorable reaction

C. Under the conditions specified here, will the reaction move to the right, the left, or is it already at equilibrium?

\[
Q = (1.67\times10^{-5})(0.033)/0.033 = 1.67\times10^{-5}
\]

\(Q\) slightly < \(K\)

Need a few more products

Reaction will move to right slightly

D. If it is not at equilibrium, can you set up an equation that you can use to find the concentrations at equilibrium? (Do not try to solve this equation - yet)

\[
1.8 \times 10^{-5} = \frac{(1.67 \times 10^{-5} + X)(0.033 + X)}{(0.033 - X)}
\]

8. (15 points) Will the number of moles of SO\(_3\) in equilibrium with SO\(_2\) and O\(_2\) in the below reaction increase, decrease, or remain constant under the following conditions?

\[
2\text{SO}_3(g) \rightleftharpoons 2\text{SO}_2(g) + \text{O}_2(g) \quad \Delta H^o = +197 \text{ kJ}
\]

a. Oxygen is added

\(\text{Moves to left, SO}_3\ \text{increases}\)

b. The pressure in increased by decreasing the volume of the container

\(\text{Smaller volume favors left side SO}_3\ \text{increases}\)

c. The pressure in increased by adding Ar gas

\(\text{Remains constant}\)

d. The temperature is increased

\(\text{Endothermic, Think of heat as a reactant, moves to right, SO}_3\ \text{decreases}\)

e. Gaseous sulfur dioxide is removed

\(\text{Moves right, SO}_3\ \text{decreases}\)
9. (5 BONUS POINTS) Solve problem 7C

\[ 1.8 \times 10^{-5} = \frac{(1.67 \times 10^{-5} + X)(0.033 + X)}{(0.033 - X)} \]

Quick and dirty

K is small so X is going to be small

Let's guess that \(0.033 + \text{ or } - X\) is not going to change

but \(0.0000167 + X\) will change because we are starting with a small number

In this case

\[ 1.8 \times 10^{-5} = (1.67 \times 10^{-5} + X)(0.033) / 0.033 \]

\[ 1.8 \times 10^{-5} = 1.67 \times 10^{-5} + X \]

\[ X = (1.8 - 1.67) \times 10^{-5} \]

\[ X = 0.13 \times 10^{-5} \]

\[ [H^+] = 1.8 \times 10^{-5}; \quad [\text{CH}_3\text{COO}^-] = 0.033 + 0.0000013 - 0.033; \quad [\text{CH}_3\text{COO}^-] = 0.033 - 0.0000013 - 0.033 \]

The long way

\[ 1.8 \times 10^{-5} = \frac{(1.67 \times 10^{-5} + X)(0.033 + X)}{(0.033 - X)} \]

\[ 5.94 \times 10^{-7} - 18 \times 10^{-5} X = 5.51 \times 10^{-7} + 0.0330167 X + X^2 \]

\[ X^2 + 0.0330167 X + 18 \times 10^{-5} X + 5.51 \times 10^{-7} - 5.94 \times 10^{-7} = X^2 + 0.03303 X - 4.3 \times 10^{-8} \]

\[ \text{quadratic} \quad \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \]

\[ = 0.03303 \pm \sqrt{(0.03303)^2 + 4(1)4.3 \times 10^{-8}} \]

\[ = 0.03303 \pm 0.00109098 + 0.00000172 \]

\[ = 0.03303 \pm 0.00109098 \]

\[ = 0.03303 \pm 0.033026 \]

\[ = -0.033 \quad \text{discard} \]

\[ + 1.3 \times 10^{-6} \]

Same answer!