1. Circle the correct answer (42 8 pts total) (2 points each)

(a) The rate constant for a reaction will change if:

- i) a catalyst is added
- ii) the concentration of reactants is increased
- iii) $T$ is lowered
- iv) all of the above
- v) (i) and (iii) only

(b) A system at equilibrium will shift from its equilibrium position if:

- i) a catalyst is added
- ii) the concentration of reactants is increased
- iii) $T$ is lowered
- iv) all of the above
- v) (ii) and (iii) only

(c) For the elementary reaction represented by $A \rightarrow B$, one can determine the rate of reaction when a specific concentration of $A$ is present by:

- i) measuring the slope of a plot of $[A]$ vs. time at the appropriate place.
- ii) using the rate law, if the rate constant is known.
- iii) measuring the time it takes for a certain (small) amount of $A$ to disappear.
- iv) all of the above.
- v) (ii) and (iii) only

(f) Given the equation $AB(s) \rightarrow A^+(aq) + B^-(aq)$, if the beaker to the right represents a system in which $Q < K$, which picture best represents what the system might look like after some time passes?

- Q < K means that $Q$ must get bigger to equal $K$, so since products are in numerator, forward reaction occurring makes $Q$ bigger. So here, ions are made.

2. Write T (True) or F (False) for the following statements. If the statement is false correct it by changing, dropping, or adding a few words (8 points in total; 2 points each)

a) The half life for a first order reaction becomes one half of its original value REMAINS CONSTANT during the course of a reaction.

**F.** (The half life remains constant during a 1st order process. It’s the concentration that becomes half its value (not the half life itself)).
b) One can write an expression for the equilibrium constant for any reaction whose balanced chemical equation is known, but one cannot always write the rate law.

T. (you need experiments to determine the orders, [unless it is an elementary step])

c) The mechanism of a reaction is the series of elementary or non-elementary steps that occur as the reactants are turned into products.

F. (must be ELEMENTARY steps only)

d) When a system comes to equilibrium, no more reaction occurs in the forward or reverse directions at equal rates

F.

Free Response Questions

3. (8 pts) Consider the elementary process $A \rightarrow B$, for which the half-life is 10.8 yr. If you have a solution in which $[A] = 0.670 \text{ M}$, what will the concentration be after 16.0 yrs?

REMEMBER THAT FOR A FIRST ORDER PROCESS, THE HALF-LIFE AND $k$ ARE RELATED BY THE EQUATION $t_{1/2} = \frac{0.693}{k}$, which can be derived easily (see answer in key to PS2) from the more general equation: $\frac{[\text{reactant}]_t}{[\text{reactant}]_0} = e^{-kt}$ which you will need for the "main" part of this question.

So in this problem, first recognize that you could use the second equation above to solve for the $[A]$ at time = 16.0 years, if only you had the value of $k$ (since the $[A]_0$ is given in this problem). So use the first equation to solve for $k$ from the half life, and then use the second equation to get the final answer:

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10.8 \text{ yr}} = 0.0642 \text{ yr}^{-1};$$

$$\frac{[A]_{16.0 \text{ yr}}}{0.670 \text{ M}} = e^{-0.0642 \text{ yr}^{-1} \cdot 16.0 \text{ yr}} \rightarrow [A]_{16.0 \text{ yr}} = (0.670 \text{ M})e^{-1.027} = 0.240 \text{ M}$$

(Answer makes sense; should be a little less than half of 0.670 M because 16.0 years is a little bit longer than the half life (10.8 years).)

4. (21 pts) Consider the following equation:

$$\text{CCl}_4(g) \rightleftharpoons \text{C(s)} + 2 \text{Cl}_2(g)$$

for which $K_c = 0.013$ at 427 °C.

(a) (4 pts) Write the equilibrium constant expression.

$$K_c = \frac{[\text{Cl}_2]_e^2}{[\text{CCl}_4]_e}$$
(b) (5 pts) If some CCl$_4$ is put into a sealed container at 427 °C., do you expect that the majority of it will be converted into products before equilibrium is established? Explain briefly.

NO. The value of $K$ is less than 1, so the reaction is “reactant favored”, meaning at equilibrium, there will be more reactants than products (so a majority would not have reacted to form products)

(c) (4 pts) If a system containing CCl$_4$(g), C(s), and Cl$_2$(g) were at equilibrium and the volume of the container were doubled, would the system shift, and if so, in which direction would net reaction occur? Explain briefly.  

FORWARD REACTION OCCURS

If V is increased, the total pressure would go down. So reaction would occur (system would shift), to make the pressure bigger again. So FORWARD reaction occurs since two moles of gas (Cl$_2$) will be made for every one mole of gas reacted (CCl$_4$). (Look at coefficients.)

(d) (6 pts) If 3.2 moles of CCl$_4$ is put into a 1.0 L container at 427 °C, set up a mathematical equation that would allow you to determine the concentrations at equilibrium. Solve this in the NEXT part.

Let $x$ = [CCl$_4$] that reacts for system to reach equil.  (Because its coefficient is 1; makes the algebra a bit simpler.)

\[
\begin{array}{c|c|c}
\text{Initial} & \text{CCl}_4 \text{ (M)} & \text{Cl}_2 \text{ (M)} \\
\hline
\text{Change} & -x & +2x \\
\hline
\text{Equilibrium} & 3.2 - x & 2x \\
\end{array}
\]

$\frac{[\text{NO}_2]^2_{\text{eq}}}{[\text{N}_2\text{O}_4]_{\text{eq}}} \Rightarrow 0.013 = \frac{(2x)^2}{(3.2 - x)}$ (sufficient answer for part d)

(e) (2 pts) Use your equation in (d) to solve for the concentrations of Cl$_2$ and CCl$_4$ at equilibrium. Comment on whether or not your answers are consistent with your prediction in (b). (NOTE: This part is only worth 2 points, so you might consider doing this after you have finished the rest of the exam.)

Simplifying yields:  $4x^2 + 0.013x - 0.0416 = 0$

Using quadratic equation yields:  $x = 0.100$ (positive root)

$[\text{CCl}_4]_{\text{eq}} = 3.2 \text{ M} - 0.10 \text{ M} = 3.1 \text{ M} = 3.1 \text{ M}$

$[\text{Cl}_2]_{\text{eq}} = 2(0.10) = 0.20 \text{ M} = 0.20 \text{ M}$

Note: One could also use the "x is small" approximation here. Although $K$ is not that small, it works here because 3.2 is so large. $x$ (which equals 0.102 here) is about 3% of 3.2.

Note also that this result is consistent with the answer to part b—only about 3% of the CCl$_4$ was converted to products!
8. (6 pts) \( K_c = 4.1 \) at 300°C for the following equation:

\[
\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow \text{PCl}_5(\text{g})
\]

If a 2.0 L box at 300°C were filled with 2.1 moles of \( \text{PCl}_3 \), 1.3 moles of \( \text{Cl}_2 \), and 7.2 moles of \( \text{PCl}_5 \), would any net reaction occur in the forward or reverse direction? Justify your answer.

\[ [\text{PCl}_3] = \frac{2.1 \text{ moles}}{2.0 \text{ L}} = 1.05 \text{ M}; [\text{Cl}_2] = \frac{1.3 \text{ mol}}{2.0 \text{ L}} = 0.65 \text{ M}; [\text{PCl}_5] = \frac{7.2 \text{ mol}}{2.0 \text{ L}} = 3.6 \text{ M} \]

\[ Q = \frac{3.6}{(1.05)(0.65)} = 5.27 > (= 4.1) \]

Since \( Q > K \), there are too many products (compared to reactants) for the system to be at equilibrium. So some (net) REVERSE reaction will occur to reach equilibrium (\( Q \) will decrease as [products] decreases).

9. (9 pts) The observed rate law for the decomposition of ozone into oxygen is rather odd (see below; please don’t let it bother you!). Two possible mechanisms are shown below.

Overall Equation: \( 2 \text{O}_3(\text{g}) \rightarrow 3 \text{O}_2(\text{g}) \)

Observed Rate Law: \( \text{Rate} = k \frac{[\text{O}_3]^2}{[\text{O}_2]} = k[\text{O}_3]^2[\text{O}_2]^{-1} \)

<table>
<thead>
<tr>
<th>Proposal #1</th>
<th>Proposal #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_3 \rightarrow \text{O}_2 + \text{O} ) (slow)</td>
<td>( \text{O}<em>3 \xrightleftharpoons{\kappa_1}{\kappa</em>{-1}} \text{O}_2 + \text{O} ) (fast, equilibrium)</td>
</tr>
<tr>
<td>( \text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 ) (fast)</td>
<td>( \text{O} + \text{O}_3 \rightarrow \text{O}_2 + \text{O}_2 ) (slow)</td>
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Is one mechanism a better candidate than the other for representing what actually happens when this reaction occurs? Back up your answer with some work!

The rate law for Proposed Mechanism 1 is simply \( \text{Rate} = k_1[\text{O}_3] \) (the rate law for the slow step). This rate law does not match the observed rate law since the order of \( \text{O}_3 \) there is 2, not 1. So this mechanism CAN’T be the one that is actually occurring (inconsistent with experiment).

The rate law for Proposed Mechanism 2 is: \( \text{Rate(overall)} = \text{Rate(slow)} = k_2[\text{O}][\text{O}_3] \), which does not appear to match the observed rate law, but that is inconclusive since there is an intermediate’s concentration in the rate law ([O]). Use the equilibrium approximation for step 1 to find [O]:

\[
\text{Rate}_1 = \text{Rate}_r, \text{ (step 1)} \Rightarrow k_1[\text{O}_3] = k_r[\text{O}_2][\text{O}] \Rightarrow [\text{O}] = \frac{k_1[\text{O}_3]}{k_r[\text{O}_2]} \]

\[
\text{Rate} = k_2[\text{O}][\text{O}_3] = k_2 \left( \frac{k_1[\text{O}_3]}{k_r[\text{O}_2]} \right)[\text{O}_3] = \frac{k_2k_1}{k_r} \frac{[\text{O}_3]^2}{[\text{O}_2]} = k' \frac{[\text{O}_3]^2}{[\text{O}_2]}, \text{ which IS consistent with the observed rate law.}
\]

So Proposal 2 is a better candidate.
10. (10 pts) (a) Which reaction (forward or reverse) has the greater activation energy?

(b) Draw a "reaction progress" diagram to the right that is qualitatively consistent with (not quantitatively!) the figure on the left. Ask me if you are not sure what I mean here.

(c) Is the reaction endothermic or exothermic?

Without memorization, you can just sketch out two PE diagrams, one for an endothermic reaction and one for an exothermic reaction. You will see that it must be the case that in an endothermic reaction, the forward reaction's activation energy is greater than the reverse's ($E_{a,f} > E_{a,r}$) [because you start lower in energy but you have to go up to the same energy (of the transition state)] and for an exothermic reaction, it is the other way around. I've labeled the $E_a$'s on the diagram up to the right to show this, even though that was not required for the problem.

(d) If $T$ is increased in this case, what, if anything, happens to $K$, and which direction (if any) would a system at equilibrium shift if $T$ were raised? **$K$ gets SMALLER; system shifts LEFT**

**Le Chatelier type argument:**
An increase in $T$ ("adding of energy") will cause a system at equilibrium to shift in the direction which will absorb the added energy—i.e., in the direction of the endothermic reaction. Since this particular reaction is exothermic, then the system will shift in the reverse direction when $T$ increases. This means that the $K$ value must have decreased, because a decrease in $K$ means that reaction has a lesser tendency to occur in the forward direction [or a greater tendency to occur in the reverse direction] (starting from the same initial concentrations). In other words, since the shift occurred to the left as a result of the $T$ increase (not any initial concentration changes!), $K$ must have gotten smaller.

**Kinetic type argument:**
When $T$ is increased, the reaction that has the greater activation energy barrier will be more affected by this $T$ increase. That is, it's $k$ value will be increased by a greater factor than the $k$ for the reaction with the smaller activation energy. (Because a smaller fraction of particles had the energy to get over initially—it needs "more help" than the reaction with the smaller $E_a$; look at the KE distribution curves in this problem to see that the % increase in area to the right of $E_{a,f}$ is greater than that to the right of $E_{a,r}$ when $T$ increases!) Since the reverse direction here has the greater $E_a$, the system will shift left. Since $K=k_f/k_r$, if $k_r$ increases by a greater factor than $k_f$, $K$ must get smaller.