Circle the correct answers  (2 points each)

1. If the half-life of a reaction depends on the concentration of the reactant, then the reaction cannot be _____ order.
   a. second  b. zero  c. first  d. third  e. none of the above

2. Choose the INCORRECT statement. The rate of a chemical reaction:
   a. usually is increased when the concentration of one of the reactants is increased
   b. is dependent on temperature
   c. may be inhibited sometimes by certain catalytic agents
   d. will be very rapid when the activation energy is large
   e. none of the above

3. Choose the INCORRECT statement:
   a. a certain amount of energy, called the activation energy, must be available if a reaction is to take place
   b. a reversible chemical reaction is one in which equilibrium is never established due to the constant decomposition of the products
   c. when the rate of the reverse reaction equals the rate of a forward reaction, equilibrium has been established
   d. changes in temperature will change the value of an equilibrium constant
   e. all of the above are correct

4. All of the following may shift the position of a reaction at equilibrium EXCEPT:
   a. temperature decrease
   b. concentration change
   c. homogeneous catalyst
   d. pressure change
   e. none of the above

5. The equilibrium constant, K_c or K_p, is constant EXCEPT when one varies the:
   a. reactant concentration
   b. reaction temperature
   c. product concentration
   d. partial pressures of reactants
   e. none of the above

6. Which of the following substances present in a chemical reaction would NOT appear in the equilibrium expression?
   a. NaCl{(s)}
   b. H_2O{(l)}
   c. NH_4Cl{(s)}
   d. solvents
   e. all of these

(10 points)
7. A chemical reaction has a rate constant of 2.00 x 10^{-9} min^{-1} at 369 K and 3.50 x 10^{-5} min^{-1} at 448 K. What is the value of the activation energy for the reaction in kJ/mol?
   (R = 8.314 J/Kmol)

\[
\ln \frac{k_1}{k_2} = \frac{E_a}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right)
\]

solve for E_a to find 170 kJ (1.70x10^{-5} J)
Fill in the blank with the correct answers (2 points each blank)

8. The three factors that in collision theory that determine the rate of a reaction are:
   a. collision frequency  
   b. activation energy  
   c. steric factor

9. (6 points)
   Consider the accompanying potential energy diagram, label the arrow which indicates the activation energy for the forward reaction, label the arrow that indicates the enthalpy change for the reaction, and sketch a curve that represents the effect of a catalyst on the reaction profile.

(3 points)
10. Refer once again to the figure in number 10. If $E_{a\,\text{forward}} = 90 \text{ kJ}$ and $E_{a\,\text{reverse}} = 30 \text{ kJ}$, what is the enthalpy change, $\Delta H$, of the reaction in the forward direction? $\Delta H = 90 \text{ kJ} - 30 \text{ kJ} = +60 \text{ kJ}$

(9 points)
11. For the gas phase reaction $2 \text{ NO} + \text{ O}_2 \rightarrow 2 \text{ NO}_2$, initial rate data are given below.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>[NO] (M)</th>
<th>[O$_2$] (M)</th>
<th>Rate (M/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.010</td>
<td>0.010</td>
<td>2.5 x 10^{-3}</td>
</tr>
<tr>
<td>2</td>
<td>0.010</td>
<td>0.020</td>
<td>5.0 x 10^{-3}</td>
</tr>
<tr>
<td>3</td>
<td>0.030</td>
<td>0.020</td>
<td>4.5 x 10^{-2}</td>
</tr>
</tbody>
</table>

(a) What is the rate law (rate equation) for this reaction (you may skip the calculation of the numerical value of $k$)? SHOW YOUR REASONING!
   From Expt. 1 to 2 [O$_2$] doubles and the rate of the reaction also doubles: therefore 1$^{st}$ order in O$_2$
   From Expt. 2 to 3 [NO] triples and the rate of the reaction increases 9x: therefore 2$^{nd}$ order in NO
   \[ \text{Rate} = k \, [\text{O}_2] \, [\text{NO}]^2 \]

(b) Is this rate law consistent with the reaction being a single step termolecular collision reaction? Briefly explain.
   YES: A single termolecular reaction (i.e. the reaction written above) would have a predicted rate law that matches the experimentally determined rate law. Despite the fact that termolecular processes are less probable does NOT mean the reaction CANNOT occur in that manner.
12. For the reaction \( A \rightarrow \) products, the following data are obtained. (16 points)

<table>
<thead>
<tr>
<th>Experiment 1</th>
<th>Experiment 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>[A], M</td>
<td>[A], M</td>
</tr>
<tr>
<td>time, minutes</td>
<td>time, minutes</td>
</tr>
<tr>
<td>1.512</td>
<td>3.024</td>
</tr>
<tr>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1.490</td>
<td>2.935</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>1.469</td>
<td>2.852</td>
</tr>
<tr>
<td>2.0</td>
<td>2.0</td>
</tr>
</tbody>
</table>

(a) Determine the AVERAGE INITIAL rate of reaction for each experiment.

Expt. (1) Rate = \( \frac{-\Delta[A]}{\Delta t} = \frac{(1.490 \text{ M} - 1.512 \text{ M})}{(1.0 \text{ min} - 0.0 \text{ min})} = 0.022 \text{ M/min} \)

Expt. (2) Rate = \( \frac{-\Delta[A]}{\Delta t} = \frac{(2.935 \text{ M} - 3.024 \text{ M})}{(1.0 \text{ min} - 0.0 \text{ min})} = 0.089 \text{ M/min} \)

(b) Determine the order of the reaction and write the rate law (including \( k \)).

In ext. (1) the starting concentration of “A”, [A]_{init}, is 1.512 M and this doubles to 3.024 M for expt. (2). The initial rate that results from this doubling of concentration is FOUR times higher. Thus, the reaction is 2\(^{nd}\) order in “A”.

Rate = \( k[A]^2 \)

We can find \( k \) for both expts (I have chosen to use the average [A] during minute one of the reaction).

Expt (1) \( k = \frac{0.022 \text{ M/min}}{(-1.50 \text{ M})^2} = 9.8 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1} \)

Expt (2) \( k = \frac{0.089 \text{ M/min}}{(-2.98 \text{ M})^2} = 1.0 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1} \)

Average \( k = 9.9 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1} \)

(c) For the first experiment, find what the concentration of A will be after 12.5 minutes.

Using the average value of \( k \) and the integrated rate law for a 2\(^{nd}\) order reaction, we find.

\[
\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} = \left(9.9 \times 10^{-3} \text{ M}^{-1} \text{ min}^{-1}\right)(12.5 \text{ min}) + \frac{1}{1.512M}
\]

Solving we find: \( [A] = 1.274 \text{ M} \)

13. The following reaction is one of the steps in the production of sulfuric acid:

\[ 2 \text{ SO}_2 (g) + \text{ O}_2 (g) \rightleftharpoons 2 \text{ SO}_3 (g) \quad \Delta H = -198 \text{ kJ} \]

(a) Predict whether the forward or reverse reaction will occur when the equilibrium of the reaction is disturbed by . . .

1. adding \( \text{SO}_3 \) gas \( \text{reaction proceeds in reverse direction (toward left)} \)
2. expanding the system at constant temperature \( \text{REVERSE reaction occurs (toward left)} \)
3. adding argon gas \( \text{no effect whatsoever} \)
4. adding \( \text{SO}_2 \) gas \( \text{forward reaction occurs (toward right)} \)
5. increasing the temperature \( \text{reaction proceeds in reverse direction (toward left)} \)

(b) Which, if any, of the above changes will alter the value of K? AND Will K become larger or smaller? The change in (5) will alter the numerical value of K. K will get SMALLER because the forward direction is EXOthermic (note the negative \( \Delta H \)).
14. For the reaction \(2 \text{A} (\text{g}) \rightleftharpoons \text{B} (\text{g}) + \text{C} (\text{g})\), \(K_c = 1.25\) at 300 K.

(a) If a 1.00 L mixture contains 0.319 mole A, 0.689 mole B, and 0.689 mole C at 300 K, will the reaction mixture be in equilibrium?

The reaction vessel is 1.00 L so the molarities are easily found (see below). Find \(Q\) compare to \(K\).

\[
Q = \frac{[B][C]}{[A]^2} = \frac{[0.689][0.689]}{[0.319]^2} = 4.665 > K
\]

The reaction is NOT at equilibrium.

(b) If not, in what direction will a net reaction occur? Explain!

\(Q > K\) The reaction has too much product (relative to reactant). Reverse reaction is indicated.

(c) Finally, what number of moles of each substance will be present at equilibrium. Use an ICE table and solve.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>2 A (g)</th>
<th>B (g)</th>
<th>+</th>
<th>C (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial, I</td>
<td>0.319 M</td>
<td>0.689 M</td>
<td></td>
<td>0.689 M</td>
</tr>
<tr>
<td>Change, C</td>
<td>+2x</td>
<td></td>
<td>-x</td>
<td></td>
</tr>
<tr>
<td>Equil., E</td>
<td>0.319+2x</td>
<td>0.689-x</td>
<td></td>
<td>0.689-x</td>
</tr>
</tbody>
</table>

\[
1.25 = \frac{[B][C]}{[A]^2} = \frac{[0.689 - x][0.689 - x]}{[0.319 + 2x]^2} = \frac{[0.689 - x]^2}{[0.319 + 2x]^2}
\]

Take square root, solve:

\[
x = 0.103\ M
\]

See table for equil. conc.

CHECK: verify that \(Q = K\) using the equilibrium concentrations. \(Q = 1.246 = K\) (GOOD)

22. For the gas phase decomposition of SO3 at 300 K, \(2 \text{SO}_3 (\text{g}) \rightleftharpoons 2 \text{SO}_2 (\text{g}) + \text{O}_2 (\text{g})\). The equilibrium concentrations are found to be:

\([\text{SO}_3] = 4.00 \times 10^{-3}\quad [\text{SO}_2] = 3.60 \times 10^{-3}\quad [\text{O}_2] = 4.40 \times 10^{-3}\)

Calculate \(K_c\) and \(K_p\) for this reaction.

\(R = 0.08206 \text{ LatmK}^{-1}\text{mole}^{-1}\)

\[
K_c = \frac{[\text{SO}_2]^2[\text{O}_2]}{[\text{SO}_3]^2} = \frac{[3.60 \times 10^{-3}]^2[4.40 \times 10^{-3}]}{[4.00 \times 10^{-3}]^2} = 3.564 \times 10^{-3}
\]

\[
K_p = K_c (RT)^{\Delta n_g} = 3.564 \times 10^{-3} \left[\left(0.0821 \text{L atm}^{-1} \text{mol}^{-1}\right)(300K)\right]^{1} = 8.778 \times 10^{-2}
\]

with \(\Delta n_g = 3 - 2 = 1\)
Consider the energy diagrams below, and answer the questions that follow.

Reaction a.

Reaction b.

(5 points, 1 point per question)

**Rxn. (b)** a. Which reaction (a, b, both, or neither) will have a forward rate constant that is greater than the reverse rate constant?

**Rxn. (b)** b. Which reaction (a, b, both, or neither) will produce an equilibrium mixture that favors the products?

**Rxn. (a)** c. If both of the reactions are allowed to reach equilibrium, which reaction (a, b, both, or neither) will shift toward product if the equilibrium mixture is heated?

**Neither** d. If both of the reactions are allowed to reach equilibrium, which reaction (a, b, both, or neither) will shift toward product if a catalyst is added?

**Both** e. If neither of the reactions have reached equilibrium, which reaction (a, b, both, or neither) will reach equilibrium more rapidly if the reaction mixtures are heated?