1)
a) ClO
b) Cl
c)
$$O_{(g)} + O_{3(g)} ---> 2O_{2(g)}$$

2)

a) D, lower concentration of reactant, decrease # of collisions.

b) I, increase concentration, increase # of collisions.

c) D, decrease # of collisions, decrease kinetic energy decrease % of collisions which are effective

d) I, increase # of collisions, increase kinetic energy-increase % of collisions which are effective

e) I, decrease activation energy, increases % of collisions which are effective.

f) R, not a reactant no change in rate



4)
a)
$$1/2 O_{2(g)} + O_{2(g)} ---> O_{3(g)}$$

b) $143kJ/mol$
c)



5)

a) Rate=k[A][B] b) 1.2 Lmol⁻¹s⁻¹ c) 4.8•10⁻⁴ molL⁻¹s⁻¹ d.i) Adding both steps gives A + 2B ---> 2C This is the same as the given reaction. d.ii) it must be the first step, rate laws are the same. 6)

a) Increasing the temperature decreases the activation energy, which increases the percentage of collisions which are effective. Additionally increasing the temperature increases the velocity of the particles causing more collisions.

b) Adding a catalyst decrease the activation energy by changing the reaction pathway. Decreasing the activation increases the percentage of reaction which are effective.

c) Catalysts are usually a surface area effect the greater the surface area the better the catalyst will work, grinding to a powder gives more surface area.

d) Increasing the concentration will increases the total number of collisions with out changing the percentage of collisions which are effective. More collisions will give more effective collisions.

7) Average score = 3.24

a) two points

order of reaction determined by the slowest step in the mechanism OR

order of reaction determined by exponents in the rate law OR

providing a counterexample where the coefficients in equation and exponents in rate law are different

b) six points

1. Rate = k[XY] or equivalent

2. k = 1/time or units consistent with student's rate equation

3. Mechanism proposed should show:

a) steps adding up to the overall reaction

b) one step starting with XY

c) rate-determining step involving XY

8) Both mechanisms sum to give the same overall equation so we need to consider the rate law. The reaction has an overall rate law of: Rate= $k[NO]^2[Br_2]$ so we want the mechanism to give the same rate law. The rate laws for each reaction require us to combine the fast steps in to the slow steps. For mechanism I the rate law of the slow step is Rate = $k[N_2O_2][Br_2]$, but N_2O_2 is not is the over all reaction. We need to substitute the value of NO in for the value of N_2O_2 . $[N_2O_2] = [NO]^2$ so the overall rate law of the first mechanism is Rate= $k[NO]^2[Br_2]$. This is consistent with the overall rate law. For the second reaction the rate of the slow step is not consistent with the overall rate law.

9) a) three points

Plot ln k or log k vs 1/T Eact = - R (slope) or - 2,303 R (slope) For partial credit, if the 2-point equation is given for the activation evergy, the student may receive a point. A student may also receive a point if it is stated that k is plotted vs 1/T or if ln K or log k is plotted vs T.

b) five points

Plot ln PA or log PA vs time. Plot 1/PA vs time. If ln PA vs time is linear, the reaction is first order. If 1/PA vs time is linear, the reaction is second order. If first order, slope = $-k_1$ or $-k_1 / 2.303$. If second order, slope = k_2 . 10)

(a) Response must clearly indicate (and distinguish between) Eact and Δ Hrxn on graph *Each earns one point*

(b) i. Response shows a softly curving line that approaches the time axis and whose slope changes continually. *No penalty if curve crosses time axis or levels*

out above time axis. Curve must drop initially and continually.

No credit earned if $[N_2O_5]$ increases

ii. Reaction rate is the **slope** of the line **tangent** to any point on the curve. (one point)

Rate must be tied somehow to slope of the graph

Answer may be indicated directly on the graph

Instantaneous rate ust be indicated rather than the average rate



iii. Since "rate = slope = $k[N_2O_5]$ ", the value of k can be determined algebraically from the slope at a known value of $[N_2O_5]$. (one point)

No penalty for "rate = $2k [N_2O_5]$ as a reaction stoichiometry could suggest this answer. Point can be earned for rate constant = slope of graph if $ln[N_2O_5]$ vs. time since reaction is first order.

Use half-life or integrated rate law to solve for k can be accepted.

iv. The value of the rate constant is independent of the reactant concentrations, so adding more reactant will not affect the value of k. (one point) *no point earned for simply stating that value of k will not change. Response must distinguish between rate and rate constant.*

(c) i. Rate = k[A] or ln([A]/[A]o) = kt. Since graph of ln[A] vs. time is linear, it must be a first-order reaction. (one point)

Either from of the rate law is acceptable, and both the equation and the brief justification are required to earn the point.

No point earned if response indicates first order because the first graph is not linear.

ii. Determine the slope of the first graph and set "k = -slope." (one point) *Response must indicate both the negative sign and the slope.*

10.

(a) Calculate the initial rate of disappearance of $Br_{2(g)}$ in experiment 1.

$$3.24 \cdot 10^{-4} \cdot \frac{1 \text{Br}_2}{2 \text{NOBr}} = 1.62 \cdot 10^{-4}$$

(b) Determine the order of the reaction with respect to each reactant, $Br_{2(g)}$ and $NO_{(g)}$. In each case, explain your reasoning. *NO second order*

Br₂ first order

(c) For the reaction,

- (i) write the rate law that is consistent with the data, and $Rate = k[NO^2] [Br_2]$
- (ii) calculate the value of the specific rate constant, *k*, and specify units. $k=1.05e2 L^2 mol^{-2} s^{-1}$
- (d) The following mechanism was proposed for the reaction:

$$Br_{2(g)} + NO_{(g)} \longrightarrow NOBr_{2(g)}$$
 slow
NOBr $+ NO \longrightarrow 2 NOBr$ fast

 $NOBr_{2(g)} + NO_{(g)} \rightarrow 2 NOBr_{(g)} \qquad fast$ Is this mechanism consistent with the given experimental observations? Justify your answer.

For the mechanism to be consistent it must sum to the over all reaction and it does.

For the mechanism to be consistent it must give a rate law that is consistent with the experimentally determined rate law. The slow step in this mechanism has a rate law of $Rate=k[NO][Br_2]$. This is not consistent with the experimental data so this mechanism should be ruled out.