Question 2

$$A(g) + B(g) \rightarrow C(g) + D(g)$$

For the gas-phase reaction represented above, the following experimental data were obtained.

Experiment	Initial [A] (mol L^{-1})	Initial [B] (mol L^{-1})	Initial Reaction Rate (mol L^{-1} s^{-1})
1	0.033	0.034	6.67×10^{-4}
2	0.034	0.137	1.08×10^{-2}
3	0.136	0.136	1.07×10^{-2}
4	0.202	0.233	?

(a) Determine the order of the reaction with respect to reactant A. Justify your answer.

Between experiments 2 and 3, [B] stays the same and [A] is quadrupled, but the initial reaction rate stays the same. This means that the initial reaction rate is not dependent on [A], so the reaction is zero order with respect to A. (May also justify using mathematics as shown in part (b).)	One point is earned for the correct order <u>and</u> for the justification.

(b) Determine the order of the reaction with respect to reactant B. Justify your answer.

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k\,[A]_2^x\,[B]_2^y}{k\,[A]_1^x\,[B]_1^y}$$

$$\frac{1.08 \times 10^{-2}}{6.67 \times 10^{-4}} = \frac{k\,(0.034)^x\,(0.137)^y}{k\,(0.033)^x\,(0.034)^y} \quad \text{where } x = 0$$

$16.2 = (4.03)^y$

$y = 2$, so the reaction is second order with respect to B

OR

Between experiments 1 and 2, [A] stays the same, [B] is multiplied by 4, and the initial reaction rate is multiplied by 16. This means that the reaction is second order with respect to B.

One point is earned for the correct order <u>and</u> for the justification.

(c) Write the rate law for the overall reaction.

rate = $k\,[B]^2$	One point is earned for the correct rate law (or a rate law consistent with the answers in part (a) and part (b)).

Question 2 (continued)

(d) Determine the value of the rate constant, k, for the reaction. Include units with your answer.

Using experiment 2: rate = $k\,[B]^2$ $k = \frac{\text{rate}}{[B]^2} = \frac{6.67 \times 10^{-4}\ \text{mol L}^{-1}\ \text{sec}^{-1}}{(0.034\ \text{mol L}^{-1})^2} = 0.577\ M^{-1}\ \text{sec}^{-1}$	One point is earned for the correct numerical value of the rate constant. One point is earned for the correct units.

(e) Calculate the initial reaction rate for experiment 4.

rate = $k\,[B]^2$ rate = $(0.577\ M^{-1}\ \text{sec}^{-1}) \times (0.233\ \text{mol L}^{-1})^2$ $= 3.13 \times 10^{-2}\ \text{mol L}^{-1}\ \text{sec}^{-1}$	One point is earned for the correct answer, including units.

(f) The following mechanism has been proposed for the reaction.

Step 1: $B + B \rightarrow E + D$ *slow*

Step 2: $E + A \rightleftarrows B + C$ *fast equilibrium*

Provide two reasons why the mechanism is acceptable.

(1) When steps 1 and 2 are added together, the overall reaction is $A + B \rightarrow C + D$. This is the stoichiometry that was given for the overall reaction. (2) The rate-determining step (slow step) is consistent with the rate law because only reactant B occurs in the rate law and it occurs to the power of 2, which is the number of B molecules colliding in the rate-determining step. (3) The rate-determining step is consistent with the rate law because A is absent from the rate-determining step and the reaction is zero order—i.e., reactant A does not appear in the rate law.	One point is earned for each correct reason, with a maximum of 2 points.

(g) In the mechanism in part (f), is species E a catalyst, or is it an intermediate? Justify your answer.

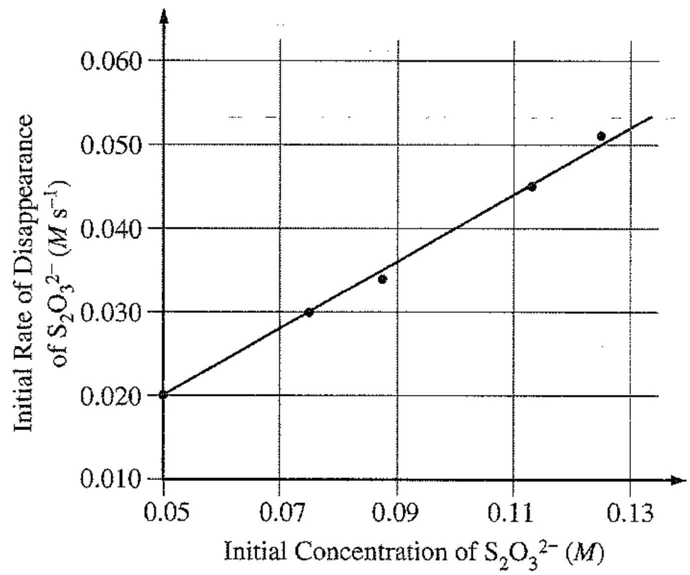
Species E is an intermediate; it is formed in step 1 and consumed in step 2. AND/OR Species E is not a catalyst because a catalyst occurs as a reactant in an earlier step and is then reproduced as a product in a later step.	One point is earned for the correct answer with justification.

Question 2 (8 points)

$$S_2O_3^{2-}(aq) \xrightarrow{H^+} SO_3^{2-}(aq) + S(s)$$

A student performed an experiment to investigate the decomposition of sodium thiosulfate, $Na_2S_2O_3$, in acidic solution, as represented by the equation above. In each trial the student mixed a different concentration of sodium thiosulfate with hydrochloric acid at constant temperature and determined the rate of disappearance of $S_2O_3^{2-}(aq)$. Data from five trials are given below in the table on the left and are plotted in the graph on the right.

Trial	Initial Concentration of $S_2O_3^{2-}(aq)$ (M)	Initial Rate of Disappearance of $S_2O_3^{2-}(aq)$ ($M\ s^{-1}$)
1	0.050	0.020
2	0.075	0.030
3	0.088	0.034
4	0.112	0.045
5	0.125	0.051



(a) Identify the independent variable in the experiment.

The initial concentration of $S_2O_3^{2-}(aq)$	One point is earned for the correct answer.

(b) Determine the order of the reaction with respect to $S_2O_3^{2-}$. Justify your answer by using the information above.

Using trials 1 and 2: $\frac{\text{rate}_2}{\text{rate}_1} = \frac{k_2[S_2O_3^{2-}]^{m_2}}{k_1[S_2O_3^{2-}]^{m_1}}$	One point is earned for the correct order.
$\frac{0.030\ M\ s^{-1}}{0.020\ M\ s^{-1}} = \frac{[0.075]^m}{[0.050]^m}$	
$1.5 = (1.5)^m$, so $m = 1$ and the reaction is **first order** with respect to $S_2O_3^{2-}$.	One point is earned for a correct justification.
Note: Other correct justifications are acceptable.	

Question 2 (continued)

(c) Determine the value of the rate constant, k, for the reaction. Include units in your answer. Show how you arrived at your answer.

$\text{rate} = k[S_2O_3^{2-}] \Rightarrow k = \dfrac{\text{rate}}{[S_2O_3^{2-}]}$ Using the data from trial 1, $k = \dfrac{0.020\ M\ s^{-1}}{0.050\ M} = \mathbf{0.40\ s^{-1}}$ **OR** the rate constant is equal to the slope of the line $k = \dfrac{(0.052 - 0.020) M\,s^{-1}}{(0.13 - 0.05) M} = \dfrac{0.032 M\,s^{-1}}{0.08 M} = \mathbf{0.40\ s^{-1}}$	One point is earned for the correct value. One point is earned for the correct units.

(d) In another trial the student mixed 0.10 M $Na_2S_2O_3$ with hydrochloric acid. Calculate the amount of time it would take for the concentration of $S_2O_3^{2-}$ to drop to 0.020 M.

$\ln[A]_t - \ln[A]_0 = -kt \Rightarrow \ln\dfrac{[A]_t}{[A]_0} = -kt$ $\ln\dfrac{[S_2O_3^{2-}]_t}{[S_2O_3^{2-}]_0} = -kt$ $\ln\dfrac{0.020}{0.10} = (-0.40\ s^{-1})(t) \Rightarrow t = \dfrac{-1.61}{-0.40\ s^{-1}} = \mathbf{4.0\ s}$	One point is earned for the correct setup. One point is earned for the correct answer with units.

(e) On the graph above, sketch the line that shows the results that would be expected if the student repeated the five trials at a temperature lower than that during the first set of trials.

The line drawn should start on the y-axis at a lower point than the line already plotted and should have a less steep slope.	One point is earned for an acceptable line.

Question 3
(9 points)

$$8\ H^+(aq) + 4\ Cl^-(aq) + MnO_4^-(aq) \rightarrow 2\ Cl_2(g) + Mn^{3+}(aq) + 4\ H_2O(l)$$

$Cl_2(g)$ can be generated in the laboratory by reacting potassium permanganate with an acidified solution of sodium chloride. The net-ionic equation for the reaction is given above.

(a) A 25.00 mL sample of 0.250 *M* NaCl reacts completely with excess $KMnO_4(aq)$. The $Cl_2(g)$ produced is dried and stored in a sealed container. At 22°C the pressure of the $Cl_2(g)$ in the container is 0.950 atm.

(i) Calculate the number of moles of $Cl^-(aq)$ present before any reaction occurs.

mol Cl^- = (0.02500 L)(0.250 *M*) = 6.25×10^{-3} mol	One point is earned for the correct numerical value.

(ii) Calculate the volume, in L, of the $Cl_2(g)$ in the sealed container.

$\text{mol } Cl_2 = \frac{\text{mol } Cl^-}{2} = \frac{6.25 \times 10^{-3} \text{ mol}}{2} = 3.125 \times 10^{-3} \text{ mol } Cl_2$	One point is earned for the correct number of moles of Cl_2 based on stoichiometry.
$V = \frac{nRT}{P} = \frac{(3.125 \times 10^{-3} \text{ mol } Cl_2)(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(295 \text{ K})}{0.950 \text{ atm}}$ = 0.0797 L Cl_2	One point is earned for substitution into ideal gas law and correct numerical result.

An initial-rate study was performed on the reaction system. Data for the experiment are given in the table below.

Trial	$[Cl^-]$	$[MnO_4^-]$	$[H^+]$	Rate of Disappearance of MnO_4^- in $M\ s^{-1}$
1	0.0104	0.00400	3.00	2.25×10^{-8}
2	0.0312	0.00400	3.00	2.03×10^{-7}
3	0.0312	0.00200	3.00	1.02×10^{-7}

Question 3 (continued)

(b) Using the information in the table, determine the order of the reaction with respect to each of the following. Justify your answers.

(i) Cl^-

The reaction is second order. Tripling $[Cl^-]$ between trials 1 and 2 with no change in $[MnO_4^-]$ results in a nine-fold increase in the rate: $$\left(\frac{0.0312\ M}{0.0104\ M}\right)^x = \frac{2.03 \times 10^{-7}}{2.25 \times 10^{-8}}$$ $$3^x = 9$$ $$x = 2$$ Thus the order of the reaction must be 2 with respect to Cl^-.	One point is earned for the correct order of reaction with justification.

(ii) MnO_4^-

The reaction is first order. Doubling $[MnO_4^-]$ between trials 3 and 2 with no change in $[Cl^-]$ results in a doubling of the rate: $$\left(\frac{0.00400\ M}{0.00200\ M}\right)^y = \frac{2.03 \times 10^{-7}}{1.02 \times 10^{-7}}$$ $$2^y = 2$$ $$y = 1$$ Thus the order of the reaction must be 1 with respect to MnO_4^-.	One point is earned for the correct order of reaction with justification.

(c) The reaction is known to be third order with respect to H^+. Using this information and your answers to part (b) above, complete both of the following:

(i) Write the rate law for the reaction.

rate = $k[Cl^-]^2[MnO_4^-][H^+]^3$	One point is earned for the correct rate law.

Question 3 (continued)

(ii) Calculate the value of the rate constant, k, for the reaction, including appropriate units.

Using data from trial 1: $2.25 \times 10^{-8}\ M\,s^{-1} = k(0.0104\ M)^2(0.00400\ M)(3.00\ M)^3$ $k = 1.93 \times 10^{-3}\ M^{-5}s^{-1}$	One point is earned for the correct numerical result. One point is earned for the correct units.

(d) Is it likely that the reaction occurs in a single elementary step? Justify your answer.

It is not likely that the reaction occurs in a single step because the orders of the reaction with respect to the reactants do not correspond to the coefficients in the balanced equation ***OR*** It is not likely that the reaction occurs in a single step because the reaction requires the collision of many (13) reactant particles and the frequency of a 13-particle collision is negligible.	One point is earned for the correct answer with justification.

Question 6
(8 points)

$$H_2(g) + Cl_2(g) \rightarrow 2\,HCl(g)$$

The table below gives data for a reaction rate study of the reaction represented above.

Experiment	Initial $[H_2]$ (mol L^{-1})	Initial $[Cl_2]$ (mol L^{-1})	Initial Rate of Formation of HCl (mol L^{-1} s^{-1})
1	0.00100	0.000500	1.82×10^{-12}
2	0.00200	0.000500	3.64×10^{-12}
3	0.00200	0.000250	1.82×10^{-12}

(a) Determine the order of the reaction with respect to H_2 and justify your answer.

The order of the reaction with respect to H_2 is 1. Comparing experiments 1 and 2, doubling the initial concentration of H_2 while keeping the initial concentration of Cl_2 constant results in a doubling of the reaction rate.	One point is earned for the correct order with justification.

(b) Determine the order of the reaction with respect to Cl_2 and justify your answer.

The order of the reaction with respect to Cl_2 is 1. Comparing experiments 2 and 3, halving the initial concentration of Cl_2 while keeping the initial concentration of H_2 constant results in a halving of the reaction rate.	One point is earned for the correct order with justification.

(c) Write the overall rate law for the reaction.

rate = $k\,[H_2][Cl_2]$	One point is earned for a rate law consistent with part (a) and part (b).

(d) Write the units of the rate constant.

$k = \dfrac{rate}{[H_2][Cl_2]} = \dfrac{\text{mol L}^{-1}\text{ s}^{-1}}{\text{mol L}^{-1}\text{ mol L}^{-1}}$ $= \dfrac{\text{s}^{-1}}{\text{mol L}^{-1}} = \text{L mol}^{-1}\text{ s}^{-1}$	One point is earned for units consistent with part (c).

Question 6 (continued)

(e) Predict the initial rate of the reaction if the initial concentration of H_2 is 0.00300 mol L^{-1} and the initial concentration of Cl_2 is 0.000500 mol L^{-1}.

For this reaction, the initial concentration of Cl_2 is the same as in Experiment 1 but the initial concentration of H_2 is three times as large. And because the reaction is first order with respect to each reactant, the initial rate of the reaction would be 5.46×10^{-12} mol L^{-1} s^{-1}, which is three times the rate of the initial rate of the reaction in Experiment 1.	One point is earned for the correct numerical answer or correct multiplier consistent with the rate law from part (c).

The gas-phase decomposition of nitrous oxide has the following two-step mechanism.

Step 1: $N_2O \rightarrow N_2 + O$

Step 2: $O + N_2O \rightarrow N_2 + O_2$

(f) Write the balanced equation for the overall reaction.

$2\,N_2O \rightarrow 2\,N_2 + O_2$	One point is earned for the correct balanced equation.

(g) Is the oxygen atom, O, a catalyst for the reaction or is it an intermediate? Explain.

The O atom is an intermediate because it is formed and then consumed during the course of the reaction. (Had it been a catalyst, it would have been present both at the beginning and the end of the reaction.)	One point is earned for the correct choice with explanation.

(h) Identify the slower step in the mechanism if the rate law for the reaction was determined to be *rate* = $k\,[N_2O]$. Justify your answer.

Step 1 is slower because N_2O appears in Step 1 as the single reactant, which is consistent with the given rate law.	One point is earned for the correct choice with justification.

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Question 6

In an experiment, all the air in a rigid 2.0 L flask is pumped out. Then some liquid ethanol is injected into the sealed flask, which is held at 35°C. The amount of liquid ethanol initially decreases, but after five minutes the amount of liquid ethanol in the flask remains constant. Ethanol has a boiling point of 78.5°C and an equilibrium vapor pressure of 100 torr at 35°C.

(a) When the amount of liquid ethanol in the flask is constant, is the pressure in the flask greater than, less than, or equal to 100 torr? Justify your answer.

The pressure would be equal to 100 torr. Because the quantity of liquid ethanol is not changing, the gas and liquid phases have reached equilibrium. Therefore the pressure of ethanol in the gas phase equals the vapor pressure.	1 point is earned for the correct choice with a valid justification.

(b) The flask is then heated to 45°C, and the pressure in the flask increases. In terms of kinetic molecular theory, provide TWO reasons that the pressure in the flask is greater at 45°C than at 35°C.

There are three possible reasons based on kinetic molecular theory. • At the higher temperature there are more ethanol molecules in the gas phase, so there will be more collisions with the flask walls, resulting in a greater pressure. • At the higher temperature the molecules will be moving faster on average, thus colliding with the flask walls more frequently, resulting in a greater pressure. • Because the molecules are moving faster on average, their collisions with the flask walls will exert a greater force, resulting in a greater pressure.	1 point is earned for each correct reason up to a maximum of 2 points.

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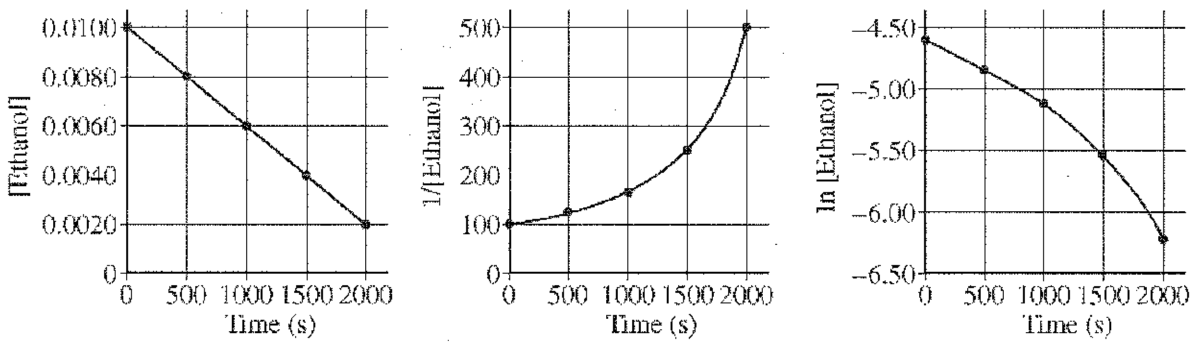
Question 6 (continued)

In a second experiment, which is performed at a much higher temperature, a sample of ethanol gas and a copper catalyst are placed in a rigid, empty 1.0 L flask. The temperature of the flask is held constant, and the initial concentration of the ethanol gas is 0.0100 *M*. The ethanol begins to decompose according to the chemical reaction represented below.

$$CH_3CH_2OH(g) \xrightarrow{Cu} CH_3CHO(g) + H_2(g)$$

The concentration of ethanol gas over time is used to create the three graphs below.



(c) Given that the reaction order is zero, one, or two, use the information in the graphs to respond to the following.

(i) Determine the order of the reaction with respect to ethanol. Justify your answer.

The order of the reaction is zero. The plot on the left is a straight line, indicating that the rate of decrease in [ethanol] is constant as [ethanol] changes. Therefore the rate of reaction does not depend on [ethanol].	1 point is earned for the correct choice with a valid justification.

(ii) Write the rate law for the reaction.

rate = k	1 point is earned for the correct rate law.

(iii) Determine the rate constant for the reaction, including units.

rate = $k = -\frac{\Delta[\text{ethanol}]}{\Delta t} = -\frac{(0.0020 - 0.0100)\text{ mol/L}}{2000\text{ s}}$ $= 4.0 \times 10^{-6}\ M\ s^{-1}$	1 point is earned for the correct setup. 1 point is earned for the correct units.

Question 6 (continued)

(d) The pressure in the flask at the beginning of the experiment is 0.40 atm. If the ethanol completely decomposes, what is the final pressure in the flask?

The final pressure is 0.80 atm (twice the original pressure because the products represent twice as many moles of gas as the reactant).	1 point is earned for the correct final pressure.