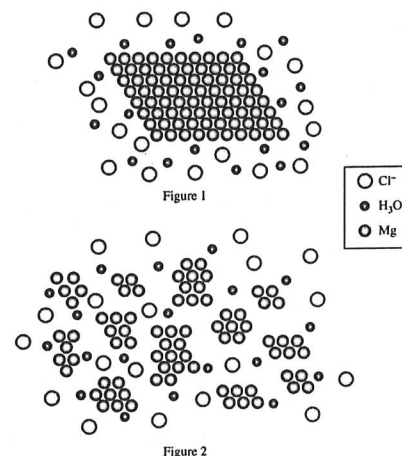
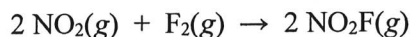


- 1) Which of the following best helps explain why an increase in temperature increases the rate of a chemical reaction?
- A) At higher temperatures, reactions have a lower activation energy. *no*
 B) At higher temperatures, reactions have a higher activation energy. *no*
 C) At higher temperatures, every collision results in the formation of product. *no*
 D) At higher temperatures, high-energy collisions happen more frequently.

- 2) Two samples of $\text{Mg}(s)$ of equal mass were placed in equal amounts of $\text{HCl}(aq)$ contained in two separate reaction vessels. Particle representations of the mixing of $\text{Mg}(s)$ and $\text{HCl}(aq)$ in the two reaction vessels are shown in Figure 1 and 2. Water molecules are not included in the particle representations. Which of the reactions will initially proceed faster, and why?



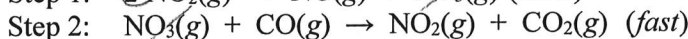
- A) The reaction in Figure 1, because the atoms of Mg are more concentrated than those in Figure 2. *opposite*
 B) The reaction in Figure 1, because the $\text{Mg}(s)$ in Figure 1 has a larger mass than the $\text{Mg}(s)$ in Figure 2. *it doesn't*
 C) The reaction in Figure 2, because more Mg atoms are exposed to $\text{HCl}(aq)$ in Figure 2 than in Figure 1. *more*
 D) The reaction in Figure 2, because the $\text{Mg}(s)$ in Figure 2 has less surface area than the $\text{Mg}(s)$ in Figure 1.
- 3) Which of the following will most likely increase the rate of the following reaction? $\text{C}_2\text{H}_4(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g)$
- A) Decreasing the temperature of the reaction system (B) Adding a heterogeneous catalyst to the reaction system
 C) Increasing the volume of the reaction vessel using a piston D) Removing some $\text{H}_2(g)$ from the reaction system



- 4) The rate law for the reaction represented by the equation above is $\text{rate} = k [\text{NO}_2][\text{F}_2]$. Which of the following could be the first elementary step of a two-step mechanism for the reaction if the first step is slow and the second step is fast?
- A) $\text{F}_2(g) \rightarrow 2 \text{F}(g)$ (B) $\text{NO}_2(g) + \text{F}_2(g) \rightarrow \text{NO}_2\text{F}(g) + \text{F}(g)$ *both first order*
 C) $\text{NO}_2(g) + \text{F}(g) \rightarrow \text{NO}_2\text{F}(g)$ D) $2 \text{NO}_2(g) + \text{F}_2(g) \rightarrow 2 \text{NO}_2\text{F}(g)$



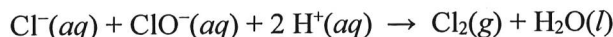
- 5) The reaction between $\text{NO}_2(g)$ and $\text{CO}(g)$ is represented above. The elementary steps of a proposed reaction mechanism are represented here:



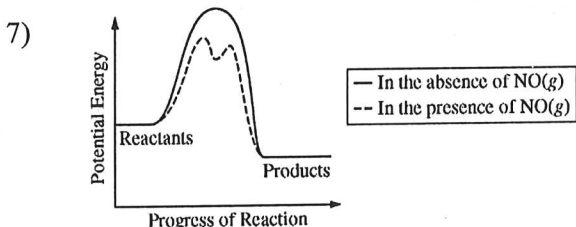
CO is not in rate determining step

Which of the following is the rate law for the overall reaction that is consistent with the proposed mechanism?

- A) $\text{Rate} = k [\text{NO}_2][\text{CO}]$ (B) $\text{Rate} = k [\text{NO}_2]^2$ C) $\text{Rate} = k [\text{NO}_3][\text{CO}]$ D) $\text{Rate} = k [\text{NO}_2][\text{NO}_3][\text{CO}]$



- 6) What effect will increasing $[\text{H}^+]$ at constant temperature have on the reaction represented above?
- A) The activation energy of the reaction will increase.
 B) The activation energy of the reaction will decrease. *no*
 C) The frequency of collisions between $\text{H}^+(aq)$ ions and $\text{ClO}^-(aq)$ ions will increase.
 D) The value of the rate constant will increase.



The decomposition of $\text{O}_3(g)$ in the upper atmosphere is represented by the equation $\text{O}_3(g) + \text{O}(g) \rightarrow 2 \text{O}_2(g)$. The potential energy diagram for the decomposition of $\text{O}_3(g)$ in the presence and absence of $\text{NO}(g)$ is given. Which of the following mechanisms for the catalyzed reaction is consistent with the equation and diagram?

- A) $2 \text{O}_3(g) + 2 \text{NO}(g) \rightarrow 4 \text{O}_2(g) + \text{N}_2(g)$ *slow*
 (B) $\text{O}_3(g) + \text{NO}(g) \rightarrow \text{NO}_2(g) + \text{O}_2(g)$ *slow*
 $\text{NO}_2(g) + \text{O}(g) \rightarrow \text{NO}(g) + \text{O}_2(g)$ *fast*
 C) $\text{NO}_2(g) + \text{O}_3(g) \rightarrow \text{NO}(g) + 2 \text{O}_2(g)$ *slow*
 $\text{NO}(g) + \text{O}(g) \rightarrow \text{NO}_2(g)$ *fast*
 D) $\text{NO}_2(g) + \text{O}(g) \rightarrow \text{NO}_3(g)$ *slow*
 $\text{NO}_3(g) + \text{O}_3(g) \rightarrow \text{NO}_2(g) + 2 \text{O}_2(g)$ *fast*

*NO is a catalyst
consumed then reformed*

Questions 8-10 refer to the investigation described below.

$\text{C}_{25}\text{H}_{30}\text{N}_3^+ (\text{aq}) + \text{OH}^- (\text{aq}) \rightarrow \text{C}_{25}\text{H}_{30}\text{N}_3\text{OH} (\text{aq})$
violet colorless

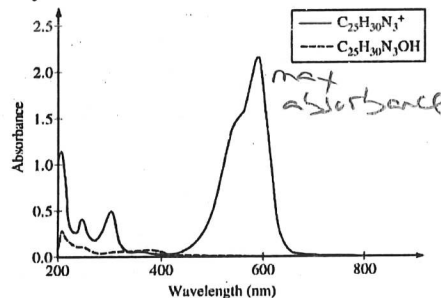
The reaction between $\text{C}_{25}\text{H}_{30}\text{N}_3^+(aq)$ and $\text{OH}^-(aq)$, as represented above, is first order with respect to $\text{C}_{25}\text{H}_{30}\text{N}_3^+(aq)$ in the presence of excess $\text{OH}^-(aq)$. A 10.0 mL sample of 0.10 M $\text{NaOH}(aq)$ is mixed with a 10.0 mL sample of $2.5 \times 10^{-5} \text{ M}$ $\text{C}_{25}\text{H}_{30}\text{N}_3^+(aq)$. A 5.0 mL sample of the mixture is quickly transferred to a clean cuvette and placed in a spectrophotometer, and the progress of the reaction is measured. The data are given in the table below.

Time (s)	0	30	60	90	120	150	180	210	240	270	300
Absorbance	0.62	0.54	0.47	0.41	0.36	0.31	0.27	0.23	0.20	0.17	0.15

- 8) Approximately how long did it take for 75 percent of the initial amount of $\text{C}_{25}\text{H}_{30}\text{N}_3^+(aq)$ to react?
A) 75 s B) 225 s C) 300 s D) 600 s
- 9) What would be the effect on the reaction rate if the solution of $\text{C}_{25}\text{H}_{30}\text{N}_3^+(aq)$ is diluted by a factor of two?
A) It would be higher.
B) It would be lower.
C) It would not change.
D) It would initially be higher but then rapidly decrease.
- Simple Kinetics

- 10) To choose a wavelength to analyze the progress of the reaction, a student records the absorbance spectra of both $\text{C}_2\text{H}_3\text{N}_3^+(\text{aq})$ and $\text{C}_2\text{H}_3\text{N}_3\text{OH}(\text{aq})$ in the range of 200-800 nm. The two spectra are presented in the graph.

The student wants to use the spectrophotometer to measure $[\text{C}_{25}\text{H}_{30}\text{N}_3^+]$ with the greatest sensitivity as the reaction progresses. Which of the following indicates the best wavelength setting and explains why it is best?



- A) 205 nm, because the colorless form of the molecule will absorb significantly at this wavelength
B) 205 nm, because both forms of the molecule will absorb significantly at this wavelength
C) 590 nm, because only the violet form of the molecule will absorb significantly at this wavelength
D) 590 nm, because this wavelength falls in the violet region of the visible light spectrum *it does not*

Use this equation for #11 - 13: $2\text{NO}_{(g)} + \text{O}_{2(g)} \rightarrow 2\text{NO}_{2(g)}$

- 11) Nitrogen monoxide and oxygen gas were combined in a flask at 25°C and allowed to react as shown above. The concentration of the reactants were varied according to the table to the right, and initial rates were calculated. Which of the following is the rate law for the reaction?

Trial	[O ₂]	[NO]	Initial Rate of Formation of NO ₂ (M s ⁻¹)
1	0.020	0.050	0.038
2	0.020	0.100	0.152
3	0.080	0.100	0.608

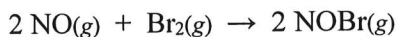
- A) Rate = $k[\text{O}_2]^2 [\text{NO}]^2$
B) Rate = $k[\text{NO}]^2$
C) Rate = $k[\text{O}_2][\text{NO}]^2$
D) Rate = $k[\text{O}_2][\text{NO}]$

- 12) Which mechanism agrees with the rate law above?

- A) Step 1: $\text{NO(g)} + \text{O}_2\text{(g)} \rightarrow \text{NO}_2\text{(g)} + \text{O(g)}$ (slow) (B)
Step 2: $\text{NO(g)} + \text{O(g)} \rightarrow \text{NO}_2\text{(g)}$ (fast)
first order w/ respect to NO

- 13) Which substance is acting as intermediate in each mechanism?
A) NO B) NO₂ C) O D) O₂

- 1) A rate study of the reaction represented below was conducted at 25°C. The data that were obtained are shown in the table. 1999 3



Experiment	Initial [NO] (mol L ⁻¹)	Initial [Br ₂] (mol L ⁻¹)	Initial Rate of Appearance of NOBr (mol L ⁻¹ s ⁻¹)
1	0.0160	0.0120	3.24 x 10 ⁻⁴
2	0.0160	0.0240	6.38 x 10 ⁻⁴
3	0.0320	0.0060	6.42 x 10 ⁻⁴

- a) Calculate the initial rate of disappearance of Br₂(g) in experiment 1. (1pt)

2:1 ratio

$$\frac{3.24 \times 10^{-4}}{2}$$

$$= -1.62 \times 10^{-4} \frac{\text{mol}}{\text{L} \cdot \text{s}}$$

- b) Determine the order of the reaction with respect to each reactant, Br₂(g) and NO(g). In each case, explain your reasoning. (3pts)

1st order w/ respect to Br₂. when [NO] was held constant, [Br₂] was doubled and the rate also doubled

2nd order w/ respect to [NO]. The rate remained constant when [NO] was doubled and [Br₂] was decreased by 4. The rate would stay constant if [NO] is 2nd order.

- c) For the reaction,

- i) write the rate law that is consistent with the data, and (1pt)

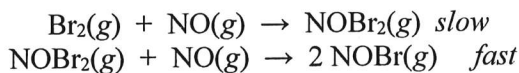
$$R = k[\text{NO}]^2[\text{Br}_2]$$

- ii) calculate the value of the specific rate constant, *k*, and specify units. (2pts)

$$k = \frac{R}{[\text{NO}]^2[\text{Br}_2]} = \frac{3.24 \times 10^{-4} \frac{\text{M}}{\text{s}}}{(0.0160 \text{ M})^2 (0.0120 \text{ M})}$$

$$= 105 \text{ M}^{-2} \text{ s}^{-1}$$

- d) The following mechanism was proposed for the reaction:



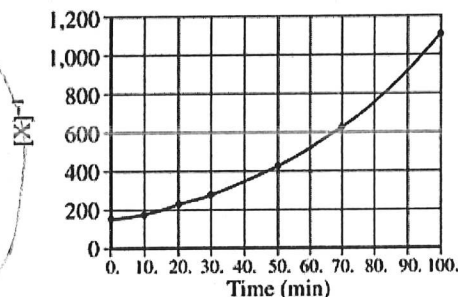
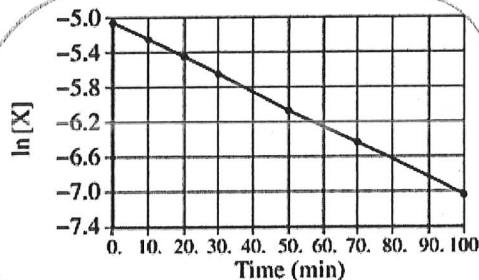
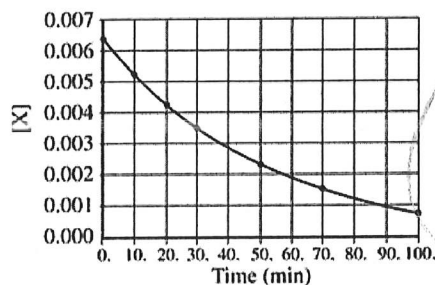
Is this mechanism consistent with the given experimental observations? Justify your answer. (2pt)

No, the mechanism suggests that NO is first order based on the slow step. It is 2nd order, so the second step should be the rate-determining step



- 5) The decomposition of gas X to produce gases Y and Z is represented by the equation above. In a certain experiment, the reaction took place in a 5.00 L flask at 428 K. Data from this experiment were used to produce the information in the table below, which is plotted in the graphs that follow. 2005B 3

Time (minutes)	[X] (mol L ⁻¹)	ln [X]	[X] - 1 (L mol ⁻¹)
0	0.00633	-5.062	158
10.	0.00520	-5.259	192
20.	0.00427	-5.456	234
30.	0.00349	-5.658	287
50.	0.00236	-6.049	424
70.	0.00160	-6.438	625
100.	0.000900	-7.013	1,110



- a) How many moles of X were initially in the flask? (1pt)

$$M = \frac{\text{mol}}{L}$$

$$0.00633 = \frac{\text{mol}}{5.00}$$

$$0.0317 \text{ mol X}$$

- b) How many molecules of Y were produced in the first 20. minutes of the reaction? (2pts)

$$0.00427 = \frac{\text{mol}}{5.00} = 0.0214 \text{ mol}$$

$$0.0317 \text{ mol} - 0.0214 \text{ mol} = 0.0104 \text{ mol used}$$

$$0.0104 \text{ mol} \times \left| \frac{2 \text{ mol Y}}{1 \text{ mol X}} \right| = 0.0208 \text{ mol Y} = 1.25 \times 10^{23} \text{ molecules Y}$$

- c) What is the order of this reaction with respect to X? Justify your answer. (1pt)

1st Order - Linear when ln[X]

- d) Write the rate law for this reaction. (1pt)

$$\text{Rate} = k[X]$$

- e) Calculate the specific rate constant for this reaction. Specify units. (2pts)

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$-5.456 - (-5.062) = -k(1200 \text{ s})$$

$$k = 3.28 \times 10^{-4} \text{ s}^{-1}$$

$$\text{or } 0.0197 \text{ min}^{-1}$$

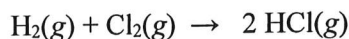
- f) Calculate the concentration of X in the flask after a total of 150. minutes of reaction. (2pts)

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\ln[A]_t = -8.014$$

$$\ln[A]_t - (-5.062) = -(3.28 \times 10^{-4} \text{ s}^{-1})(9000 \text{ s})$$

$$[X] = 3.31 \times 10^{-4} \text{ M}$$



- 9) The table gives data for a reaction rate study of the reaction represented above.

2010B 6

Experiment	Initial $[\text{H}_2]$ (mol L ⁻¹)	Initial $[\text{Cl}_2]$ (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. (1pt)

1st Order - when $[\text{H}_2]$ is doubled and $[\text{Cl}_2]$ remains constant, the rate doubles

- b) Determine the order of the reaction with respect to Cl_2 and justify your answer. (1pt)

1st Order - when $[\text{Cl}_2]$ is halved and $[\text{H}_2]$ is constant, the rate is also halved.

- c) Write the overall rate law for the reaction. $R = k[\text{H}_2][\text{Cl}_2]$ (1pt)

- d) Write (determine) the units of the rate constant. (1pt)

$$\frac{\text{M}}{\text{s}} = k(\text{M})(\text{M}) \quad \boxed{k = \frac{1}{\text{M} \cdot \text{s}}} \quad \text{or} \quad \frac{\text{L}}{\text{mol} \cdot \text{s}}$$

- 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. (1pt)

Find k :

$$1.82 \times 10^{-12} \frac{\text{M}}{\text{s}} = k(0.00100 \text{ M})(0.000500 \text{ M})$$

$$k = 3.64 \times 10^{-6} \frac{1}{\text{M} \cdot \text{s}}$$

Find Rate:

$$R = (3.64 \times 10^{-6} \frac{1}{\text{M} \cdot \text{s}})(0.00300 \text{ M})(0.000500 \text{ M})$$

$$\boxed{R = 5.46 \times 10^{-12} \frac{\text{M}}{\text{s}}}$$

(or do 3x the first rate based on data)

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

Step 1: $\text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}$

Step 2: $\text{O} + \text{N}_2\text{O} \rightarrow \text{N}_2 + \text{O}_2$

- f) Write the balanced equation for the overall reaction. (1pt)



- g) Is the oxygen atom, O, a catalyst for the reaction or is it an intermediate? Explain. (1pt)

Intermediate - produced then immediately reacted

- h) Identify the slower step in the mechanism if the rate law for the reaction was determined to be $\text{rate} = k[\text{N}_2\text{O}]$. Justify your answer. (1pt)

Step 1 - only 1 N_2O appears. This is consistent with the first order rate law.

The first-order decomposition of a colored chemical species, X, into colorless products is monitored with a spectrophotometer by measuring changes in absorbance over time. Species X has a molar absorptivity constant of $5.00 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$ and the path length of the cuvette containing the reaction mixture is 1.00 cm. The data from the experiment are given in the table.

20043

[X] (M)	Absorbance	Time (min)
?	0.600	0.0
4.00×10^{-5}	0.200	35.0
3.00×10^{-5}	0.150	44.2
1.50×10^{-5}	0.075	?

- a) Calculate the initial concentration of the colored species. (1pt)

$$A = \epsilon bc$$

$$c = \frac{A}{\epsilon b} = \frac{(0.600)}{(5.00 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})} = 1.20 \times 10^{-4} \text{ M}$$

- b) Calculate the rate constant for the first-order reaction using the values given for concentration and time. Include units with your answer. (2pts)

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$k = 0.0314 \text{ min}^{-1}$$

$$\ln[4.00 \times 10^{-5}] - \ln[1.20 \times 10^{-4}] = -k(35 \text{ min})$$

- c) Calculate the number of minutes it takes for the absorbance to drop from 0.600 to 0.075. (2pts)

$$(1.20 \times 10^{-4} \text{ M}) \quad (1.50 \times 10^{-5} \text{ M})$$

$$\ln[1.50 \times 10^{-5}] - \ln[1.20 \times 10^{-4}] = -(0.0314)(t)$$

$$t = 66.2 \text{ min}$$

- d) Calculate the half-life of the reaction. Include units with your answer. (2pts)

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0314 \text{ min}^{-1}} = 22.1 \text{ min}$$