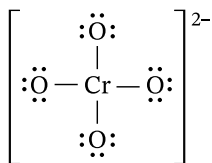


Question 2: Version J

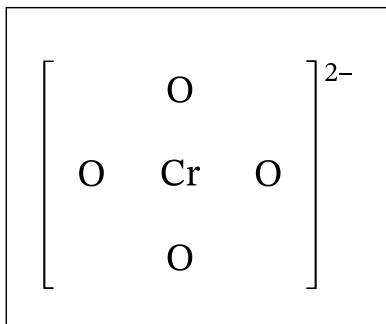
2. Answer the following questions about the chromate ion, CrO_4^{2-} , and the dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$.

Part A

The bonds between chromium and oxygen in CrO_4^{2-} can be represented as covalent bonds. One possible Lewis diagram for the CrO_4^{2-} ion is shown in Figure 1.

Figure 1

- Based on VSEPR theory, **predict** the molecular geometry of the CrO_4^{2-} ion.
- On Figure 2, **draw** a complete Lewis diagram for a resonance structure of CrO_4^{2-} that results in a formal charge of zero on two of the O atoms and a formal charge of -1 on the other two O atoms. Your diagram should contain the same number of valence electrons as in Figure 1.

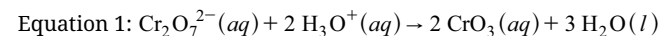
Figure 2**Part B**

When reacted with a strong acid like $\text{HNO}_3(aq)$, $\text{CrO}_4^{2-}(aq)$ can be converted to $\text{Cr}_2\text{O}_7^{2-}(aq)$ and $\text{H}_2\text{O}(l)$ in a reversible reaction.

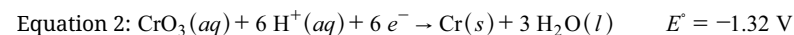
- Write** a balanced net ionic equation for the reaction between $\text{CrO}_4^{2-}(aq)$ and a strong acid.
- Is the reaction a redox reaction? **Justify** your answer based on the oxidation number of Cr.

The following information applies to parts C and D.

In acidic solutions, $\text{Cr}_2\text{O}_7^{2-}(aq)$ reacts to form $\text{CrO}_3(aq)$ according to Equation 1.



$\text{CrO}_3(aq)$ can be electrolyzed to plate objects with a thin layer of chromium metal according to Equation 2.

**Part C**

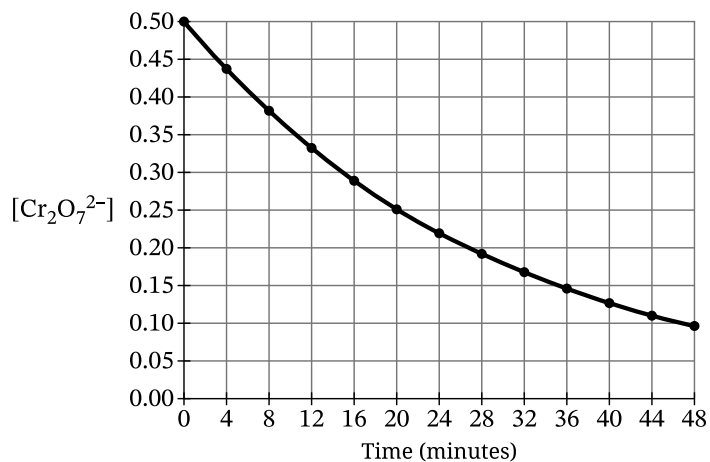
Is the reaction represented by Equation 2 thermodynamically favorable or unfavorable under standard conditions? **Justify** your answer with a calculation of ΔG° . Show the work that leads to your answer.

Part D

Calculate the number of grams of $\text{Cr}(s)$ that could be plated onto the surface of a steel rod when 15.0 A of current is applied for 3250 seconds. Show the work that leads to your answer.

Part E

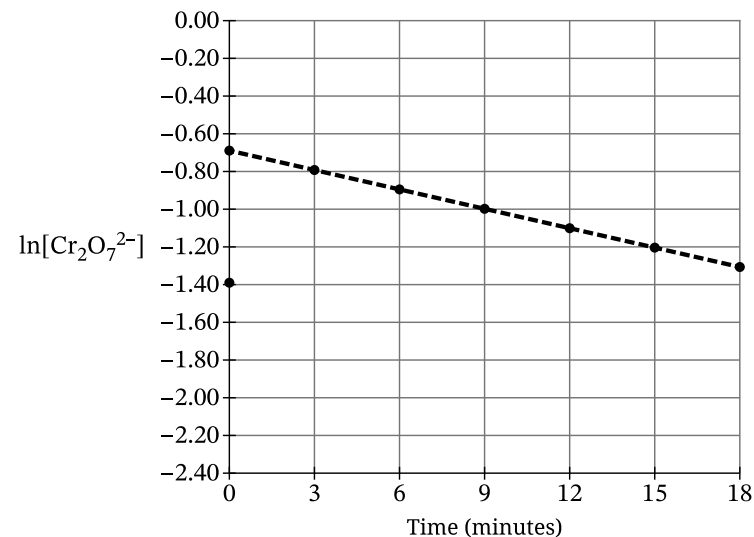
In a separate experiment, an iron wire is placed directly in a solution of $0.50\text{ M Cr}_2\text{O}_7^{2-}(aq)$ with $\text{pH} = 1.99$. The concentration of $\text{Cr}_2\text{O}_7^{2-}(aq)$ remaining is recorded over time, and the results are presented in Figure 3.

Figure 3

Explain how the data in Figure 3 support the conclusion that the reaction is first order with respect to $\text{Cr}_2\text{O}_7^{2-}$.

The following information applies to parts F and G.

The student creates a plot of $\ln[\text{Cr}_2\text{O}_7^{2-}]$ versus time for a trial with an initial concentration of $0.50\text{ M Cr}_2\text{O}_7^{2-}(aq)$, as shown in Figure 4.

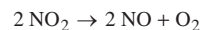
Figure 4**Part F**

Calculate the value of the rate constant, k , for the reaction. Report your answer in units of min^{-1} . Show the work that leads to your answer.

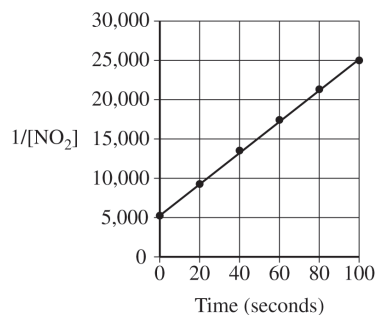
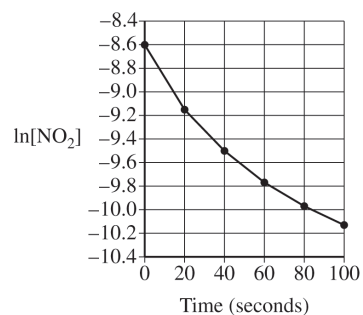
Part G

The student then runs a second trial of the experiment under identical conditions but uses an initial concentration of $0.25\text{ M Cr}_2\text{O}_7^{2-}(aq)$ instead of $0.50\text{ M Cr}_2\text{O}_7^{2-}(aq)$. On Figure 4, carefully **draw** the plot of $\ln[\text{Cr}_2\text{O}_7^{2-}]$ versus time that would be expected for the second experiment. The point at time zero has already been plotted.

6. At elevated temperatures, NO_2 undergoes decomposition in the gas phase, forming NO and O_2 as represented by the following equation.



A scientist measures the change in $[\text{NO}_2]$ over the first 100. s of the reaction at 546°C . The scientist uses the data collected from the experiment to generate the following two graphs.



Based on these data, the scientist makes the claim that the rate law for the reaction is $\text{rate} = k[\text{NO}_2]^2$.

- (a) Explain how the graphs indicate that the reaction is second order with respect to NO_2 .

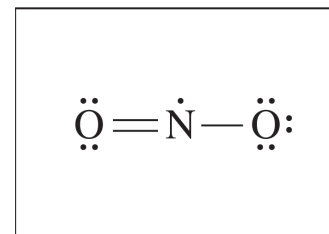
- (b) At a certain point in the reaction, the rate of disappearance of NO_2 is determined to be $6.52 \times 10^{-7} \text{ M/s}$.

Determine the rate of appearance, in M/s , of O_2 at this same point in the reaction.

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Continue your response to **QUESTION 6** on this page.

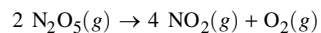
- (c) NO_2 is a molecule that contains an odd number of electrons and can be oxidized to form the NO_2^+ ion. In NO_2 , the unpaired electron is presumed to be localized on the nitrogen atom, as shown in the Lewis diagram in the box on the left.



- (i) In the box on the right, complete the Lewis diagram for NO_2^+ . Be sure to show all bonding and nonbonding electrons.
- (ii) A student makes the claim that the bond angles in NO_2 and NO_2^+ are different from each other. Do you agree or disagree with the student's claim? Justify your answer.

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The following equation represents the decomposition of N_2O_5 , for which the rate law is $\text{rate} = k[\text{N}_2\text{O}_5]$.

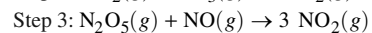
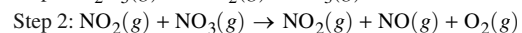
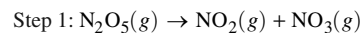


A sample of pure $\text{N}_2\text{O}_5(g)$ is placed in an evacuated container and allowed to decompose at a constant temperature of 300 K. The concentration of $\text{N}_2\text{O}_5(g)$ in the container is measured over a period of time, and the measurements are recorded in the following table.

Time (hr)	$[\text{N}_2\text{O}_5](M)$
0	0.160
1.67	0.0800
3.33	0.0400
5.00	0.0200

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

(b) The following mechanism is proposed for the decomposition of $\text{N}_2\text{O}_5(g)$.



Identify which step of the proposed mechanism (1, 2, or 3) is the rate-determining step. Justify your answer in terms of the rate law given.

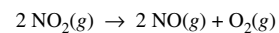
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Continue your response to **QUESTION 5** on this page.

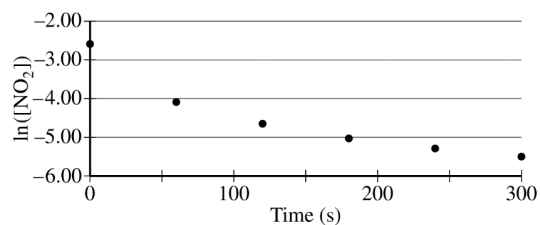
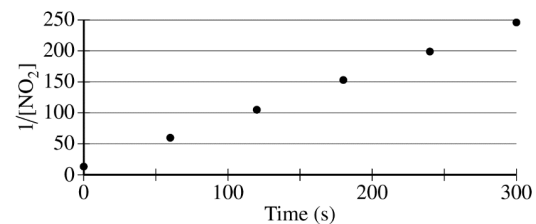
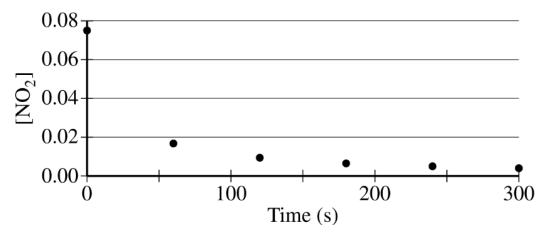
(c) If this experiment was repeated at the same temperature but with twice the initial concentration of N_2O_5 , would the value of k increase, decrease, or remain the same? Explain your reasoning.

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6. Nitrogen dioxide, $\text{NO}_2(g)$, is produced as a by-product of the combustion of fossil fuels in internal combustion engines. At elevated temperatures $\text{NO}_2(g)$ decomposes according to the equation below.



The concentration of a sample of $\text{NO}_2(g)$ is monitored as it decomposes and is recorded on the graph directly below. The two graphs that follow it are derived from the original data.

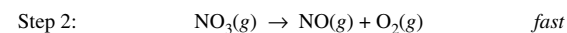
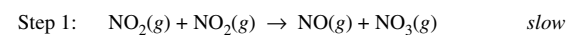


- (a) Explain how the graphs indicate that the reaction is second order.
- (b) Write the rate law for the decomposition of $\text{NO}_2(g)$.

- (c) Consider two possible mechanisms for the decomposition reaction.

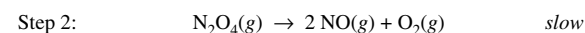
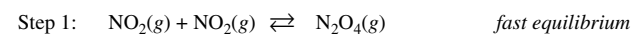
- (i) Is the rate law described by mechanism I shown below consistent with the rate law you wrote in part (b)? Justify your answer.

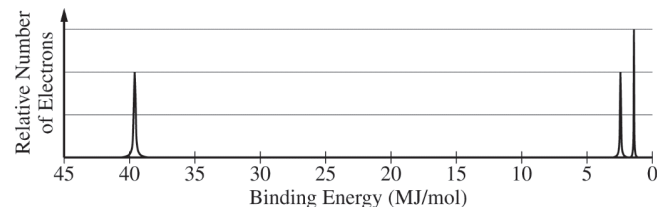
Mechanism I



- (ii) Is the rate law described by mechanism II shown below consistent with the rate law you wrote in part (b)? Justify your answer.

Mechanism II





7. The complete photoelectron spectrum of an element is represented above.

(a) Identify the element.

A radioactive isotope of the element decays with a half-life of 10. minutes.

(b) Calculate the value of the rate constant, k , for the radioactive decay. Include units with your answer.

(c) If 64 atoms of the radioactive isotope are originally present in a sample, what is the expected amount of time that will pass until only one atom of the isotope remains? Show how you arrived at your answer.

STOP

END OF EXAM

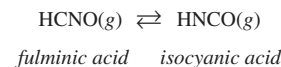
2. Answer the following questions about the isomers fulminic acid and isocyanic acid.

Two possible Lewis electron-dot diagrams for fulminic acid, HCNO, are shown below.



(a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

Fulminic acid can convert to isocyanic acid according to the equation below.



Fulminic Acid	Isocyanic Acid
$\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$	$\text{H}-\ddot{\text{N}}=\text{C}=\ddot{\text{O}}:$

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of ΔH° for the reaction of HCNO(g) to form HNCO(g).

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N–O	201	C=N	615	H–C	413
C=O	745	C≡N	891	H–N	391

(c) A student claims that ΔS° for the reaction is close to zero. Explain why the student's claim is accurate.

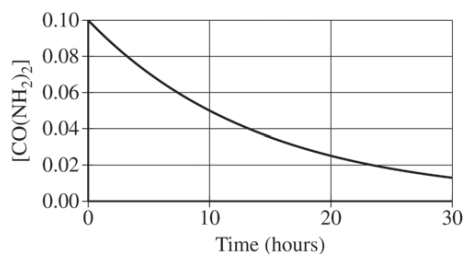
(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

The ammonium salt of isocyanic acid is a product of the decomposition of urea, $\text{CO}(\text{NH}_2)_2$, represented below.

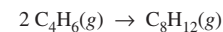


A student studying the decomposition reaction runs the reaction at 90°C. The student collects data on the concentration of urea as a function of time, as shown by the data table and the graph below.

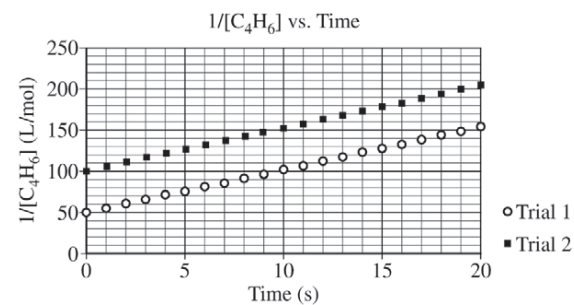
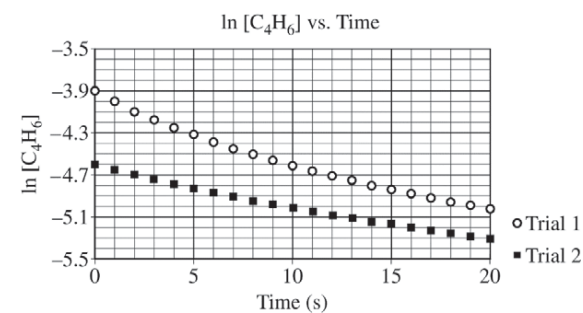
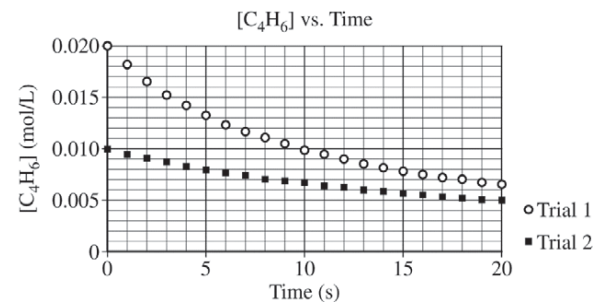
Time (hours)	[CO(NH ₂) ₂]
0	0.1000
5	0.0707
10	0.0500
15	0.0354
20	0.0250
25	0.0177
30	0.0125



- (e) The student proposes that the rate law is $rate = k[CO(NH_2)_2]$.
- Explain how the data support the student's proposed rate law.
 - Using the proposed rate law and the student's results, determine the value of the rate constant, k . Include units with your answer.
- (f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $OH^-(aq)$.

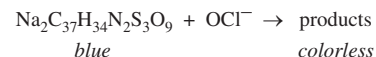


5. At high temperatures the compound C_4H_6 (1,3-butadiene) reacts according to the equation above. The rate of the reaction was studied at 625 K in a rigid reaction vessel. Two different trials, each with a different starting concentration, were carried out. The data were plotted in three different ways, as shown below.

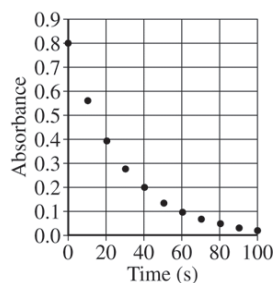


- (a) For trial 1, calculate the initial pressure, in atm, in the vessel at 625 K. Assume that initially all the gas present in the vessel is C_4H_6 .
- (b) Use the data plotted in the graphs to determine the order of the reaction with respect to C_4H_6 .
- (c) The initial rate of the reaction in trial 1 is $0.0010 \text{ mol/(L}\cdot\text{s)}$. Calculate the rate constant, k , for the reaction at 625 K.

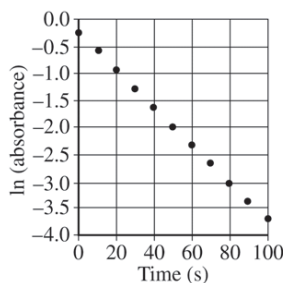
AP Chemistry: 2015



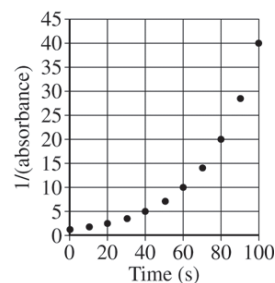
5. Blue food coloring can be oxidized by household bleach (which contains OCl^-) to form colorless products, as represented by the equation above. A student used a spectrophotometer set at a wavelength of 635 nm to study the absorbance of the food coloring over time during the bleaching process. In the study, bleach is present in large excess so that the concentration of OCl^- is essentially constant throughout the reaction. The student used data from the study to generate the graphs below.



Graph I



Graph II

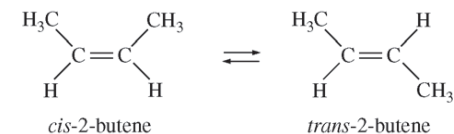


Graph III

- (a) Based on the graphs above, what is the order of the reaction with respect to the blue food coloring?
- (b) The reaction is known to be first order with respect to bleach. In a second experiment, the student prepares solutions of food coloring and bleach with concentrations that differ from those used in the first experiment. When the solutions are combined, the student observes that the reaction mixture reaches an absorbance near zero too rapidly. In order to correct the problem, the student proposes the following three possible modifications to the experiment.
- Increasing the temperature
 - Increasing the concentration of the food coloring
 - Increasing the concentration of the bleach

Circle the one proposed modification above that could correct the problem, and explain how that modification increases the time for the reaction mixture to reach an absorbance near zero.

- (c) In another experiment, a student wishes to study the oxidation of red food coloring with bleach. How would the student need to modify the original experimental procedure to determine the order of the reaction with respect to the red food coloring?



7. The half-life ($t_{1/2}$) of the catalyzed isomerization of *cis*-2-butene gas to produce *trans*-2-butene gas, represented above, was measured under various conditions, as shown in the table below.

Trial Number	Initial $P_{\text{cis-2-butene}}$ (torr)	V (L)	T (K)	$t_{1/2}$ (s)
1	300.	2.00	350.	100.
2	600.	2.00	350.	100.
3	300.	4.00	350.	100.
4	300.	2.00	365	50.

- (a) The reaction is first order. Explain how the data in the table are consistent with a first-order reaction.
- (b) Calculate the rate constant, k , for the reaction at 350. K. Include appropriate units with your answer.
- (c) Is the initial rate of the reaction in trial 1 greater than, less than, or equal to the initial rate in trial 2? Justify your answer.
- (d) The half-life of the reaction in trial 4 is less than the half-life in trial 1. Explain why, in terms of activation energy.

STOP

END OF EXAM