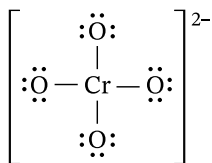


Question 2: Version J

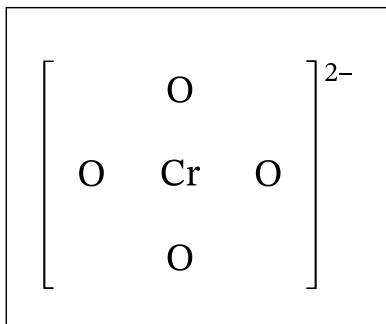
2. Answer the following questions about the chromate ion, CrO_4^{2-} , and the dichromate ion, $\text{Cr}_2\text{O}_7^{2-}$.

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

- i. Based on VSEPR theory, **predict** the molecular geometry of the CrO_4^{2-} ion.
- ii. 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.

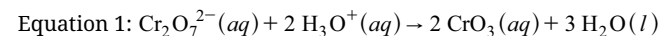
Figure 2**Part B**

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.

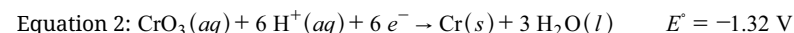
- i. **Write** a balanced net ionic equation for the reaction between $\text{CrO}_4^{2-}(aq)$ and a strong acid.
- ii. Is the reaction a redox reaction? **Justify** your answer based on the oxidation number of Cr.

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**

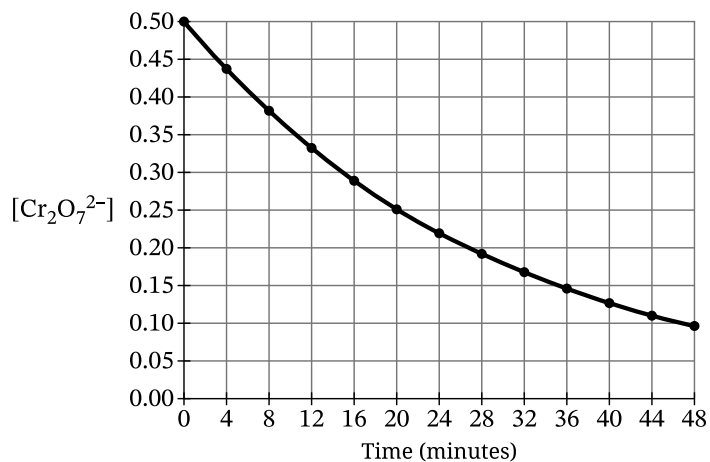
Is the reaction represented by Equation 2 thermodynamically favorable or unfavorable under standard conditions? **Justify** your answer with a calculation of ΔG° . Show the work that leads to your answer.

Part D

Calculate the number of grams of 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

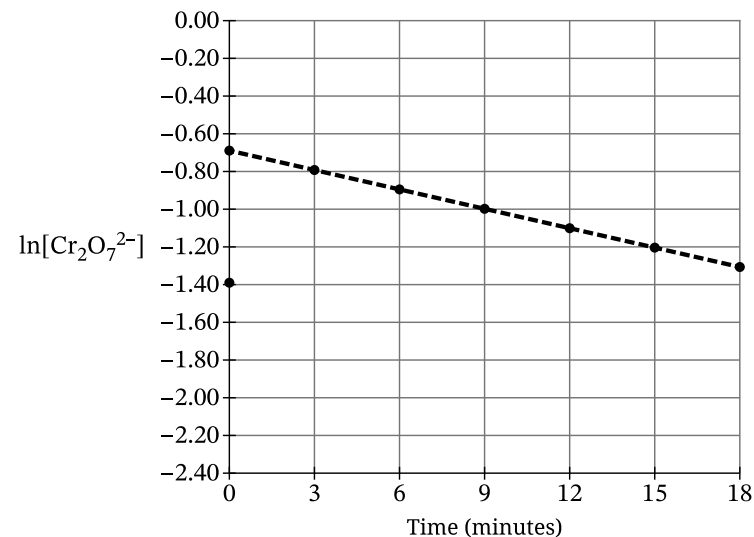
In a separate experiment, an iron wire is placed directly in a solution of $0.50\text{ M Cr}_2\text{O}_7^{2-}(aq)$ with $\text{pH} = 1.99$. The concentration of $\text{Cr}_2\text{O}_7^{2-}(aq)$ remaining is recorded over time, and the results are presented in Figure 3.

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.

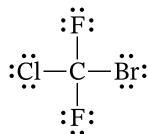
Part G

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.

Question 5

The following information applies to parts A and B.

5. The Lewis diagram of CBrClF_2 is shown.

**Part A**

Which of the bonds in CBrClF_2 (C–Br, C–Cl, or C–F) is the most polar? **Justify** your answer.

Part B

In a molecule of CBrClF_2 , the F–C–F bond angle is 106.8° and the Br–C–Cl bond angle is 112.3° . **Explain** the difference in bond angles using principles of atomic structure and VSEPR theory.

Part C

Lewis diagrams and boiling points for CBr_4 and CBrClF_2 are given in the following table.

Formula	CBr_4	CBrClF_2
Lewis diagram	<pre> :Br: :Br—C—Br: :Br: </pre>	<pre> :F: :Cl—C—Br: :F: </pre>
Boiling point	463 K	269 K

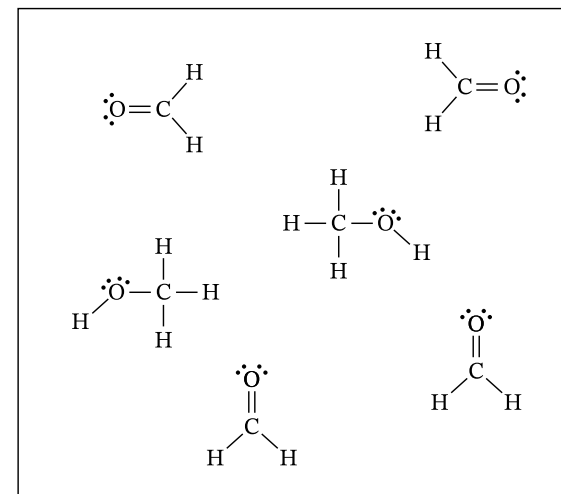
i. Clearly **identify** all the intermolecular forces in pure $\text{CBr}_4(l)$ and in pure $\text{CBrClF}_2(l)$.

$\text{CBr}_4(l)$:

$\text{CBrClF}_2(l)$:

ii. In terms of the relative strengths of all the intermolecular forces, **explain** why pure $\text{CBr}_4(l)$ has a higher boiling point than pure $\text{CBrClF}_2(l)$ does.

4. A scientist is investigating the properties of a mixture of CH_3OH and H_2CO . The scientist generates the following diagram to represent the mixture.



A. Identify the hybridization of the valence orbitals of the C atom in the H_2CO molecule.

B. In the diagram provided, draw a SINGLE dashed line (---) to represent a strong hydrogen-bonding attraction between one CH_3OH molecule and one H_2CO molecule in the mixture.

C. The scientist plans to cool a gaseous mixture of CH_3OH and H_2CO to form a liquid mixture and finds data on the two compounds. The data are summarized in the table.

Substance	Melting Point (K)	Boiling Point (K)	Enthalpy of Vaporization (kJ/mol)
CH_3OH	176	338	37.6
H_2CO	181	254	24.2

i. Propose a temperature to which the mixture should be cooled such that CH_3OH and H_2CO will both be liquids.

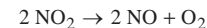
ii. The scientist analyzes the mixture after it is cooled and determines that 8.59 g of $\text{CH}_3\text{OH}(l)$ is present. Calculate the amount of thermal energy, in kJ, that was removed to condense the 8.59 g of CH_3OH (molar mass 32.04 g/mol) at its boiling point.

5. Complete Lewis diagrams and some physical properties for compounds X and Y are given.

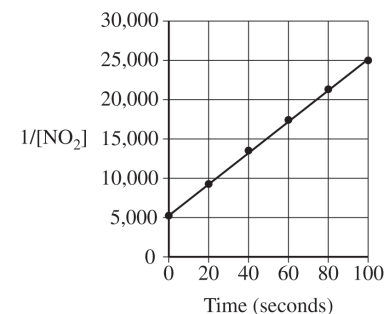
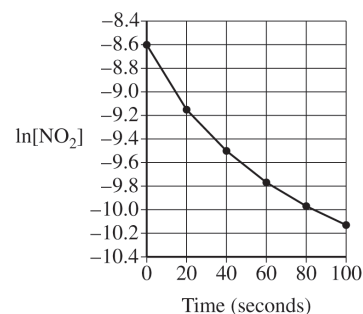
Compound	X	Y
Lewis diagram		
Molar mass	74.1 g/mol	90.2 g/mol
Boiling point	82°C	98°C

- A. Based on VSEPR theory, predict the geometry around the Si atom in compound Y.
- B. A student claims that compound Y has a higher boiling point than that of compound X because compound Y has stronger London dispersion forces. Do you agree or disagree? Justify your answer.
- C. An equimolar mixture of the two compounds is heated. When the mixture reaches 82°C, which compound will have the higher vapor pressure? Justify your answer.
- D. The mixture is heated to 198°C in a sealed, rigid 12.5 L container, at which point both substances are gases and the total pressure in the container is 2.30 atm. Calculate the number of moles of gas particles in the container.

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 $\text{rate} = k[\text{NO}_2]^2$.

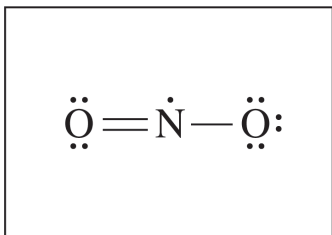
(a) Explain how the graphs indicate that the reaction is second order with respect to NO_2 .

(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.

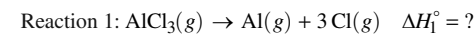
- (c) NO_2 is a molecule that contains an odd number of electrons and can be oxidized to form the NO_2^+ ion. In NO_2 , the unpaired electron is presumed to be localized on the nitrogen atom, as shown in the Lewis diagram in the box on the left.



- (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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2. In the gas phase, AlCl_3 is a molecular substance. A reaction of gaseous AlCl_3 at high temperature is represented by the following balanced equation.



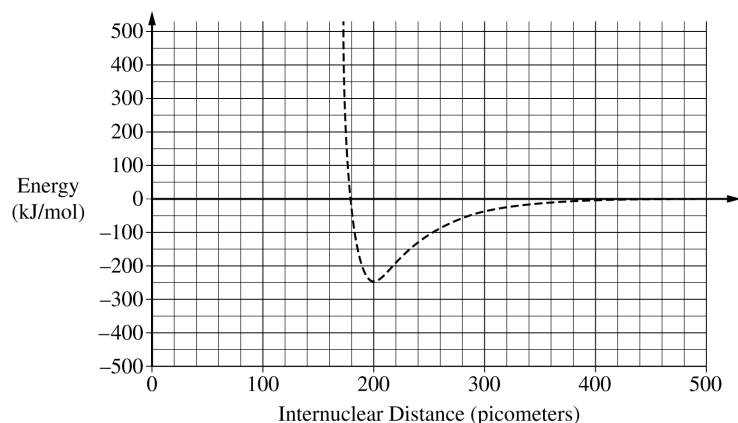
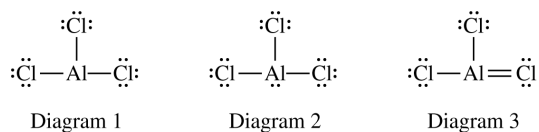
- (a) How many grams of $\text{Cl}(g)$ can be formed from 1.25 mol of $\text{AlCl}_3(g)$?

Additional reactions that involve Al or Cl are shown in the following table.

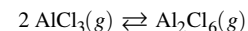
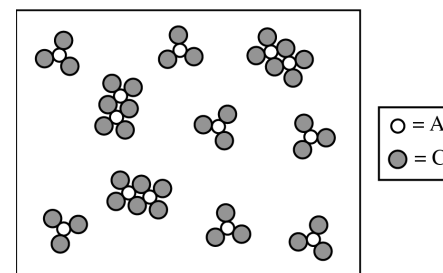
Reaction Number	Equation	ΔH_{rxn}° (kJ/mol _{rxn})
2	$\text{Al}(s) + \frac{3}{2} \text{Cl}_2(g) \rightarrow \text{AlCl}_3(g)$	-583
3	$\text{Al}(s) \rightarrow \text{Al}(g)$	+326
4	$\text{Cl}_2(g) \rightarrow 2 \text{Cl}(g)$	+243

- (b) Calculate the value of ΔH_1° , in kJ/mol_{rxn}, for reaction 1 above using reactions 2, 3, and 4.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 1** on this page.(c) A potential energy diagram for Cl_2 is shown in the following graph.(i) Based on the graph, what is the bond length, in picometers, for Cl_2 ? _____(ii) A student finds that the average $\text{Al} - \text{Cl}$ bond length is 220 picometers and the average bond energy is 425 kJ/mol. Draw the potential energy curve for the average $\text{Al} - \text{Cl}$ bond on the preceding graph.(d) Three proposed Lewis diagrams for the $\text{AlCl}_3(g)$ molecule are shown.(i) The $\text{AlCl}_3(g)$ molecule has a trigonal planar geometry. Which diagram (1, 2, or 3) can be eliminated based on geometry? Justify your choice based on VSEPR theory.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 2** on this page.(ii) Which of the three diagrams is the best representation for the bonding in AlCl_3 ? Justify your choice based on formal charges. AlCl_3 is known to dimerize reversibly in the gas phase. The dimerization equilibrium is represented by the following equation.(e) Write the expression for the equilibrium constant, K_p , for this reaction.A particle-level diagram of an equilibrium mixture of $\text{AlCl}_3(g)$ and $\text{Al}_2\text{Cl}_6(g)$ at 400°C in a 25 L closed container is shown.(f) Using the particle-level diagram, calculate the value of K_p for the reaction if the total pressure in the container is 22.1 atm.

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. A Lewis electron-dot diagram of the oxalate ion, $\text{C}_2\text{O}_4^{2-}$, is shown.

(a) Identify the hybridization of the valence orbitals of either carbon atom in the oxalate ion.

(b) Silver oxalate, $\text{Ag}_2\text{C}_2\text{O}_4(s)$, is slightly soluble in water. The value of K_{sp} for $\text{Ag}_2\text{C}_2\text{O}_4$ is 5.40×10^{-12} .

(i) Write the expression for the solubility-product constant, K_{sp} , for $\text{Ag}_2\text{C}_2\text{O}_4$.

(ii) Calculate the molar solubility of $\text{Ag}_2\text{C}_2\text{O}_4$ in neutral distilled water.

(iii) The molar solubility of $\text{Ag}_2\text{C}_2\text{O}_4$ increases when it is dissolved in $0.5\text{ M HClO}_4(aq)$ instead of neutral distilled water. Write a balanced, net-ionic equation for the process that occurs between species in solution that contributes to the increased solubility of $\text{Ag}_2\text{C}_2\text{O}_4(aq)$ in $\text{HClO}_4(aq)$.

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STOP

END OF EXAM

CHEMISTRY

Section II

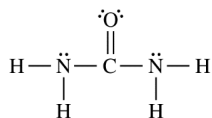
Time—1 hour and 45 minutes

7 Questions

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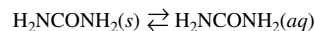
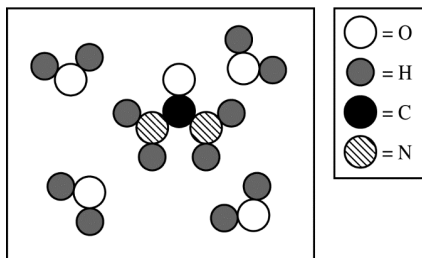
Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

Write your response in the space provided following each question. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.



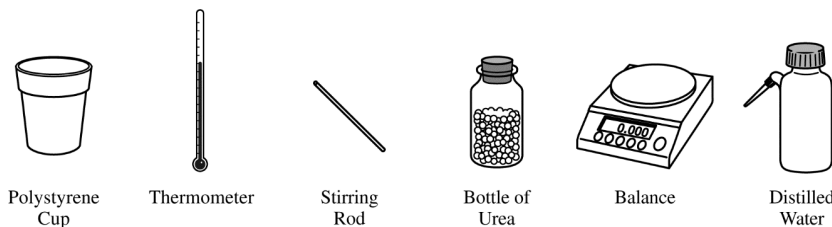
1. The compound urea, H_2NCONH_2 , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

- (a) Identify the hybridization of the valence orbitals of the carbon atom in the urea molecule.
- (b) Urea has a high solubility in water, due in part to its ability to form hydrogen bonds. A urea molecule and four water molecules are represented in the box below. Draw ONE dashed line (----) to indicate a possible location of a hydrogen bond between a water molecule and the urea molecule.



The dissolution of urea is represented by the equation above. A student determines that 5.39 grams of H_2NCONH_2 (molar mass 60.06 g/mol) can dissolve in water to make 5.00 mL of a saturated solution at 20.°C.

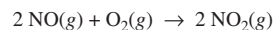
- (c) Calculate the concentration of urea, in mol/L, in the saturated solution at 20.°C.
- (d) The student also determines that the concentration of urea in a saturated solution at 25°C is 19.8 *M*. Based on this information, is the dissolution of urea endothermic or exothermic? Justify your answer in terms of Le Chatelier's principle.



- (e) The equipment shown above is provided so that the student can determine the value of the molar heat of solution for urea. Knowing that the specific heat of the solution is 4.18 J/(g·°C), list the specific measurements that are required to be made during the experiment.

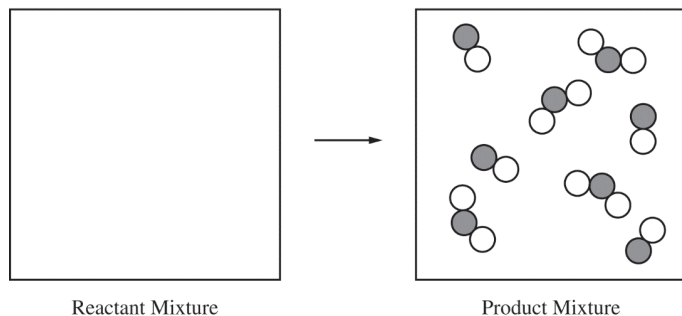
	S° (J/(mol·K))
$\text{H}_2\text{NCONH}_2(s)$	104.6
$\text{H}_2\text{NCONH}_2(aq)$	?

- (f) The entropy change for the dissolution of urea, $\Delta S^\circ_{\text{soln}}$, is 70.1 J/(mol·K) at 25°C. Using the information in the table above, calculate the absolute molar entropy, S° , of aqueous urea.
- (g) Using particle-level reasoning, explain why $\Delta S^\circ_{\text{soln}}$ is positive for the dissolution of urea in water.
- (h) The student claims that ΔS° for the process contributes to the thermodynamic favorability of the dissolution of urea at 25°C. Use the thermodynamic information above to support the student's claim.

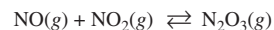


2. A student investigates the reactions of nitrogen oxides. One of the reactions in the investigation requires an equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$, which the student produces by using the reaction represented above.

- (a) The particle-level representation of the equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$ in the flask at the completion of the reaction between $\text{NO}(g)$ and $\text{O}_2(g)$ is shown below in the box on the right. In the box below on the left, draw the particle-level representation of the reactant mixture of $\text{NO}(g)$ and $\text{O}_2(g)$ that would yield the product mixture shown in the box on the right. In your drawing, represent oxygen atoms and nitrogen atoms as indicated below.



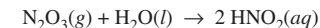
The student reads in a reference text that $\text{NO}(g)$ and $\text{NO}_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.



ΔH_{298}°	ΔS_{298}°	ΔG_{298}°
$-40.4 \text{ kJ/mol}_{\text{rxn}}$	$-138.5 \text{ J/(K} \cdot \text{mol}_{\text{rxn}})$	$0.87 \text{ kJ/mol}_{\text{rxn}}$

- (b) The student begins with an equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$ in a rigid reaction vessel and the mixture reaches equilibrium at 298 K.
- Calculate the value of the equilibrium constant, K , for the reaction at 298 K.
 - If both P_{NO} and P_{NO_2} in the vessel are initially 1.0 atm, will $P_{\text{N}_2\text{O}_3}$ at equilibrium be equal to 1.0 atm? Justify your answer.
- (c) The student hypothesizes that increasing the temperature will increase the amount of $\text{N}_2\text{O}_3(g)$ in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

$\text{N}_2\text{O}_3(g)$ reacts with water to form nitrous acid, $\text{HNO}_2(aq)$, a compound involved in the production of acid rain. The reaction is represented below.



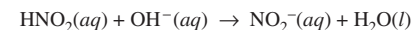
(d) The skeletal structure of the HNO_2 molecule is shown in the box below.

- (i) Complete the Lewis electron-dot diagram of the HNO_2 molecule in the box below, including any lone pairs of electrons.

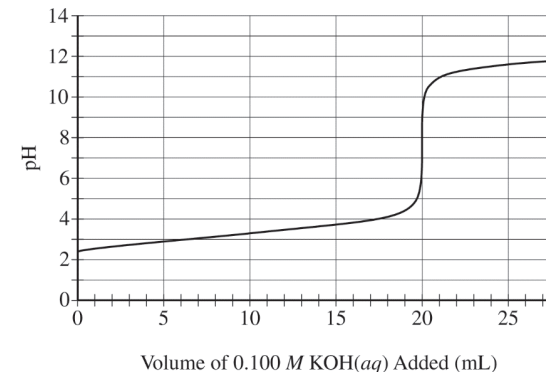


- (ii) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the HNO_2 molecule.

To produce an aqueous solution of HNO_2 , the student bubbles $\text{N}_2\text{O}_3(g)$ into distilled water. Assume that the reaction goes to completion and that HNO_2 is the only species produced. To determine the concentration of $\text{HNO}_2(aq)$ in the resulting solution, the student titrates a 100. mL sample of the solution with 0.100 M $\text{KOH}(aq)$. The neutralization reaction is represented below.



The following titration curve shows the change in pH of the solution during the titration.



- (e) Use the titration curve and the information above to
- determine the initial concentration of the $\text{HNO}_2(aq)$ solution
 - estimate the value of $\text{p}K_a$ for $\text{HNO}_2(aq)$
- (f) During the titration, after a volume of 15 mL of 0.100 M $\text{KOH}(aq)$ has been added, which species, $\text{HNO}_2(aq)$ or $\text{NO}_2^-(aq)$, is present at a higher concentration in the solution? Justify your answer.

CHEMISTRY

Section II

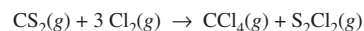
7 Questions

Time—1 hour and 45 minutes

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

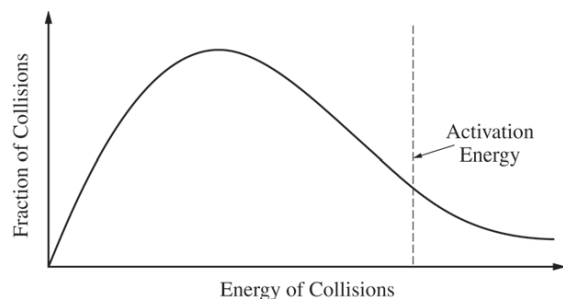
Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

Write your response in the space provided following each question. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. Pay attention to significant figures.



1. Carbon tetrachloride, $\text{CCl}_4(g)$, can be synthesized according to the reaction represented above. A chemist runs the reaction at a constant temperature of 120°C in a rigid 25.0 L container.

- (a) Chlorine gas, $\text{Cl}_2(g)$, is initially present in the container at a pressure of 0.40 atm.
- How many moles of $\text{Cl}_2(g)$ are in the container?
 - How many grams of carbon disulfide, $\text{CS}_2(g)$, are needed to react completely with the $\text{Cl}_2(g)$?
- (b) At 30°C the reaction is thermodynamically favorable, but no reaction is observed to occur. However, at 120°C , the reaction occurs at an observable rate.
- Explain how the higher temperature affects the collisions between the reactant molecules so that the reaction occurs at an observable rate at 120°C .
 - The graph below shows a distribution for the collision energies of reactant molecules at 120°C . Draw a second curve on the graph that shows the distribution for the collision energies of reactant molecules at 30°C .

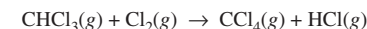


- (c) S_2Cl_2 is a product of the reaction.

- (i) In the box below, complete the Lewis electron-dot diagram for the S_2Cl_2 molecule by drawing in all of the electron pairs.

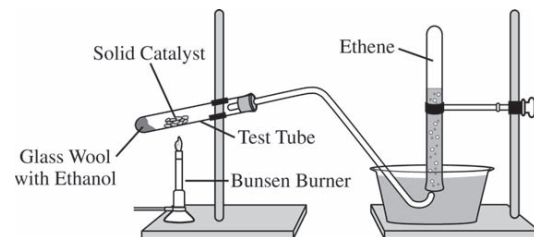


- (ii) What is the approximate value of the Cl-S-S bond angle in the S_2Cl_2 molecule that you drew in part (c)(i)? (If the two Cl-S-S bond angles are not equal, include both angles.)
- (d) $\text{CCl}_4(g)$ can also be produced by reacting $\text{CHCl}_3(g)$ with $\text{Cl}_2(g)$ at 400°C , as represented by the equation below.

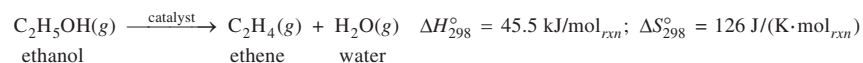


At the completion of the reaction a chemist successfully separates the $\text{CCl}_4(g)$ from the $\text{HCl}(g)$ by cooling the mixture to 70°C , at which temperature the $\text{CCl}_4(g)$ condenses while the $\text{HCl}(g)$ remains in the gaseous state.

- Identify all types of intermolecular forces present in $\text{HCl}(l)$.
- What can be inferred about the relative strengths of the intermolecular forces in $\text{CCl}_4(l)$ and $\text{HCl}(l)$? Justify your answer in terms of the information above.



2. Ethene, $\text{C}_2\text{H}_4(g)$ (molar mass 28.1 g/mol), may be prepared by the dehydration of ethanol, $\text{C}_2\text{H}_5\text{OH}(g)$ (molar mass 46.1 g/mol), using a solid catalyst. A setup for the lab synthesis is shown in the diagram above. The equation for the dehydration reaction is given below.



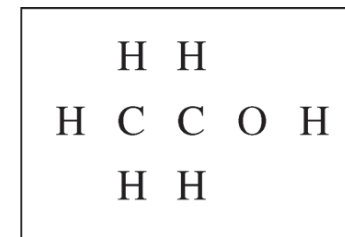
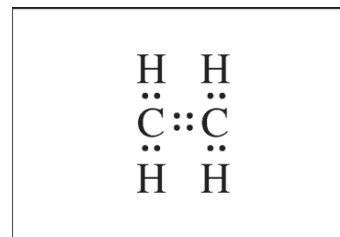
A student added a 0.200 g sample of $\text{C}_2\text{H}_5\text{OH}(l)$ to a test tube using the setup shown above. The student heated the test tube gently with a Bunsen burner until all of the $\text{C}_2\text{H}_5\text{OH}(l)$ evaporated and gas generation stopped. When the reaction stopped, the volume of collected gas was 0.0854 L at 0.822 atm and 305 K. (The vapor pressure of water at 305 K is 35.7 torr.)

- (a) Calculate the number of moles of $\text{C}_2\text{H}_4(g)$
- that are actually produced in the experiment and measured in the gas collection tube and
 - that would be produced if the dehydration reaction went to completion.
- (b) Calculate the percent yield of $\text{C}_2\text{H}_4(g)$ in the experiment.

Because the dehydration reaction is not observed to occur at 298 K, the student claims that the reaction has an equilibrium constant less than 1.00 at 298 K.

- (c) Do the thermodynamic data for the reaction support the student's claim? Justify your answer, including a calculation of ΔG_{298}° for the reaction.

- (d) The Lewis electron-dot diagram for C_2H_4 is shown below in the box on the left. In the box on the right, complete the Lewis electron-dot diagram for $\text{C}_2\text{H}_5\text{OH}$ by drawing in all of the electron pairs.



- (e) What is the approximate value of the C–O–H bond angle in the ethanol molecule?
- (f) During the dehydration experiment, $\text{C}_2\text{H}_4(g)$ and unreacted $\text{C}_2\text{H}_5\text{OH}(g)$ passed through the tube into the water. The C_2H_4 was quantitatively collected as a gas, but the unreacted $\text{C}_2\text{H}_5\text{OH}$ was not. Explain this observation in terms of the intermolecular forces between water and each of the two gases.

Nonmetal	C	N	O	Ne	Si	P	S	Ar
Formula of Compound	CF ₄	NF ₃	OF ₂	No compound	SiF ₄	PF ₃	SF ₂	No compound

5. Some binary compounds that form between fluorine and various nonmetals are listed in the table above. A student examines the data in the table and poses the following hypothesis: the number of F atoms that will bond to a nonmetal is always equal to 8 minus the number of valence electrons in the nonmetal atom.

- (a) Based on the student's hypothesis, what should be the formula of the compound that forms between chlorine and fluorine?
- (b) In an attempt to verify the hypothesis, the student researches the fluoride compounds of the other halogens and finds the formula ClF₃. In the box below, draw a complete Lewis electron-dot diagram for a molecule of ClF₃.

- (c) Two possible geometric shapes for the ClF₃ molecule are trigonal planar and T-shaped. The student does some research and learns that the molecule has a dipole moment. Which of the two shapes is consistent with the fact that the ClF₃ molecule has a dipole moment? Justify your answer in terms of bond polarity and molecular structure.

In an attempt to resolve the existence of the ClF₃ molecule with the hypothesis stated above, the student researches the compounds that form between halogens and fluorine, and assembles the following list.

Halogen	Formula(s)
F	F ₂
Cl	
Br	BrF, BrF ₃ , BrF ₅
I	IF, IF ₃ , IF ₅ , IF ₇

- (d) Based on concepts of atomic structure and periodicity, propose a modification to the student's previous hypothesis to account for the compounds that form between halogens and fluorine.