Week 4

AP Chemistry

Homework bundle for this week

本周作业合集

exercises.lol

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AP Chemistry   Name: ____________   Score: ______

1. A metal transfers electrons to a nonmetal. What bond forms?
   - ☐ ionic
   - ☐ covalent
   - ☐ metallic
2. On a potential-energy versus distance curve, the bond length is at the...
   - ☐ lowest point of the well
   - ☐ far right where energy is zero
   - ☐ highest point
3. An ionic solid conducts electricity...
   - ☐ only when molten or dissolved
   - ☐ always, even as a solid
   - ☐ never, under any condition
4. What carries electric current through a solid metal?
   - ☐ delocalized electrons
   - ☐ moving positive ions
   - ☐ neutrons
5. What is the first step in drawing a Lewis diagram?
   - ☐ count the total valence electrons
   - ☐ guess the shape
   - ☐ add double bonds everywhere
6. A deeper potential-energy well means a stronger bond.

   ☐ True   ☐ False
7. How many valence electrons does CO_2 have? ($C = 4$, $O = 6$ each)

   ____
8. An oxygen atom (6 valence) has 4 lone electrons and 4 bonding electrons. Its formal charge?

   ____

9. A lattice of metal cations in a shared sea of electrons is a ______ bond.

____

10. A higher lattice energy generally means a higher melting point.

☐ True ☐ False

AP Chemistry

1. **ionic**

   Electron transfer between a metal and nonmetal makes an ionic bond.

2. **lowest point of the well**

   The minimum is the stable separation – the bond length.

3. **only when molten or dissolved**

   Ions must be free to move – that happens when melted or dissolved.

4. **delocalized electrons**

   Free (delocalized) electrons move and carry the charge.

5. **count the total valence electrons**

   You must know the total electron count before placing anything.

6. **True**

   The well depth is the bond energy needed to break the bond.

7. **16**

   $4 + 2 \times 6 = 16$ valence electrons.

8. **0**

   $FC = 6 - 4 - \frac{1}{2}(4) = 6 - 4 - 2 = 0$.

9. **metallic**

   This "sea of electrons" model describes a metallic bond.

10. **True**

    More energy holds the lattice, so more heat is needed to break it apart.

2.1 Types of Chemical Bonds

Name: ______________ Class: __________ Date: ____________ **Total: 11 marks**

KEY WORDS ionic 离子键 • covalent 共价键 • polar covalent 极性共价 • metallic 金属键 • electronegativity differe

Objective

Build the skills to answer exam questions on **types of chemical bonds** — deciding whether a bond is ionic, covalent, or metallic.

You must be able to:

- distinguish **ionic 离子键**, **covalent 共价键**, and **metallic 金属键** bonding
- use **electronegativity difference 电负性差** to classify a bond as ionic, polar covalent, or nonpolar covalent
- link bond type to the elements involved (metal + nonmetal, nonmetal + nonmetal, metal + metal)

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The three bond types

- **Ionic**: electrons **transferred** from a metal to a nonmetal, giving + and − ions that attract (e.g. NaCl).
- **Covalent**: electrons **shared** between nonmetals (e.g. H_2O).
- **Metallic**: metal atoms share a "sea" of delocalized electrons (e.g. copper).

■ Classifying by electronegativity difference

Let ΔEN be the difference in electronegativity:

- ΔEN large ($\gtrsim 1.7$): **ionic**;
- ΔEN moderate: **polar covalent 极性共价** (unequal sharing);
- $\Delta \text{EN} \approx 0$: **nonpolar covalent** (equal sharing).

■ A worked classification

HCl: H (2.1) and Cl (3.0), $\Delta \text{EN} = 0.9$ — a **polar covalent** bond, with Cl slightly negative. Cl_2: $\Delta \text{EN} = 0$, **nonpolar covalent**.

■ **Bonding continuum**

Bonding is a continuum: as ΔEN grows, sharing becomes more unequal, then a full transfer. Use the elements' positions (metal vs nonmetal) as a first guide.

2 Practice

Now apply the methods above.

2.1 State the bond type in KBr (K is a metal, Br a nonmetal). [1]

2.2 Classify the bond in O_2 as polar or nonpolar covalent, with a reason. [2]

2.3 For a bond between elements with $\Delta EN = 2.1$, state the likely bond type. [1]

3 Exam-style questions

3.1 Which compound is most likely to contain **ionic** bonds? [1]

- **A** CO_2
- **B** CH_4
- **C** MgO
- **D** N_2

3.2 Consider the bonds in HF and F_2 (electronegativities: H 2.1, F 4.0).

(a) Find ΔEN for each. [2]

(b) Classify each bond. [2]

3.3 Explain, in terms of electrons, how metallic bonding differs from ionic bonding. [2]

Solutions

2.1 Ionic.

2.2 Nonpolar covalent — two identical atoms, so $\Delta EN = 0$ and the electrons are shared equally.

2.3 Ionic.

3.1 **C** — MgO is a metal + nonmetal, so it is ionic; the others are nonmetal–nonmetal (covalent).

3.2 (a) HF: $|4.0 - 2.1| = 1.9$; F_2: 0. (b) HF polar covalent (or borderline ionic); F_2 nonpolar covalent.

3.3 In metallic bonding the electrons are **delocalized** and shared across all the metal atoms (a ”sea”); in ionic bonding electrons are **transferred** to form fixed + and − ions held by electrostatic attraction.

Question 5

The following information applies to parts A and B.

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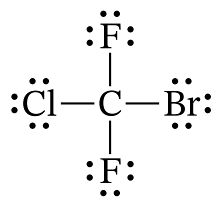
5. The Lewis diagram of $CBrClF_2$ is shown.



Part A

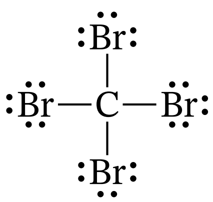
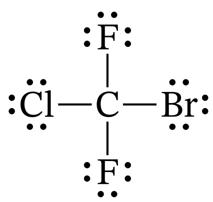
Which of the bonds in $CBrClF_2$ (C−Br, C−Cl, or C−F) is the most polar? **Justify** your answer.

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		
Boiling point	463 K	269 K

i. Clearly **identify** all the intermolecular forces in pure $CBr_4(l)$ and in pure $CBrClF_2(l)$.

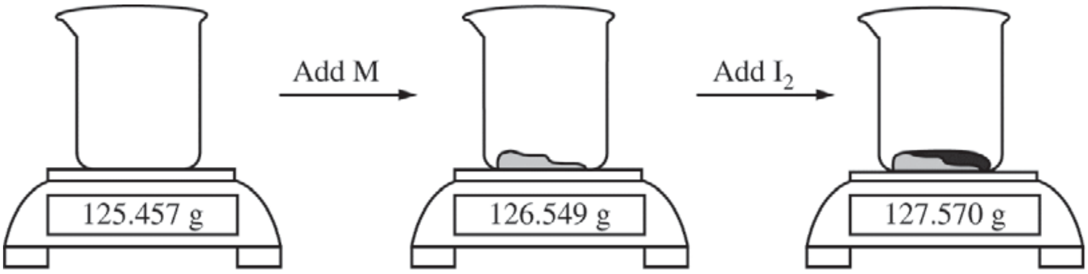
$CBr_4(l)$:

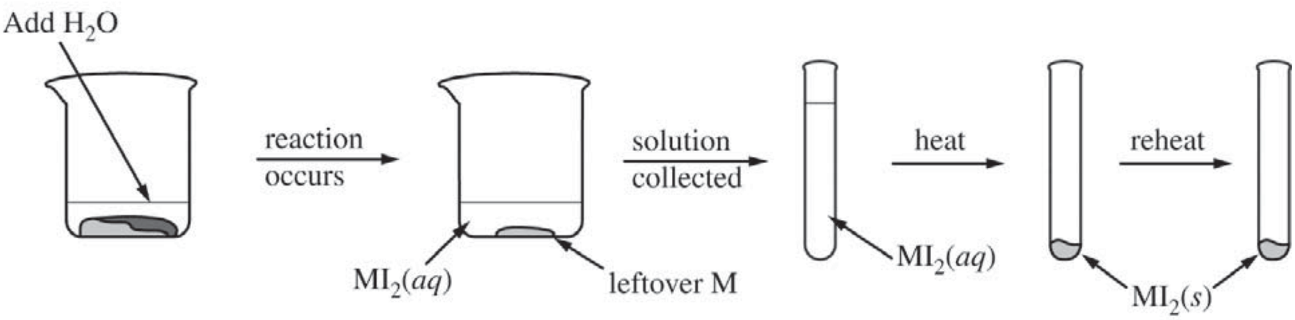
$CBrClF_2(l)$:

ii. In terms of the relative strengths of all the intermolecular forces, **explain** why pure $CBr_4(l)$ has a higher boiling point than pure $CBrClF_2(l)$ does.

$$M + I_2 \rightarrow MI_2$$

3. To determine the molar mass of an unknown metal, M, a student reacts iodine with an excess of the metal to form the water-soluble compound MI_2, as represented by the equation above. The reaction proceeds until all of the I_2 is consumed. The $MI_2(aq)$ solution is quantitatively collected and heated to remove the water, and the product is dried and weighed to constant mass. The experimental steps are represented below, followed by a data table.





Data for Unknown Metal Lab	
Mass of beaker	125.457 g
Mass of beaker + metal M	126.549 g
Mass of beaker + metal M + I_2	127.570 g
Mass of MI_2, first weighing	1.284 g
Mass of MI_2, second weighing	1.284 g

(a) Given that the metal M is in excess, calculate the number of moles of I_2 that reacted.

(b) Calculate the molar mass of the unknown metal M.

The student hypothesizes that the compound formed in the synthesis reaction is ionic.

(c) Propose an experimental test the student could perform that could be used to support the hypothesis. Explain how the results of the test would support the hypothesis if the substance was ionic.

The student hypothesizes that Br_2 will react with metal M more vigorously than I_2 did because Br_2 is a liquid at room temperature.

(d) Explain why I_2 is a solid at room temperature whereas Br_2 is a liquid. Your explanation should clearly reference the types and relative strengths of the intermolecular forces present in each substance.

While cleaning up after the experiment, the student wishes to dispose of the unused solid I_2 in a responsible manner. The student decides to convert the solid I_2 to $I^-(aq)$ anion. The student has access to three solutions, $H_2O_2(aq)$, $Na_2S_2O_3(aq)$, and $Na_2S_4O_6(aq)$, and the standard reduction table shown below.

Half reaction	$E°$ (V)
$S_4O_6^{2-}(aq) + 2\,e^- \rightarrow 2\,S_2O_3^{2-}(aq)$	0.08
$I_2(s) + 2\,e^- \rightarrow 2\,I^-(aq)$	0.54
$O_2(g) + 2\,H^+(aq) + 2\,e^- \rightarrow H_2O_2(aq)$	0.68

(e) Which solution should the student add to $I_2(s)$ to reduce it to $I^-(aq)$? Circle your answer below. Justify your answer, including a calculation of $E°$ for the overall reaction.

$H_2O_2(aq)$ $\quad$ $Na_2S_2O_3(aq)$ $\quad$ $Na_2S_4O_6(aq)$

(f) Write the balanced net-ionic equation for the reaction between I_2 and the solution you selected in part (e).

Compound	Melting Point (°C)
LiI	449
KI	686
LiF	845
NaF	993

6. A student learns that ionic compounds have significant covalent character when a cation has a polarizing effect on a large anion. As a result, the student hypothesizes that salts composed of small cations and large anions should have relatively low melting points.

(a) Select two compounds from the table and explain how the data support the student's hypothesis.

(b) Identify a compound from the table that can be dissolved in water to produce a basic solution. Write the net ionic equation for the reaction that occurs to cause the solution to be basic.

AP CHEMISTRY • EXERCISE SHEET

2.2 Intramolecular Force and Potential Energy

Name: ____________ Class: ________ Date: __________ **Total: 9 marks**

KEY WORDS bond length 键长 • potential energy 势能 • bond energy 键能 • ionic bond 离子键

Objective

Build the skills to answer exam questions on **intramolecular force and potential energy** — the Coulombic picture of a bond.

You must be able to:

- read a **potential-energy vs distance 势能-距离** curve for two atoms
- identify the **bond length 键长** (minimum) and **bond energy 键能** (well depth)
- link stronger bonds to deeper, narrower wells

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The potential-energy curve

As two atoms approach, attraction lowers the energy until repulsion of the nuclei takes over. The curve has a **minimum**: that distance is the **bond length**, and the depth of the well below zero is the **bond energy** (energy to separate the atoms).

■ Reading the curve

- The x-position of the minimum = bond length.
- The depth of the minimum = bond energy (how strongly bonded).
- To the left of the minimum, energy rises steeply — nuclei repel.

■ Comparing bonds

A **stronger** bond has a **deeper** well (larger bond energy) and usually a **shorter** bond length. A triple bond is deeper and shorter than a double, which is deeper and shorter than a single.

■ Coulomb's law link

Bond strength grows with the product of the charges and shrinks with distance ($E \propto \frac{q_1 q_2}{r}$). Smaller, more highly charged ions bond more strongly.

2 Practice

Now apply the methods above.

2.1 On a potential-energy curve, what does the position of the minimum represent? [1]

2.2 What does the depth of the well represent? [1]

2.3 Two bonds A and B have well depths 400 and 250 kJ/mol. Which is stronger? [1]

3 Exam-style questions

3.1 On a potential-energy vs distance curve, the bond length is the distance where the energy is [1]

- **A** zero
- **B** maximum
- **C** minimum
- **D** infinite

3.2 Two diatomic molecules have potential-energy curves. Molecule X has its minimum at 110 pm with depth 500 kJ/mol; molecule Y at 130 pm with depth 300 kJ/mol.

(a) Which has the shorter bond? [1]

(b) Which has the stronger bond? [1]

(c) State the relationship between bond length and bond strength suggested here. [1]

3.3 Using Coulomb's law, explain why the ionic bond in MgO (ions 2+ and 2−) is stronger than in NaCl (ions 1+ and 1−). [2]

Solutions

2.1 The bond length (the equilibrium separation of the atoms).

2.2 The bond energy — the energy needed to break the bond.

2.3 A (deeper well, 400 kJ/mol).

3.1 **C** — the bond length is at the energy minimum.

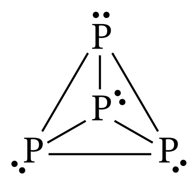
3.2 (a) X (110 pm). (b) X (500 kJ/mol). (c) Shorter bonds tend to be stronger.

3.3 Coulomb's law $E \propto \frac{q_1 q_2}{r}$: MgO has charges $2 \times 2 = 4$ vs $1 \times 1 = 1$ for NaCl, so the attraction (and bond strength) is much greater.

Question 4

4. White phosphorus, $P_4(g)$, can decompose into $P_2(g)$ at elevated temperatures. A balanced chemical equation, K_p expression, and Lewis diagrams for the chemical species involved in the reaction are given.

$$P_4(g) \rightleftarrows 2\,P_2(g) \qquad K_p = \frac{(P_{P_2})^2}{P_{P_4}} = \ ?$$

Compound	P_4	P_2
Lewis diagram		$:P{\equiv}P:$

Part A

The average bond length in P_4 molecules is 221 pm, whereas the average bond length in P_2 molecules is 189 pm. **Explain** why the average bond length in P_4 is greater than the average bond length in P_2.

Part B

A sample of $P_4(s)$ is placed in a sealed rigid container and heated to 1600. K, at which point the initial partial pressure of $P_4(g)$ is 0.470 atm. Some of the $P_4(g)$ decomposes into $P_2(g)$ as the system reaches equilibrium. At equilibrium, the partial pressure of $P_2(g)$ is determined to be 0.630 atm.

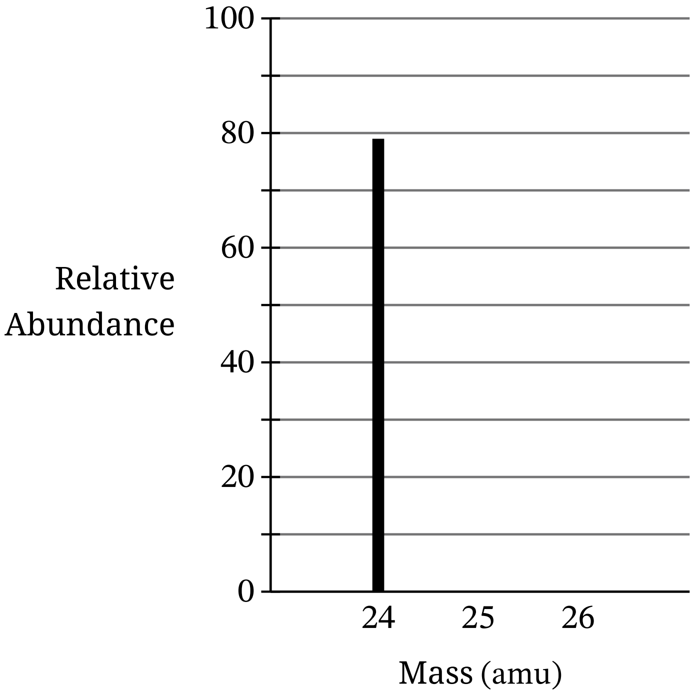
Calculate the value of the equilibrium constant, K_p, for the reaction at 1600. K. Show the work that leads to your answer.

Part C

The reaction is thermodynamically favorable under standard conditions only at temperatures above 1500 K. A student claims that the reaction must be endothermic because it is favorable only at high temperatures. Do you agree or disagree? **Justify** your answer using ΔS°_{rxn} and ΔG°_{rxn}.

1. Answer the following questions about magnesium.

A. An incomplete mass spectrum for magnesium is shown in the diagram.

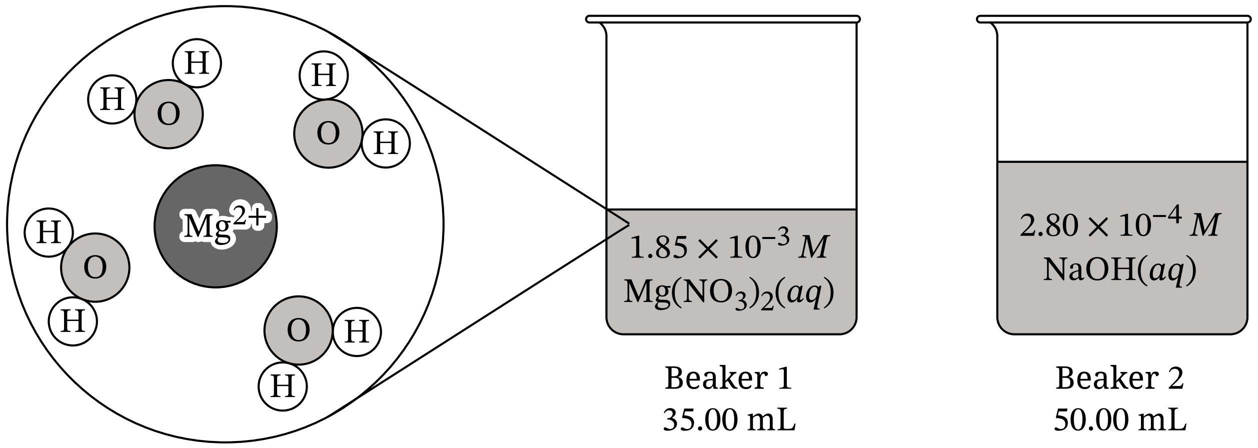


The percent abundance of magnesium-24 is 79%. The percent abundances of the other two natural isotopes of magnesium, magnesium-25 and magnesium-26, are approximately equal.

i. Complete the mass spectrum in part A by drawing thick lines in the appropriate locations to represent the percent abundance of magnesium-25 and magnesium-26.

ii. Describe the difference in atomic structure that accounts for the difference in mass between magnesium-25 and magnesium-26.

A student prepares a 1.85×10^{-3} M solution of $Mg(NO_3)_2(aq)$ in beaker 1 and a 2.80×10^{-4} M solution of $NaOH(aq)$ in beaker 2, as shown.



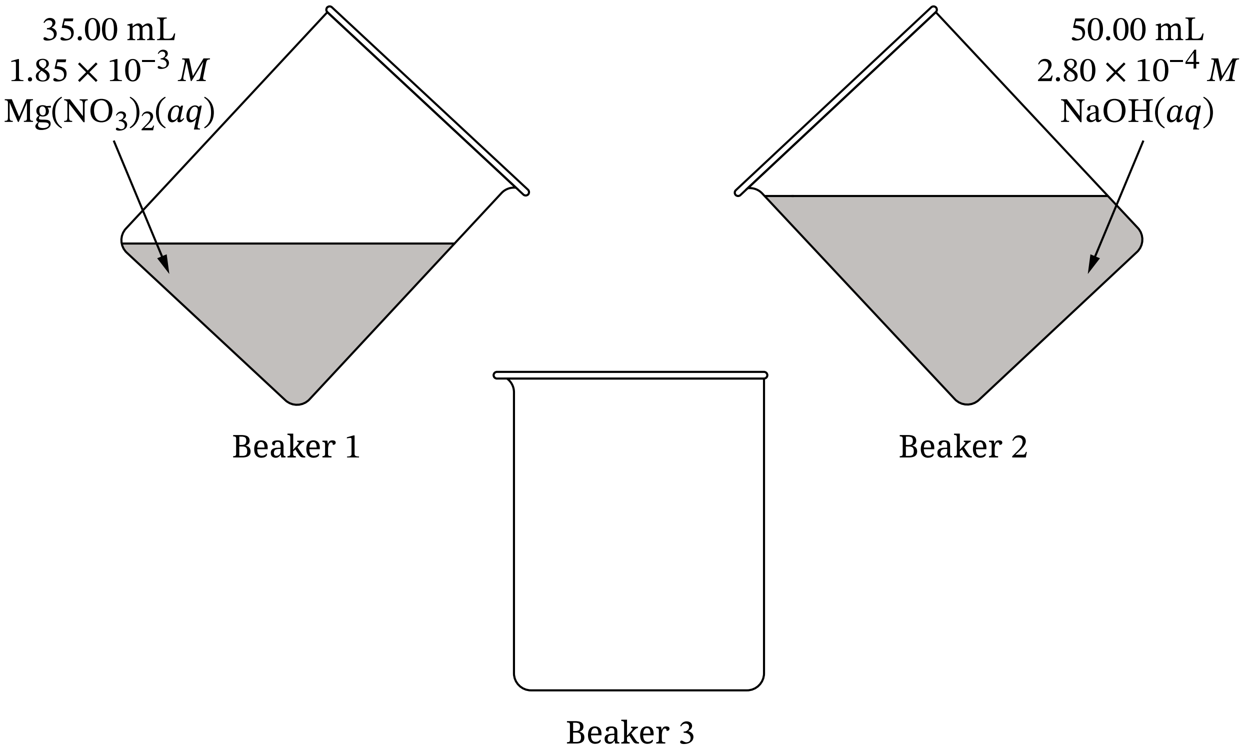
B. The particle diagram shown represents a magnesium ion, Mg^{2+}, in beaker 1. A sodium ion, Na^{+}, in beaker 2 has a weaker attraction to water than the Mg^{2+} does. Explain this phenomenon using Coulomb's law and each of the following.

i. The relative charge of the ions

ii. The relative radii of the ions

C. Calculate the pH of the solution in beaker 2.

D. A student combines 35.00 mL of 1.85×10^{-3} M $Mg(NO_3)_2(aq)$ with 50.00 mL of 2.80×10^{-4} M $NaOH(aq)$, as shown in the diagram. Calculate $[Mg^{2+}]$ after the two solutions are combined but before any reaction takes place. (Assume that volumes are additive.)



E. The dissolution of magnesium hydroxide is represented by the following equation.

$$Mg(OH)_2(s) \rightleftarrows Mg^{2+}(aq) + 2\ OH^-(aq) \quad K_{sp} = 5.61\times10^{-12}$$

i. Write the expression for the solubility product constant, K_{sp}.

ii. After the two solutions are combined in beaker 3 as described in part D, but before any reaction takes place, $[OH^-] = 1.65\times10^{-4}$ M. Using your answer to part D, calculate the value of the reaction quotient, Q.

iii. Using the reaction quotient, Q, predict whether a precipitate should form as the mixture in beaker 3 approaches equilibrium. Justify your answer.

F. In a separate experiment, the student adds $HNO_3(aq)$ to decrease the pH of a saturated solution containing undissolved $Mg(OH)_2(s)$. Does the amount of undissolved $Mg(OH)_2(s)$ increase, decrease, or remain the same as the $HNO_3(aq)$ is added? Justify your answer.

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.

$$\text{Reaction 1: } AlCl_3(g) \rightarrow Al(g) + 3\,Cl(g) \quad \Delta H_1^\circ = ?$$

(a) How many grams of $Cl(g)$ can be formed from 1.25 mol of $AlCl_3(g)$?

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

Reaction Number	Equation	ΔH°_{rxn} (kJ/mol$_{rxn}$)
2	$Al(s) + \frac{3}{2}\,Cl_2(g) \rightarrow AlCl_3(g)$	−583
3	$Al(s) \rightarrow Al(g)$	+326
4	$Cl_2(g) \rightarrow 2\,Cl(g)$	+243

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

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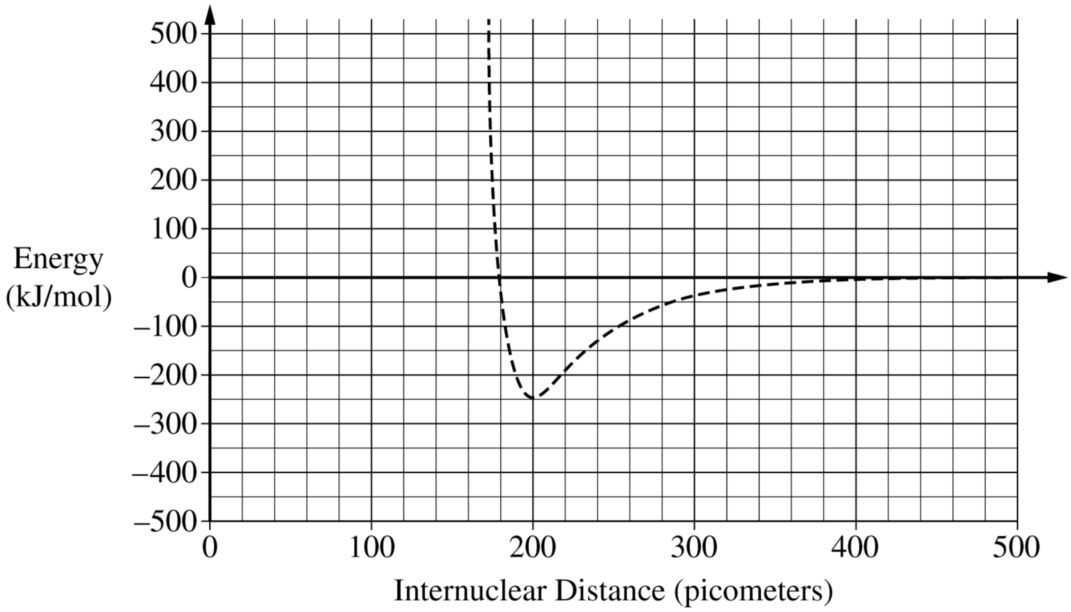
Continue your response to **QUESTION 2** on this page.

(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 Al – Cl bond length is 220 picometers and the average bond energy is 425 kJ/mol. Draw the potential energy curve for the average Al – Cl bond on the preceding graph.

(d) Three proposed Lewis diagrams for the $AlCl_3(g)$ molecule are shown.

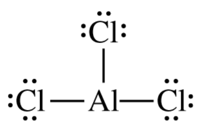


Diagram 1

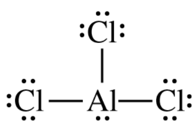


Diagram 2

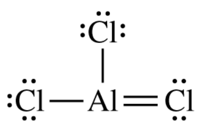


Diagram 3

(i) The $AlCl_3(g)$ 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.

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Continue your response to **QUESTION 2** on this page.

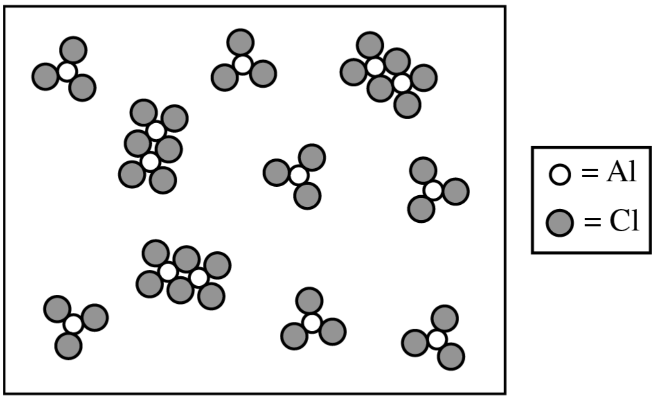
(ii) Which of the three diagrams is the best representation for the bonding in $AlCl_3$? Justify your choice based on formal charges.

$AlCl_3$ is known to dimerize reversibly in the gas phase. The dimerization equilibrium is represented by the following equation.

$$2\ AlCl_3(g) \rightleftarrows Al_2Cl_6(g)$$

(e) Write the expression for the equilibrium constant, K_p, for this reaction.

A particle-level diagram of an equilibrium mixture of $AlCl_3(g)$ and $Al_2Cl_6(g)$ 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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. Answer the following questions related to $HBr(l)$ and $HF(l)$.

(a) In the following table, list all of the types of intermolecular forces present in pure samples of $HBr(l)$ and $HF(l)$.

Liquid	$HBr(l)$	$HF(l)$
Intermolecular forces present		

(b) The enthalpy of vaporization, ΔH°_{vap}, for each liquid is provided in the following table.

Liquid	$HBr(l)$	$HF(l)$
ΔH°_{vap}	17.3 kJ / mol	25.2 kJ / mol

(i) Based on the types and relative strengths of intermolecular forces, explain why ΔH°_{vap} of $HF(l)$ is greater than that of $HBr(l)$.

(ii) Calculate the amount of thermal energy, in kJ, required to vaporize 6.85 g of $HF(l)$.

GO ON TO THE NEXT PAGE.

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

(c) Based on the arrangement of electrons in the Br and F atoms, explain why the bond length in an HBr molecule is greater than that in an HF molecule.

GO ON TO THE NEXT PAGE.

2. Answer the following questions relating to the chemistry of the halogens.

   (a) The molecular formulas of diatomic bromine, chlorine, fluorine, and iodine are written below. Circle the formula of the molecule that has the longest bond length. Justify your choice in terms of atomic structure.

   Br_2 $\qquad$ Cl_2 $\qquad$ F_2 $\qquad$ I_2

A chemistry teacher wants to prepare Br_2. The teacher has access to the following three reagents: $NaBr(aq)$, $Cl_2(g)$, and $I_2(s)$.

Half-Reaction	$E°$ at 25°C (V)
$Br_2 + 2\,e^- \rightarrow 2\,Br^-$	1.07
$Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$	1.36
$I_2 + 2\,e^- \rightarrow 2\,I^-$	0.53

   (b) Using the data in the table above, write the balanced equation for the thermodynamically favorable reaction that will produce Br_2 when the teacher combines two of the reagents. Justify that the reaction is thermodynamically favorable by calculating the value of $E°$ for the reaction.

Br_2 and Cl_2 can react to form the compound $BrCl$.

   (c) The boiling point of Br_2 is 332 K, whereas the boiling point of $BrCl$ is 278 K. Explain this difference in boiling point in terms of all the intermolecular forces present between molecules of <u>each</u> substance.

The compound $BrCl$ can decompose into Br_2 and Cl_2, as represented by the balanced chemical equation below.

$$2\,BrCl(g) \rightleftarrows Br_2(g) + Cl_2(g) \qquad \Delta H° = 1.6\ \text{kJ/mol}_{rxn}$$

A 0.100 mole sample of pure $BrCl(g)$ is placed in a previously evacuated, rigid 2.00 L container at 298 K. Eventually the system reaches equilibrium according to the equation above.

   (d) Calculate the pressure in the container before equilibrium is established.

   (e) Write the expression for the equilibrium constant, K_{eq}, for the decomposition of $BrCl$.

After the system has reached equilibrium, 42 percent of the original $BrCl$ sample has decomposed.

   (f) Determine the value of K_{eq} for the decomposition reaction of $BrCl$ at 298 K.

   (g) Calculate the bond energy of the Br-Cl bond, in kJ/mol, using $\Delta H°$ for the reaction (1.6 kJ/mol$_{rxn}$) and the information in the following table.

Bond	Bond Energy (kJ/mol)
Br – Br	193
Cl – Cl	243
Br – Cl	?

3. Answer the following questions relating to Fe and its ions, Fe^{2+} and Fe^{3+}.

(a) Write the ground-state electron configuration of the Fe^{2+} ion.

Ion	Ionic Radius (pm)
Fe^{2+}	92
Fe^{3+}	79

(b) The radii of the ions are given in the table above. Using principles of atomic structure, explain why the radius of the Fe^{2+} ion is larger than the radius of the Fe^{3+} ion.

(c) Fe^{3+} ions interact more strongly with water molecules in aqueous solution than Fe^{2+} ions do. Give one reason for this stronger interaction, and justify your answer using Coulomb's law.

A student obtains a solution that contains an unknown concentration of $Fe^{2+}(aq)$. To determine the concentration of $Fe^{2+}(aq)$ in the solution, the student titrates a sample of the solution with $MnO_4^-(aq)$, which converts $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$, as represented by the following equation.

$$5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) \rightarrow 5\ Fe^{3+}(aq) + Mn^{2+}(aq) + 4\ H_2O(l)$$

(d) Write the balanced equation for the half-reaction for the oxidation of $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$.

(e) The student titrates a 10.0 mL sample of the $Fe^{2+}(aq)$ solution. Calculate the value of $[Fe^{2+}]$ in the solution if it takes 17.48 mL of added 0.0350 M $KMnO_4(aq)$ to reach the equivalence point of the titration.

To deliver the 10.0 mL sample of the $Fe^{2+}(aq)$ solution in part (e), the student has the choice of using one of the pieces of glassware listed below.

- 25 mL buret
- 25 mL graduated cylinder
- 25 mL beaker
- 25 mL volumetric flask

(f) Explain why the 25 mL volumetric flask would be a poor choice to use for delivering the required volume of the $Fe^{2+}(aq)$ solution.

In a separate experiment, the student is given a sample of powdered $Fe(s)$ that contains an inert impurity. The student uses a procedure to oxidize the $Fe(s)$ in the sample to $Fe_2O_3(s)$. The student collects the following data during the experiment.

Mass of $Fe(s)$ with inert impurity	6.724 g
Mass of $Fe_2O_3(s)$ produced	7.531 g

(g) Calculate the number of moles of Fe in the $Fe_2O_3(s)$ produced.

(h) Calculate the percent by mass of Fe in the original sample of powdered $Fe(s)$ with the inert impurity.

(i) If the oxidation of the $Fe(s)$ in the original sample was incomplete so that some of the 7.531 g of product was $FeO(s)$ instead of $Fe_2O_3(s)$, would the calculated mass percent of $Fe(s)$ in the original sample be higher, lower, or the same as the actual mass percent of $Fe(s)$? Justify your answer.

AP CHEMISTRY • EXERCISE SHEET

2.3 Structure of Ionic Solids

Name: ______________ Class: __________ Date: ____________ **Total: 11 marks**

KEY WORDS lattice 晶格 • lattice energy 晶格能 • ionic solid 离子固体

Objective

Build the skills to answer exam questions on the **structure of ionic solids**.

You must be able to:

- describe an ionic solid as a **lattice 晶格** of alternating + and − ions
- explain properties (high melting point, brittle, conducts only when molten/dissolved) from the structure
- link **lattice energy 晶格能** to ion charge and size

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The ionic lattice

An ionic solid is a giant regular array (**lattice**) of cations and anions, each surrounded by ions of opposite charge. Strong electrostatic forces act in all directions.

■ Properties from structure

- **High melting point** — many strong ionic attractions must be broken.
- **Brittle** — a shifted layer puts like charges together, and they repel, cracking the crystal.
- **Conducts electricity only when molten or dissolved** — ions are then free to move; in the solid they are locked in place.

■ Lattice energy

The **lattice energy** (energy to separate the ions) rises with **larger ion charges** and **smaller ion sizes** ($E \propto \frac{q_1 q_2}{r}$). MgO has a much larger lattice energy than NaCl.

■ Predicting melting point

More lattice energy ⇒ higher melting point. Compare compounds by their ion charges first, then their sizes.

2 Practice

Now apply the methods above.

2.1 Why do ionic solids have high melting points? [1]

2.2 Why does solid NaCl not conduct electricity, but molten NaCl does? [2]

2.3 State two factors that increase lattice energy. [2]

3 Exam-style questions

3.1 An ionic solid conducts electricity when [1]

- **A** solid
- **B** molten or dissolved in water
- **C** cooled
- **D** never

3.2 Compare NaF and MgO.

(a) State which has the larger lattice energy, with a reason. [2]

(b) Predict which has the higher melting point. [1]

3.3 Explain why ionic solids are brittle, in terms of what happens when a layer of ions is shifted. [2]

Solutions

2.1 Many strong electrostatic attractions between oppositely charged ions must be overcome.

2.2 In the solid the ions are fixed in the lattice and cannot move; when molten the ions are free to move and carry charge.

2.3 Larger ion charges; smaller ion sizes.

3.1 **B** — when molten or dissolved, so the ions can move.

3.2 (a) MgO — its ions have charges $2+/2-$ vs $1+/1-$ for NaF, giving a much larger lattice energy. (b) MgO.

3.3 Shifting a layer brings ions of the **same** charge next to each other; they repel, so the crystal splits.

Question 7

The following information applies to parts A and B.

7. Sodium metal reacts with oxygen gas according to Equation 1.

$$\text{Equation 1: } 4\ \mathrm{Na}(s) + \mathrm{O_2}(g) \rightarrow 2\ \mathrm{Na_2O}(s) \qquad \Delta H^{\circ}_{rxn} = -828\ \mathrm{kJ/mol}_{rxn}$$

Standard enthalpies of formation are provided in Table 1.

Table 1

Substance	ΔH°_f (kJ/mol)
$Na(s)$	0
$O_2(g)$	0
$Na_2O(s)$	?

Part A

Based on the information given, **calculate** the value of ΔH°_f for $Na_2O(s)$. Show the work that leads to your answer.

Part B

An 18.4 g sample of $Na(s)$ reacts with 12.8 g of $O_2(g)$ according to Equation 1. **Calculate** the total amount of heat, in kilojoules, released during this process. Show the work that leads to your answer.

Part C

Lattice enthalpy can be defined as the energy required to separate an ionic crystal into gaseous ions. $Rb_2O\,(s)$ and $Na_2O\,(s)$ have similar crystal structures, and their lattice enthalpies are given in Table 2.

Table 2

Compound	Lattice Enthalpy (kJ/mol)
$Na_2O\,(s)$	2481
$Rb_2O\,(s)$	2163

Using Coulomb's law, **explain** why the lattice enthalpy of $Rb_2O\,(s)$ is smaller than that of $Na_2O\,(s)$.

STOP

END OF EXAM

6. A student is studying the properties of $CaSO_4$ and $PbSO_4$. The student has samples of both compounds, which are white powders.

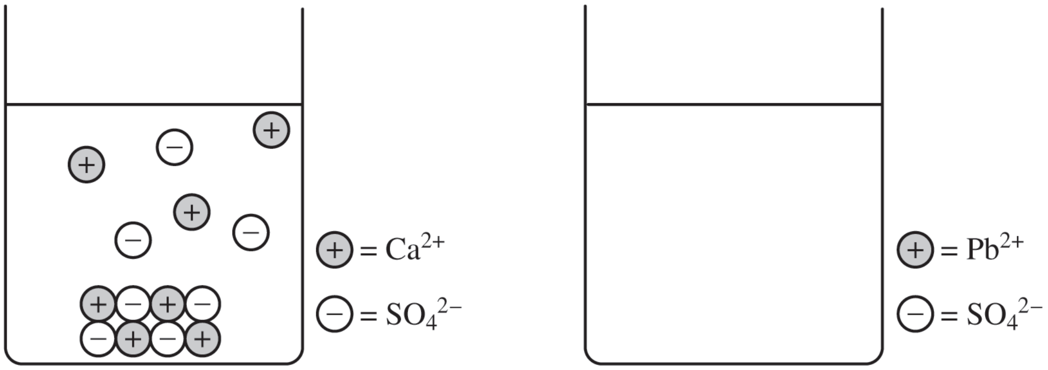
(a) The student tests the electrical conductivity of each solid and observes that neither solid conducts electricity. Describe the structures of the solids that account for their inability to conduct electricity.

The student places excess $CaSO_4(s)$ in a beaker containing $100\ \text{mL}$ of water and places excess $PbSO_4(s)$ in another beaker containing $100\ \text{mL}$ of water. The student stirs the contents of the beakers and then measures the electrical conductivity of the solution in each beaker. The student observes that the conductivity of the solution in the beaker containing the $CaSO_4(s)$ is higher than the conductivity of the solution in the beaker containing the $PbSO_4(s)$.

(b) Which compound is more soluble in water, $CaSO_4(s)$ or $PbSO_4(s)$? Justify your answer based on the results of the conductivity test.

GO ON TO THE NEXT PAGE.

The left side of the diagram below shows a particulate representation of the contents of the beaker containing the $CaSO_4(s)$ from the solution conductivity experiment.



Higher Conductivity Solution

Lower Conductivity Solution

(c) Draw a particulate representation of $PbSO_4(s)$ and the ions dissolved in the solution in the beaker on the right in the diagram. Draw the particles to look like those shown to the right of the beaker. Draw an appropriate number of dissolved ions relative to the number of dissolved ions in the beaker on the left.

(d) The student attempts to increase the solubility of $CaSO_4(s)$ by adding 10.0 mL of 2 M $H_2SO_4(aq)$ to the beaker, and observes that additional precipitate forms in the beaker. Explain this observation.

6. Answer the following questions about $Mg(OH)_2$. At 25°C, the value of the solubility product constant, K_{sp}, for $Mg(OH)_2(s)$ is 1.8×10^{-11}.

(a) Calculate the number of grams of $Mg(OH)_2$ (molar mass 58.32 g/mol) that is dissolved in 100. mL of a saturated solution of $Mg(OH)_2$ at 25°C.

(b) The energy required to separate the ions in the $Mg(OH)_2$ crystal lattice into individual $Mg^{2+}(g)$ and $OH^{-}(g)$ ions, as represented in the table below, is known as the lattice energy of $Mg(OH)_2(s)$. As shown in the table, the lattice energy of $Sr(OH)_2(s)$ is less than the lattice energy of $Mg(OH)_2(s)$. Explain why in terms of periodic properties and Coulomb's law.

Reaction	Lattice Energy (kJ/mol)
$Mg(OH)_2(s) \rightarrow Mg^{2+}(g) + 2\ OH^{-}(g)$	2900
$Sr(OH)_2(s) \rightarrow Sr^{2+}(g) + 2\ OH^{-}(g)$	2300

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. A student investigates the enthalpy of solution, ΔH_{soln}, for two alkali metal halides, LiCl and NaCl. In addition to the salts, the student has access to a calorimeter, a balance with a precision of ±0.1 g, and a thermometer with a precision of ±0.1°C.

   (a) To measure ΔH_{soln} for LiCl, the student adds 100.0 g of water initially at 15.0°C to a calorimeter and adds 10.0 g of LiCl(s), stirring to dissolve. After the LiCl dissolves completely, the maximum temperature reached by the solution is 35.6°C.

   (i) Calculate the magnitude of the heat absorbed by the solution during the dissolution process, assuming that the specific heat capacity of the solution is 4.18 J/(g·°C). Include units with your answer.

   (ii) Determine the value of ΔH_{soln} for LiCl in kJ/mol$_{rxn}$.

   To explain why ΔH_{soln} for NaCl is different than that for LiCl, the student investigates factors that affect ΔH_{soln} and finds that ionic radius and lattice enthalpy (which can be defined as the ΔH associated with the separation of a solid crystal into gaseous ions) contribute to the process. The student consults references and collects the data shown in the table below.

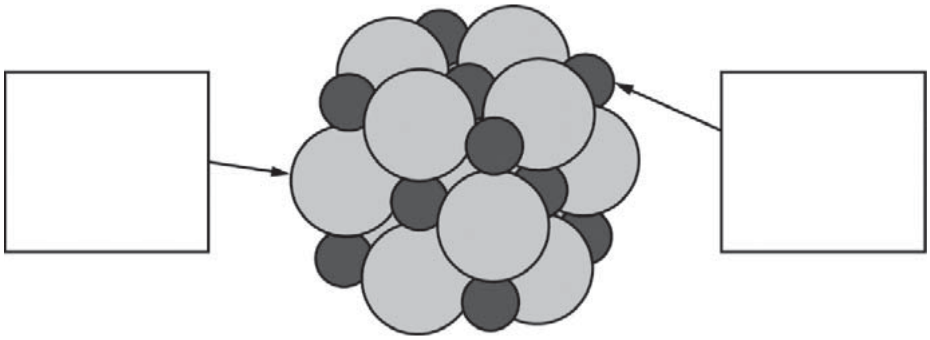
Ion	Ionic Radius (pm)
Li^+	76
Na^+	102

(b) Write the complete electron configuration for the Na^+ ion in the ground state.

(c) Using principles of atomic structure, explain why the Na^+ ion is larger than the Li^+ ion.

(d) Which salt, $LiCl$ or $NaCl$, has the greater lattice enthalpy? Justify your answer.

(e) Below is a representation of a portion of a crystal of $LiCl$. Identify the ions in the representation by writing the appropriate formulas (Li^+ or Cl^-) in the boxes below.



(f) The lattice enthalpy of $LiCl$ is positive, indicating that it takes energy to break the ions apart in $LiCl$. However, the dissolution of $LiCl$ in water is an exothermic process. Identify all particle-particle interactions that contribute significantly to the dissolution process being exothermic. For each interaction, include the particles that interact and the specific type of intermolecular force between those particles.

2.4 Structure of Metals and Alloys

Name: ______________ Class: __________ Date: ____________ **Total: 12 marks**

KEY WORDS alloy 合金 • delocalized 离域 • sea of delocalized electrons 离域电子 • metallic bond 金属键 • lattice 晶格

Objective

Build the skills to answer exam questions on the **structure of metals and alloys**.

You must be able to:

- describe metallic bonding as cations in a **sea of delocalized electrons** 离域电子
- explain metallic properties (conductive, malleable, ductile) from this model
- describe **interstitial** and **substitutional** alloys

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The electron-sea model

A metal is a lattice of **cations** immersed in a "sea" of **delocalized** valence electrons that move freely throughout the whole solid.

■ Properties from the model

- **Conducts electricity and heat** — the mobile electrons carry charge and energy.
- **Malleable and ductile** — layers of cations slide past one another while the electron sea keeps holding them together, so the metal bends rather than shatters.
- **Lustrous** — the free electrons reflect light.

■ Alloys

An **alloy** 合金 mixes a metal with other elements:

- **Substitutional** — similar-sized atoms replace some of the host atoms (e.g. brass: zinc in copper).
- **Interstitial** — small atoms fit in the **gaps** between the metal atoms (e.g. carbon in iron → steel).

> ■ **Why alloys are often harder**
> The different-sized atoms disrupt the regular layers, so they no longer slide easily — the alloy is **harder** and stronger than the pure metal.

2 Practice

Now apply the methods above.

2.1 What carries the electric current in a metal? [1]

2.2 Explain why metals are malleable. [2]

2.3 Name the two types of alloy. [2]

3 Exam-style questions

3.1 Metallic bonding is best described as [1]

- **A** shared pairs of electrons between two atoms
- **B** transfer of electrons to form ions
- **C** cations in a sea of delocalized electrons
- **D** no electron interaction

3.2 Steel is an alloy of iron and a small amount of carbon.

(a) State whether it is interstitial or substitutional, with a reason. [2]

(b) Explain why steel is harder than pure iron. [2]

3.3 Explain why metals conduct electricity in both the solid and molten states, unlike ionic compounds. [2]

Solutions

2.1 The delocalized (free) electrons.

2.2 Layers of metal cations can slide over each other while the delocalized electrons still hold them together, so the metal deforms without breaking.

2.3 Substitutional and interstitial.

3.1 **C** — cations in a sea of delocalized electrons.

3.2 (a) Interstitial — carbon atoms are much smaller than iron and fit in the gaps between iron atoms. (b) The carbon atoms disrupt the regular layers so they cannot slide easily, making the metal harder.

3.3 In a metal the delocalized electrons are mobile in both the solid and the molten state; an ionic compound needs its ions to move, which happens only when molten or dissolved.

Begin your response to **QUESTION 3** on this page.

3. Sterling silver is an alloy that is commonly used to make jewelry and consists of 92.5% silver and 7.5% other metals, such as copper, by mass. Over time, the alloy can form a tarnish of $Ag_2S(s)$ when it reacts with hydrogen sulfide, as represented by the following equation.

$$2\ Ag(s) + H_2S(g) \rightarrow Ag_2S(s) + H_2(g)$$

(a) What are the oxidation numbers of silver in $Ag(s)$ and $Ag_2S(s)$?

$Ag(s)$__________ $Ag_2S(s)$__________

(b) The following table contains the atomic radii for silver and copper.

Element	Silver (Ag)	Copper (Cu)
Atomic radius (pm)	165	145

(i) Explain why sterling silver is better classified as a substitutional alloy than as an interstitial alloy.

(ii) Using principles of atomic structure and Coulomb's law, explain why silver has a larger atomic radius than copper does.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

The Ag_2S tarnish on sterling silver can be removed until only sterling silver remains. A student weighs a tarnished sterling silver sample both before and after removing the $Ag_2S(s)$ (molar mass 247.80 g / mol) and records the data in the following table.

	Before Tarnish Removal	After Tarnish Removal
Mass	409.21 g	398.94 g

(c) Assuming that only $Ag_2S(s)$ is removed, calculate the number of moles of silver atoms removed.

Rhodium plating is a process used to protect sterling silver from tarnishing. This involves electroplating (depositing) solid rhodium, $Rh(s)$, onto the surface of the metal from an acidified solution of $Rh_2(SO_4)_3(aq)$. Oxygen gas is produced during this process.

(d) A table of half-reactions related to the overall reaction is provided.

Half-Reaction	$E°$ (V)
$Rh^{3+}(aq) + 3\,e^- \rightarrow Rh(s)$	+0.80
$O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)$	+1.23

(i) Write the balanced net ionic equation for plating $Rh(s)$ from the acidified $Rh_2(SO_4)_3(aq)$ solution.

(ii) Calculate the value of E°_{cell} for the reaction in part (d)(i).

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

(iii) Based on your answer to part (d)(ii), explain why this process requires the use of an external power source.

(e) Calculate the length of time, in seconds, required to plate $2.8\ \text{g}$ of $\text{Rh}(s)$ onto a piece of sterling silver if $2.0\ \text{C / s}$ of current is applied.

GO ON TO THE NEXT PAGE.

2.5 Lewis Diagrams

Name: ____________ Class: ________ Date: __________ **Total: 10 marks**

KEY WORDS lone pairs 孤对电子 • valence electrons 价电子 • lewis diagram 路易斯结构 • octet 八隅体

Objective

Build the skills to answer exam questions on **Lewis diagrams** — drawing the shared and lone pairs of a molecule.

You must be able to:

- count total **valence electrons 价电子** for a molecule or ion
- arrange bonding pairs and **lone pairs 孤对电子** to satisfy the octet
- use double or triple bonds when needed

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Counting valence electrons

Add the valence electrons of every atom; for an **ion**, add one electron per negative charge and subtract one per positive charge. For CO_2: $4 + 2(6) = 16$.

■ Building the skeleton

Put the least electronegative atom in the centre (usually not H), connect atoms with single bonds, then add lone pairs to complete octets (H needs only 2).

■ Using multiple bonds

If the central atom is short of an octet, form **double or triple bonds**. For CO_2, each O shares a double bond with C: $O = C = O$, all octets satisfied, 16 electrons used.

■ Checking

Count electrons: each bond is 2, each lone pair is 2. The total must equal your valence-electron count, and every atom (except H) should have an octet.

2 Practice

Now apply the methods above.

2.1 Count the total valence electrons in H_2O. [1]

2.2 Count the total valence electrons in NH_3. [1]

2.3 How many lone pairs are on the oxygen in a water molecule? [1]

3 Exam-style questions

3.1 The number of valence electrons to use in the Lewis diagram of NO_3^- is [1]

- **A** 22
- **B** 23
- **C** 24
- **D** 5

3.2 Draw the Lewis diagram of CO_2.

(a) State the total number of valence electrons. [1]

(b) Describe the bonding (single/double/triple) between C and each O. [2]

3.3 For N_2, state the total valence electrons and the bond order (single/double/triple) needed to satisfy both octets. [3]

Solutions

2.1 $2(1) + 6 = 8$.

2.2 $5 + 3(1) = 8$.

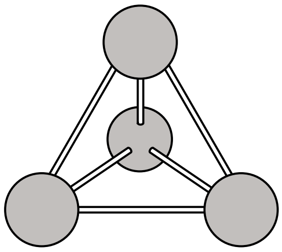
2.3 Two lone pairs.

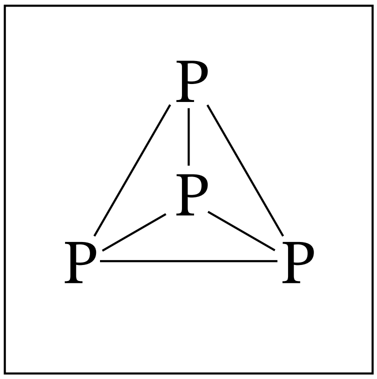
3.1 **C** — $5 + 3(6) + 1 = 24$ (the +1 for the negative charge).

3.2 (a) 16. (b) Each O forms a **double** bond with C, so all atoms reach an octet.

3.3 N_2: $2(5) = 10$ valence electrons; a **triple** bond between the N atoms, leaving one lone pair on each N.

3. White phosphorus is composed of P_4 molecules with a tetrahedral structure, as shown in the diagram on the left. Each P atom is bonded to the other three P atoms by single bonds, as shown in the incomplete Lewis diagram on the right.





A. In the box in part A, complete the Lewis diagram for P_4 by drawing the nonbonding electrons.

B. The reaction of white phosphorus with oxygen to form $P_4O_{10}(s)$ is thermodynamically favorable at 298 K. The reaction is represented by equation 1.

$$\text{Equation 1: } P_4(s) + 5\ O_2(g) \rightarrow P_4O_{10}(s)$$

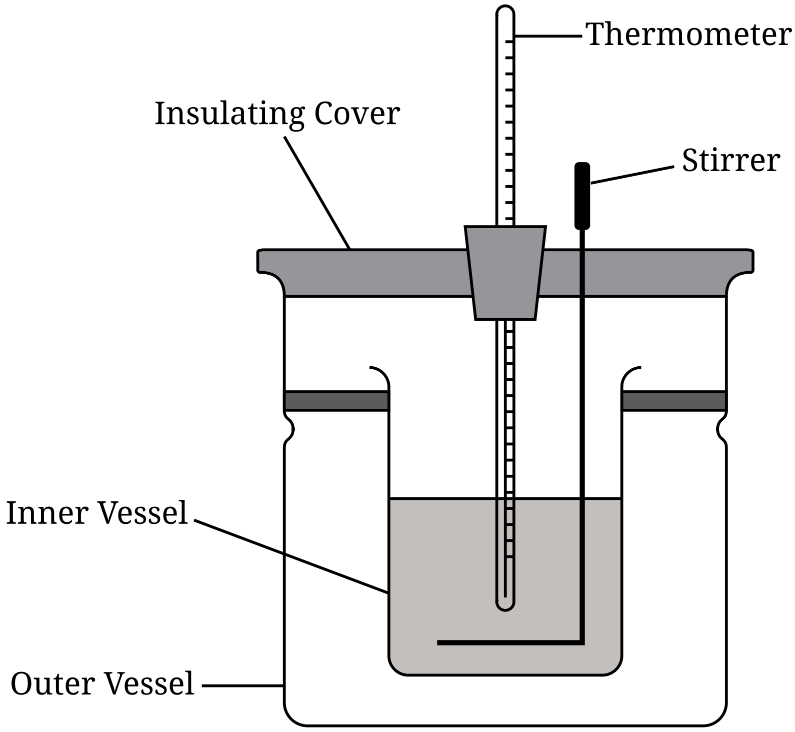
i. The entropy change of the reaction, ΔS°, is negative. Using particle-level reasoning, explain why the entropy decreases as the reaction progresses.

ii. The enthalpy change of the reaction, ΔH°, is also negative. A student claims that the favorability of the reaction is driven by enthalpy and **not** by entropy. Is the student's claim correct? Justify your answer by using the relationship between ΔG°, ΔH°, and ΔS°.

$P_4O_{10}(s)$ reacts exothermically with water to form phosphoric acid, as represented by equation 2.

$$\text{Equation 2: } P_4O_{10}(s) + 6\ H_2O(l) \rightarrow 4\ H_3PO_4(aq)$$

A chemist uses a calorimetry experiment to determine the enthalpy change for the reaction, as represented by the following diagram.



C. The chemist carries out the calorimetry experiment and records the following information.

Mass of P_4O_{10}	0.100 g
Mass of H_2O	100.0 g
Initial temperature	22.00° C
Final temperature	22.38° C
Molar mass of P_4O_{10}	283.9 g/mol
Specific heat of H_2O	4.18 $J/(g{\cdot}°C)$

i. Calculate the amount of heat, q, released during the experiment, in kJ. Assume that the specific heat of the solution is the same as that of water.

ii. Calculate the value of ΔH°_{rxn} for equation 2 in kJ/mol_{rxn}. Include the sign in your answer.

D. The chemist weighed out 0.100 g P_4O_{10} of and 100.0 g of H_2O to perform a second trial. In the second trial, some of the solid P_4O_{10} stuck to the weighing paper and was not transferred to the calorimeter. Given that P_4O_{10} is the limiting reactant, would ΔT for the second trial be greater than, less than, or equal to the value in the first trial? Justify your answer.

$P_4(s)$ also reacts readily with $Cl_2(g)$ to produce phosphorus trichloride, $PCl_3(g)$, which in turn reacts with $Cl_2(g)$ in an equilibrium process to produce $PCl_5(g)$. The reactions are represented by equations 3 and 4.

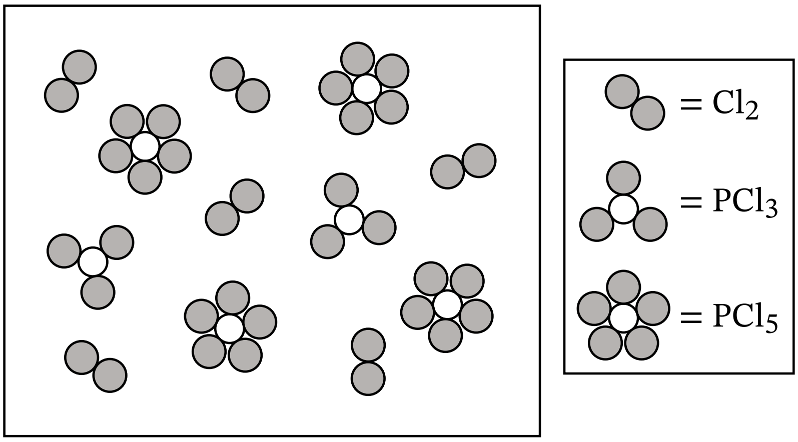
$$\text{Equation 3: } P_4(s) + 6\ Cl_2(g) \rightarrow 4\ PCl_3(g) \qquad \Delta H_1^\circ = -\ 1148\ \text{kJ/mol}_{rxn}$$

$$\text{Equation 4: } PCl_3(g) + Cl_2(g) \rightleftarrows PCl_5(g) \qquad \Delta H_2^\circ = -\ 88\ \text{kJ/mol}_{rxn}$$

E. Calculate the standard enthalpy of formation of $PCl_5(g)$ represented by equation 5.

$$\text{Equation 5: } \tfrac{1}{4}P_4(s) + \tfrac{5}{2}Cl_2(g) \rightarrow PCl_5(g) \qquad \Delta H_f^\circ = ?$$

The following particle-level diagram represents the contents of the vessel in an equilibrium mixture at 546 K involving equation 4.



F. Equation 4 for the reaction that occurs is shown.

$$\text{Equation 4: } PCl_3(g) + Cl_2(g) \rightleftarrows PCl_5(g) \qquad \Delta H_2^\circ = -\ 88\ \text{kJ/mol}_{rxn}$$

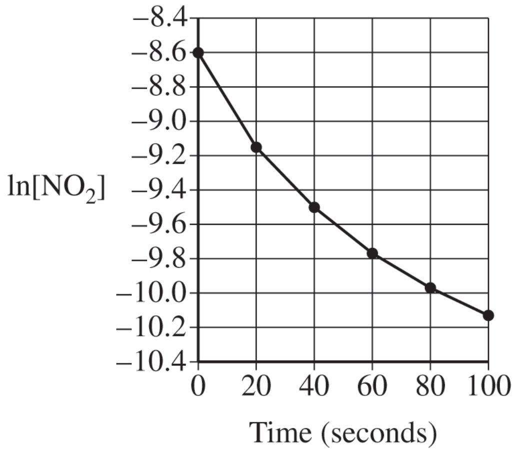
i. If each particle in the diagram represents a partial pressure of 1.00 atm, what is the value of K_p for the equilibrium mixture at 546 K?

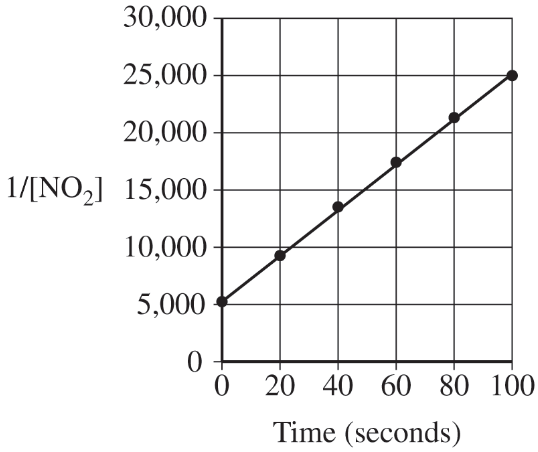
ii. Does the value of K_p increase, decrease, or remain the same when the temperature is increased to 596 K? Justify your answer based on ΔH_2°.

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

$$2\ NO_2 \rightarrow 2\ NO + O_2$$

A scientist measures the change in $[NO_2]$ 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 $rate = k[NO_2]^2$.

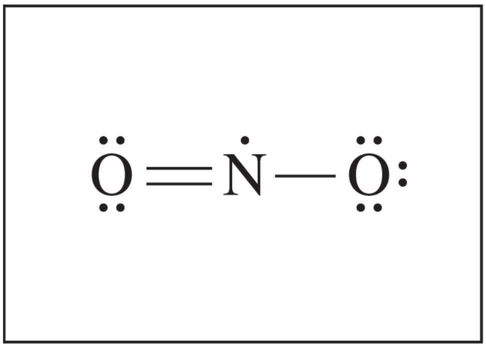
(a) Explain how the graphs indicate that the reaction is second order with respect to NO_2.

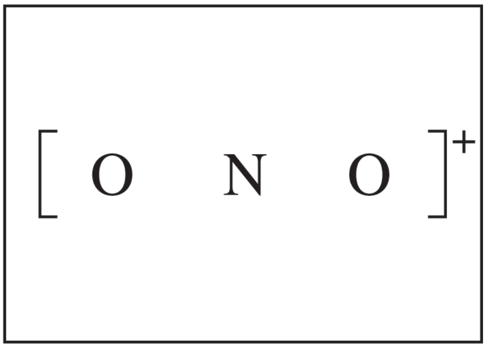
(b) At a certain point in the reaction, the rate of disappearance of NO_2 is determined to be $6.52 \times 10^{-7}\ M/s$. Determine the rate of appearance, in M/s, of O_2 at this same point in the reaction.

GO ON TO THE NEXT PAGE.

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.

GO ON TO THE NEXT PAGE.

$$CH_3OH(g) \rightleftarrows CO(g) + 2\ H_2(g) \qquad \Delta H° = \ 90.0\ \text{kJ / mol}_{rxn}$$

. Methanol vapor decomposes to form carbon monoxide gas and hydrogen gas at high temperatures in the presence of a platinum catalyst, as represented by the balanced chemical equation given.

(a) Are the hydrogen atoms oxidized or are they reduced in the forward reaction? Justify your answer in terms of oxidation numbers.

(b) In the following box, draw the complete Lewis electron-dot diagram for the carbon monoxide molecule in which every atom obeys the octet rule. Show all bonding and nonbonding valence electrons.

C O

(c) The values of the standard molar entropies of the compounds involved in the reaction are given in the following table.

Substance	$S°$ (J/(K·mol))
$CH_3OH(g)$	240.
$CO(g)$	198
$H_2(g)$	131

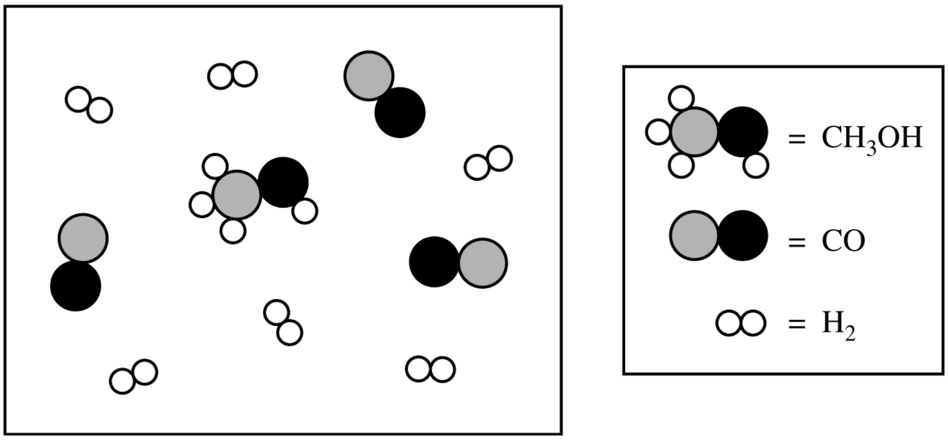
(i) Use the data in the table to calculate the value of the standard entropy change, $\Delta S°$, in J/(K·mol$_{rxn}$), for the reaction.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 2** on this page.

(ii) Calculate the value of $\Delta G°$, in kJ/mol$_{rxn}$, for the reaction at 375 K. Assume that $\Delta H°$ and $\Delta S°$ are independent of temperature.

The following particle-level diagram shows a representative sample of the equilibrium mixture represented by the equation given.



(d) Use information from the particle diagram to calculate the partial pressure of CO at equilibrium when the total pressure of the equilibrium mixture is 12.0 atm.

(e) Write the expression for the equilibrium constant, K_p, for the reaction.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 2** on this page.

$$CH_3OH(g) \rightleftarrows CO(g) + 2\ H_2(g)$$

The reaction system represented by the equation is allowed to achieve equilibrium at a different temperature. The following table gives the partial pressure of each species in the equilibrium mixture.

Substance	Partial Pressure at Different Temperature
$CH_3OH(g)$	2.7 atm
$CO(g)$	4.2 atm
$H_2(g)$	8.4 atm

(f) Use the information in the table to calculate the value of the equilibrium constant, K_p, at the new temperature.

(g) The volume of the container is rapidly doubled with no change in temperature. As equilibrium is re-established, does the number of moles of $CH_3OH(g)$ increase, decrease, or remain the same? Justify your answer by comparing the value of the reaction quotient, Q, with the value of the equilibrium constant, K_p.

GO ON TO THE NEXT PAGE.

CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

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.

For each question, show your work for each part in the space provided after that part. 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.

$$\mathrm{HCOOH}(aq) + \mathrm{H_2O}(l) \rightleftarrows \mathrm{H_3O^+}(aq) + \mathrm{HCOO^-}(aq) \qquad K_a = 1.8 \times 10^{-4}$$

1. Methanoic acid, HCOOH, ionizes according to the equation above.

(a) Write the expression for the equilibrium constant, K_a, for the reaction.

(b) Calculate the pH of a 0.25 M solution of HCOOH.

GO ON TO THE NEXT PAGE.

(c) In the box below, complete the Lewis electron-dot diagram for HCOOH. Show all bonding and nonbonding valence electrons.

O

H C O H

$$H_2NNH_2(aq) + H_2O(l) \rightleftarrows H_2NNH_3^{+}(aq) + OH^{-}(aq) \qquad K_b = 1.3 \times 10^{-6}$$

(d) In aqueous solution, the compound H_2NNH_2 reacts according to the equation above. A 50.0 mL sample of 0.25 M $H_2NNH_2(aq)$ is combined with a 50.0 mL sample of 0.25 M $HCOOH(aq)$.

(i) Write the balanced net ionic equation for the reaction that occurs when H_2NNH_2 is combined with HCOOH.

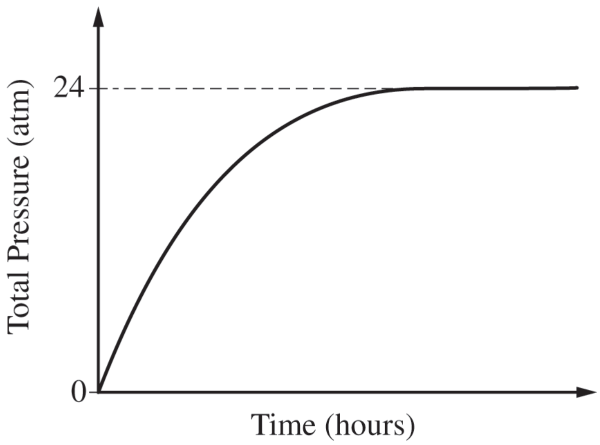
(ii) Is the resulting solution acidic, basic, or neutral? Justify your answer.

GO ON TO THE NEXT PAGE.

When a catalyst is added to a solution of $HCOOH(aq)$, the reaction represented by the following equation occurs.

$$HCOOH(aq) \rightarrow H_2(g) + CO_2(g)$$

(e) Is the reaction a redox reaction? Justify your answer.



(f) The reaction occurs in a rigid 4.3 L vessel at 25°C, and the total pressure is monitored, as shown in the graph above. The vessel originally did not contain any gas. Calculate the number of moles of $CO_2(g)$ produced in the reaction. (Assume that the amount of $CO_2(g)$ dissolved in the solution is negligible.)

(g) After the reaction has proceeded for several minutes, does the amount of catalyst increase, decrease, or remain the same? Justify your answer.

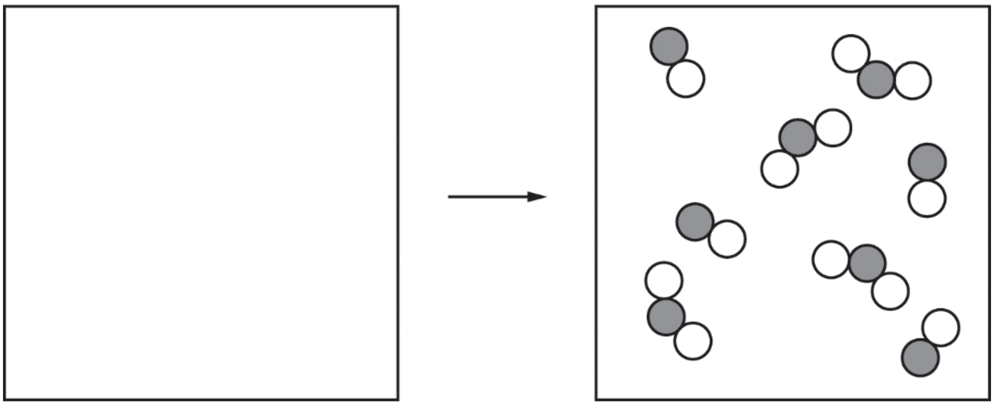
GO ON TO THE NEXT PAGE.

$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

2. A student investigates the reactions of nitrogen oxides. One of the reactions in the investigation requires an equimolar mixture of $NO(g)$ and $NO_2(g)$, which the student produces by using the reaction represented above.

(a) The particle-level representation of the equimolar mixture of $NO(g)$ and $NO_2(g)$ in the flask at the completion of the reaction between $NO(g)$ and $O_2(g)$ 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 $NO(g)$ and $O_2(g)$ 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.

Oxygen atom = ○ Nitrogen atom = ●



Reactant Mixture Product Mixture

The student reads in a reference text that $NO(g)$ and $NO_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.

$$NO(g) + NO_2(g) \rightleftarrows N_2O_3(g)$$

ΔH°_{298}	ΔS°_{298}	ΔG°_{298}
$-40.4\ kJ/mol_{rxn}$	$-138.5\ J/(K \cdot mol_{rxn})$	$0.87\ kJ/mol_{rxn}$

(b) The student begins with an equimolar mixture of $NO(g)$ and $NO_2(g)$ in a rigid reaction vessel and the mixture reaches equilibrium at 298 K.

(i) Calculate the value of the equilibrium constant, K, for the reaction at 298 K.

(ii) If both P_{NO} and P_{NO_2} in the vessel are initially 1.0 atm, will $P_{N_2O_3}$ at equilibrium be equal to 1.0 atm? Justify your answer.

(c) The student hypothesizes that increasing the temperature will increase the amount of $N_2O_3(g)$ in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

$N_2O_3(g)$ reacts with water to form nitrous acid, $HNO_2(aq)$, a compound involved in the production of acid rain. The reaction is represented below.

$$N_2O_3(g) + H_2O(l) \rightarrow 2\ HNO_2(aq)$$

(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.

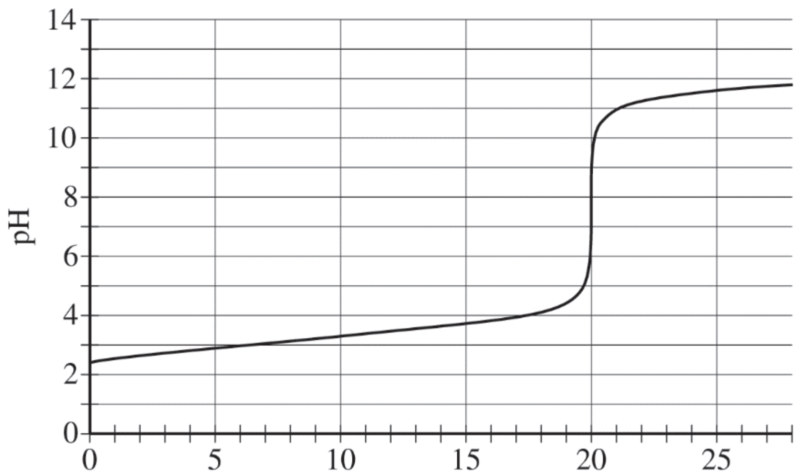
H O N O

(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 $N_2O_3(g)$ into distilled water. Assume that the reaction goes to completion and that HNO_2 is the only species produced. To determine the concentration of $HNO_2(aq)$ in the resulting solution, the student titrates a 100. mL sample of the solution with 0.100 M KOH(aq). The neutralization reaction is represented below.

$$HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$$

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



Volume of 0.100 M KOH(aq) Added (mL)

(e) Use the titration curve and the information above to

(i) determine the initial concentration of the $HNO_2(aq)$ solution

(ii) estimate the value of pK_a for $HNO_2(aq)$

(f) During the titration, after a volume of 15 mL of 0.100 M KOH(aq) has been added, which species, $HNO_2(aq)$ or $NO_2^-(aq)$, 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.

$$CS_2(g) + 3\ Cl_2(g) \rightarrow CCl_4(g) + S_2Cl_2(g)$$

1. Carbon tetrachloride, $CCl_4(g)$, 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, $Cl_2(g)$, is initially present in the container at a pressure of 0.40 atm.

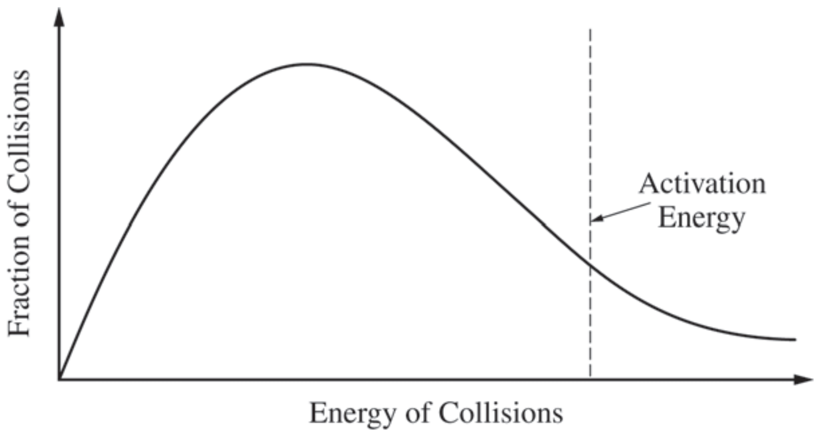
(i) How many moles of $Cl_2(g)$ are in the container?

(ii) How many grams of carbon disulfide, $CS_2(g)$, are needed to react completely with the $Cl_2(g)$?

(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.

(i) Explain how the higher temperature affects the collisions between the reactant molecules so that the reaction occurs at an observable rate at 120°C.

(ii) 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.

Cl S S Cl

(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) $CCl_4(g)$ can also be produced by reacting $CHCl_3(g)$ with $Cl_2(g)$ at 400°C, as represented by the equation below.

$$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$$

At the completion of the reaction a chemist successfully separates the $CCl_4(g)$ from the $HCl(g)$ by cooling the mixture to 70°C, at which temperature the $CCl_4(g)$ condenses while the $HCl(g)$ remains in the gaseous state.

(i) Identify all types of intermolecular forces present in $HCl(l)$.

(ii) What can be inferred about the relative strengths of the intermolecular forces in $CCl_4(l)$ and $HCl(l)$? Justify your answer in terms of the information above.

$$NaHCO_3(s) + HC_2H_3O_2(aq) \rightarrow NaC_2H_3O_2(aq) + H_2O(l) + CO_2(g)$$

2. A student designs an experiment to study the reaction between $NaHCO_3$ and $HC_2H_3O_2$. The reaction is represented by the equation above. The student places 2.24 g of $NaHCO_3$ in a flask and adds 60.0 mL of 0.875 M $HC_2H_3O_2$. The student observes the formation of bubbles and that the flask gets cooler as the reaction proceeds.

(a) Identify the reaction represented above as an acid-base reaction, precipitation reaction, or redox reaction. Justify your answer.

(b) Based on the information above, identify the limiting reactant. Justify your answer with calculations.

(c) The student observes that the bubbling is rapid at the beginning of the reaction and gradually slows as the reaction continues. Explain this change in the reaction rate in terms of the collisions between reactant particles.

(d) In thermodynamic terms, a reaction can be driven by enthalpy, entropy, or both.

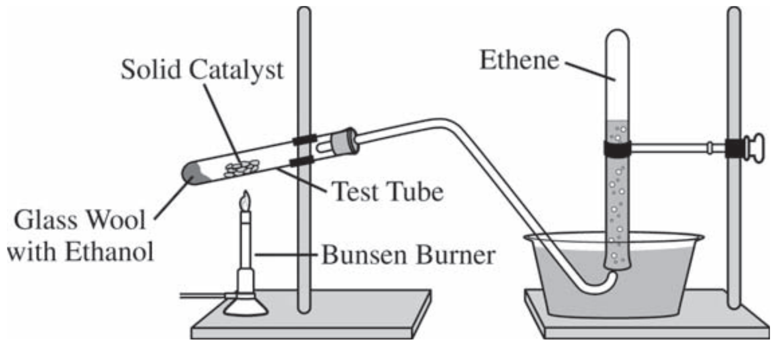
(i) Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between $NaHCO_3(s)$ and $HC_2H_3O_2(aq)$? Answer by drawing a circle around one of the choices below.

Enthalpy only | Entropy only | Both enthalpy and entropy

(ii) Justify your selection in part (d)(i) in terms of $\Delta G°$.

(e) The HCO_3^- ion has three carbon-to-oxygen bonds. Two of the carbon-to-oxygen bonds have the same length and the third carbon-to-oxygen bond is longer than the other two. The hydrogen atom is bonded to one of the oxygen atoms. In the box below, draw a Lewis electron-dot diagram (or diagrams) for the HCO_3^- ion that is (are) consistent with the given information.

(f) A student prepares a solution containing equimolar amounts of $HC_2H_3O_2$ and $NaC_2H_3O_2$. The pH of the solution is measured to be 4.7. The student adds two drops of 3.0 M $HNO_3(aq)$ and stirs the sample, observing that the pH remains at 4.7. Write a balanced, net-ionic equation for the reaction between $HNO_3(aq)$ and the chemical species in the sample that is responsible for the pH remaining at 4.7.



2. Ethene, $C_2H_4(g)$ (molar mass 28.1 g/mol), may be prepared by the dehydration of ethanol, $C_2H_5OH(g)$ (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.

$$\underset{\text{ethanol}}{C_2H_5OH(g)} \xrightarrow{\text{catalyst}} \underset{\text{ethene}}{C_2H_4(g)} + \underset{\text{water}}{H_2O(g)} \quad \Delta H^\circ_{298} = 45.5\ \text{kJ/mol}_{rxn};\ \Delta S^\circ_{298} = 126\ \text{J/(K}\cdot\text{mol}_{rxn})$$

A student added a 0.200 g sample of $C_2H_5OH(l)$ to a test tube using the setup shown above. The student heated the test tube gently with a Bunsen burner until all of the $C_2H_5OH(l)$ 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 $C_2H_4(g)$

(i) that are actually produced in the experiment and measured in the gas collection tube and

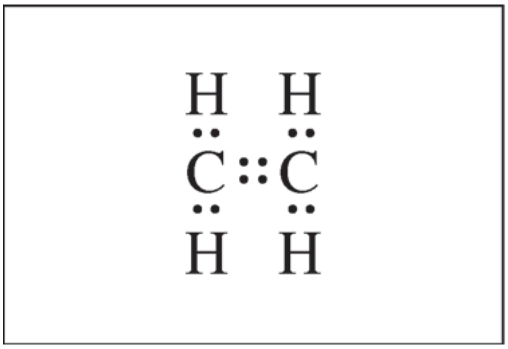
(ii) that would be produced if the dehydration reaction went to completion.

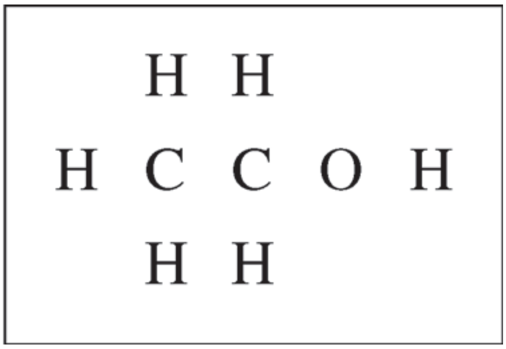
(b) Calculate the percent yield of $C_2H_4(g)$ in the experiment.

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 C_2H_5OH 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, $C_2H_4(g)$ and unreacted $C_2H_5OH(g)$ passed through the tube into the water. The C_2H_4 was quantitatively collected as a gas, but the unreacted C_2H_5OH 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 ClF_3. In the box below, draw a complete Lewis electron-dot diagram for a molecule of ClF_3.

(c) Two possible geometric shapes for the ClF_3 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 ClF_3 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 ClF_3 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.

AP CHEMISTRY • EXERCISE SHEET

2.6 Resonance and Formal Charge

Name: ______________ Class: __________ Date: ____________ **Total: 10 marks**

KEY WORDS formal charge 形式电荷 • resonance 共振 • lewis diagram 路易斯结构

Objective

Build the skills to answer exam questions on **resonance and formal charge**.

You must be able to:

- draw **resonance** 共振 structures when more than one valid Lewis diagram exists
- calculate **formal charge** 形式电荷 $= (\text{valence } e^-) - (\text{lone } e^-) - \frac{1}{2}(\text{bonding } e^-)$
- use formal charge to choose the best structure

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

Resonance

When electrons could be placed in more than one equally valid way, the molecule is a **blend** (resonance hybrid) of those structures. In O_3 (ozone) the double bond is shared between both O–O positions, so both bonds are identical.

Formal charge

For each atom,

$$\text{FC} = (\text{valence } e^-) - (\text{nonbonding } e^-) - \tfrac{1}{2}(\text{bonding } e^-).$$

A worked formal charge

In CO_2, the carbon: valence 4, lone 0, bonding 8 (two double bonds): $\text{FC} = 4-0-4 = 0$. Each oxygen: $6-4-2=0$. All zero — a good structure.

Choosing the best structure

The **best** Lewis structure has formal charges **closest to zero**, and any negative formal charge on the **most electronegative** atom. Use this to pick between candidates.

2 Practice

Now apply the methods above.

2.1 Write the formula for formal charge. [1]

2.2 Find the formal charge on N in NH_4^+ (valence 5, 0 lone electrons, 8 bonding electrons). [2]

2.3 What does it mean that ozone O_3 has resonance structures? [1]

3 Exam-style questions

3.1 The preferred Lewis structure has formal charges that are [1]

- **A** as large as possible
- **B** as close to zero as possible
- **C** all positive
- **D** all on carbon

3.2 In one resonance structure of NO_3^-, an oxygen has 6 nonbonding electrons and 2 bonding electrons (a single bond).

(a) Find the formal charge on that oxygen. [2]

(b) State what the true structure looks like given resonance. [1]

3.3 Explain why all three N–O bonds in NO_3^- have the same length, using the idea of resonance. [2]

Solutions

2.1 FC $=$ (valence e^-) $-$ (nonbonding e^-) $-$ $\frac{1}{2}$(bonding e^-).

2.2 FC $= 5 - 0 - \frac{1}{2}(8) = 5 - 4 = +1$.

2.3 The molecule is a blend (hybrid) of the equivalent structures, not switching between them.

3.1 **B** — formal charges as close to zero as possible.

3.2 (a) FC $= 6 - 6 - \frac{1}{2}(2) = 6 - 6 - 1 = -1$. (b) The real ion is a resonance hybrid — the extra bond and charge are spread equally over all three oxygens.

3.3 Resonance spreads the double-bond character equally over all three N–O positions, so each bond is identical (an average of single and double), giving equal lengths.

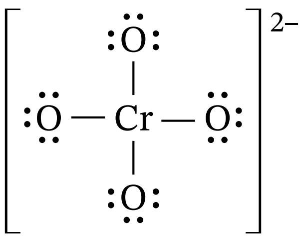
Question 2: Version J

2. Answer the following questions about the chromate ion, CrO_4^{2-}, and the dichromate ion, $Cr_2O_7^{2-}$.

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.

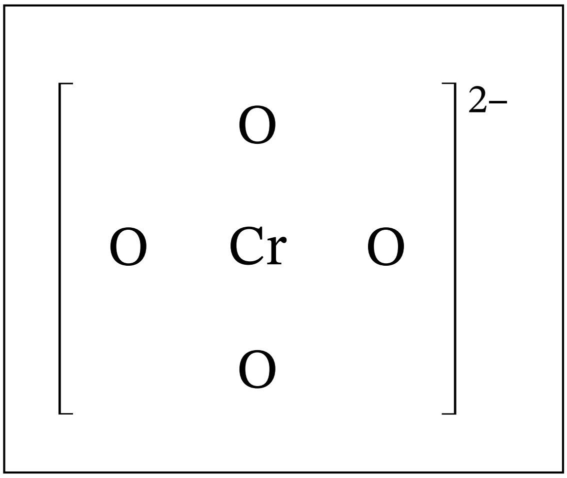
Figure 1



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 $HNO_3(aq)$, $CrO_4^{2-}(aq)$ can be converted to $Cr_2O_7^{2-}(aq)$ and $H_2O(l)$ in a reversible reaction.

i. **Write** a balanced net ionic equation for the reaction between $CrO_4^{2-}(aq)$ 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, $Cr_2O_7^{2-}(aq)$ reacts to form $CrO_3(aq)$ according to Equation 1.

$$\text{Equation 1: } Cr_2O_7^{2-}(aq) + 2\ H_3O^+(aq) \rightarrow 2\ CrO_3(aq) + 3\ H_2O(l)$$

$CrO_3(aq)$ can be electrolyzed to plate objects with a thin layer of chromium metal according to Equation 2.

$$\text{Equation 2: } CrO_3(aq) + 6\ H^+(aq) + 6\ e^- \rightarrow Cr(s) + 3\ H_2O(l) \qquad E^\circ = -1.32\ \text{V}$$

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.

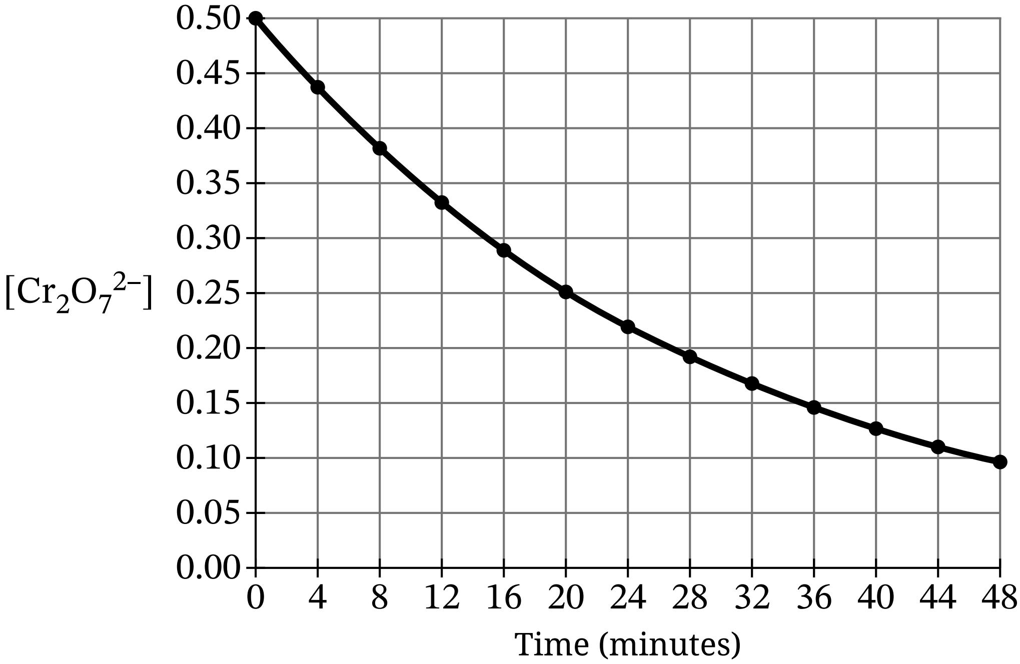
Part D

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 $0.50\ M\ Cr_2O_7^{2-}(aq)$ with $pH = 1.99$. The concentration of $Cr_2O_7^{2-}(aq)$ remaining is recorded over time, and the results are presented in Figure 3.

Figure 3

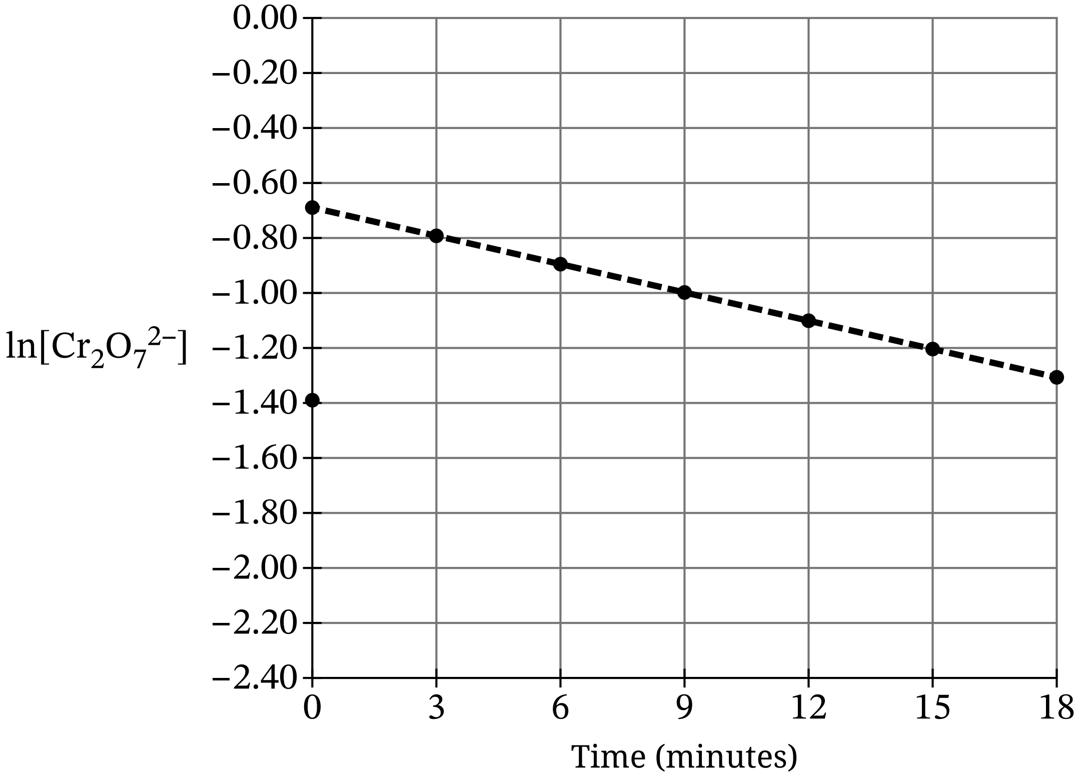


Explain how the data in Figure 3 support the conclusion that the reaction is first order with respect to $Cr_2O_7^{2-}$.

The following information applies to parts F and G.

The student creates a plot of $\ln\left[Cr_2O_7^{2-}\right]$ versus time for a trial with an initial concentration of $0.50\ M\ Cr_2O_7^{2-}(aq)$, 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 $0.25\ M\ Cr_2O_7^{2-}(aq)$ instead of $0.50\ M\ Cr_2O_7^{2-}(aq)$. On Figure 4, carefully **draw** the plot of $\ln\left[Cr_2O_7^{2-}\right]$ versus time that would be expected for the second experiment. The point at time zero has already been plotted.

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.

$$\text{Reaction 1: } AlCl_3(g) \rightarrow Al(g) + 3\,Cl(g) \quad \Delta H_1^\circ = ?$$

(a) How many grams of $Cl(g)$ can be formed from 1.25 mol of $AlCl_3(g)$?

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

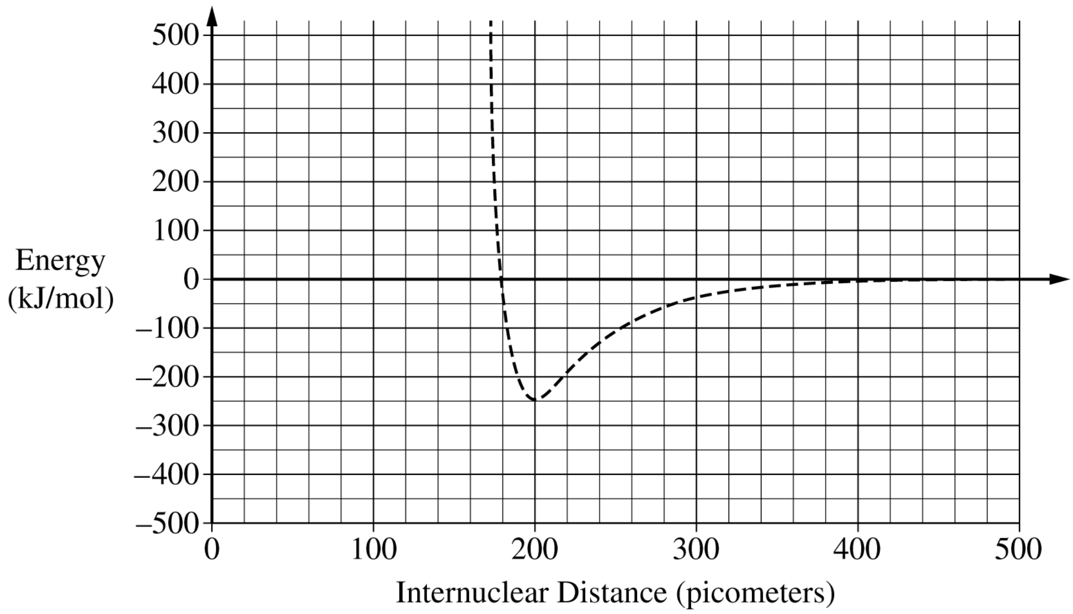
Reaction Number	Equation	ΔH_{rxn}° (kJ/mol$_{rxn}$)
2	$Al(s) + \frac{3}{2}\,Cl_2(g) \rightarrow AlCl_3(g)$	−583
3	$Al(s) \rightarrow Al(g)$	+326
4	$Cl_2(g) \rightarrow 2\,Cl(g)$	+243

(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 2** 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 Al – Cl bond length is 220 picometers and the average bond energy is 425 kJ/mol. Draw the potential energy curve for the average Al – Cl bond on the preceding graph.

(d) Three proposed Lewis diagrams for the $AlCl_3(g)$ molecule are shown.

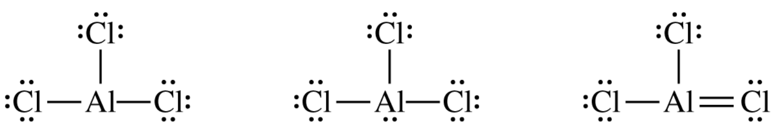


Diagram 1 Diagram 2 Diagram 3

(i) The $AlCl_3(g)$ 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.

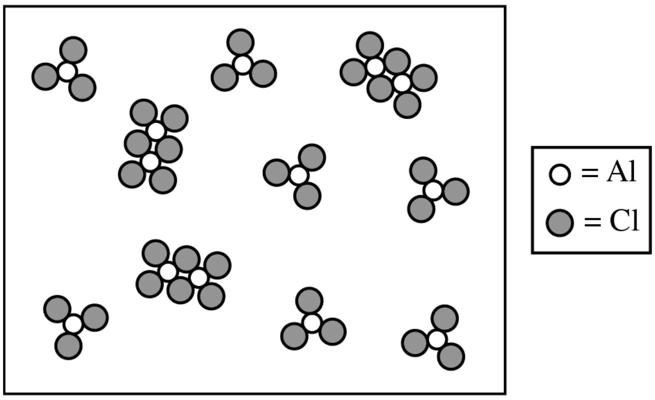
(ii) Which of the three diagrams is the best representation for the bonding in $AlCl_3$? Justify your choice based on formal charges.

$AlCl_3$ is known to dimerize reversibly in the gas phase. The dimerization equilibrium is represented by the following equation.

$$2\ AlCl_3(g) \rightleftarrows Al_2Cl_6(g)$$

(e) Write the expression for the equilibrium constant, K_p, for this reaction.

A particle-level diagram of an equilibrium mixture of $AlCl_3(g)$ and $Al_2Cl_6(g)$ 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.

GO ON TO THE NEXT PAGE.

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.

$$\mathrm{H{-}C{\equiv}N{-}\underset{\cdot\cdot}{\ddot{O}}\colon} \qquad\qquad \mathrm{H{-}\ddot{C}{=}N{=}\ddot{O}\colon}$$

(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.

$$HCNO(g) \rightleftarrows HNCO(g)$$

fulminic acid *isocyanic acid*

Fulminic Acid	Isocyanic Acid
$\mathrm{H{-}C{\equiv}N{-}\underset{\cdot\cdot}{\ddot{O}}\colon}$	$\mathrm{H{-}\ddot{N}{=}C{=}\ddot{O}\colon}$

(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 $\Delta H°$ 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 $\Delta S°$ for the reaction is close to zero. Explain why the student's claim is accurate.

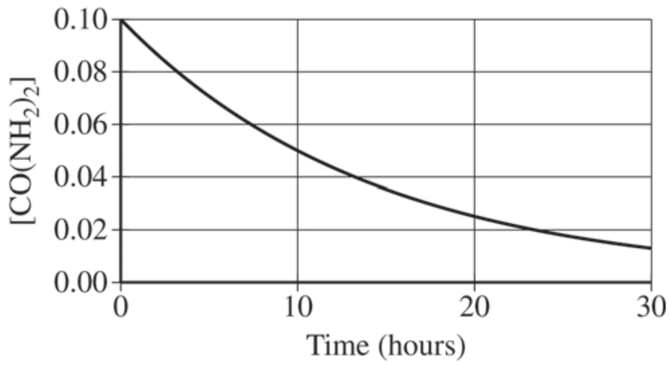
(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

The ammonium salt of isocyanic acid is a product of the decomposition of urea, $CO(NH_2)_2$, represented below.

$$CO(NH_2)_2(aq) \rightleftarrows NH_4^+(aq) + OCN^-(aq)$$

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 $rate = k[CO(NH_2)_2]$.

(i) Explain how the data support the student's proposed rate law.

(ii) 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 $OH^-(aq)$.

$$NaHCO_3(s) + HC_2H_3O_2(aq) \rightarrow NaC_2H_3O_2(aq) + H_2O(l) + CO_2(g)$$

2. A student designs an experiment to study the reaction between $NaHCO_3$ and $HC_2H_3O_2$. The reaction is represented by the equation above. The student places 2.24 g of $NaHCO_3$ in a flask and adds 60.0 mL of 0.875 M $HC_2H_3O_2$. The student observes the formation of bubbles and that the flask gets cooler as the reaction proceeds.

(a) Identify the reaction represented above as an acid-base reaction, precipitation reaction, or redox reaction. Justify your answer.

(b) Based on the information above, identify the limiting reactant. Justify your answer with calculations.

(c) The student observes that the bubbling is rapid at the beginning of the reaction and gradually slows as the reaction continues. Explain this change in the reaction rate in terms of the collisions between reactant particles.

(d) In thermodynamic terms, a reaction can be driven by enthalpy, entropy, or both.

(i) Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between $NaHCO_3(s)$ and $HC_2H_3O_2(aq)$? Answer by drawing a circle around one of the choices below.

Enthalpy only Entropy only Both enthalpy and entropy

(ii) Justify your selection in part (d)(i) in terms of $\Delta G°$.

(e) The HCO_3^- ion has three carbon-to-oxygen bonds. Two of the carbon-to-oxygen bonds have the same length and the third carbon-to-oxygen bond is longer than the other two. The hydrogen atom is bonded to one of the oxygen atoms. In the box below, draw a Lewis electron-dot diagram (or diagrams) for the HCO_3^- ion that is (are) consistent with the given information.

(f) A student prepares a solution containing equimolar amounts of $HC_2H_3O_2$ and $NaC_2H_3O_2$. The pH of the solution is measured to be 4.7. The student adds two drops of 3.0 M $HNO_3(aq)$ and stirs the sample, observing that the pH remains at 4.7. Write a balanced, net-ionic equation for the reaction between $HNO_3(aq)$ and the chemical species in the sample that is responsible for the pH remaining at 4.7.

2.7 VSEPR and Bond Hybridization

Name: ______________ Class: __________ Date: ____________ **Total: 11 marks**

KEY WORDS hybridization 杂化 • vsepr 价层电子对互斥 • electron domains 电子域 • lone pairs 孤对电子

Objective

Build the skills to answer exam questions on **VSEPR and hybridization** — predicting molecular shape.

You must be able to:

- count **electron domains 电子域** (bonds + lone pairs) around the central atom
- use **VSEPR 价层电子对互斥** to predict the shape and bond angles
- assign **hybridization** (sp, sp^2, sp^3) from the domain count

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

Count the domains

Electron domains repel and spread as far apart as possible. Count bonding groups (a double/triple bond counts as **one** domain) plus lone pairs on the central atom.

Shape from domains

domains	arrangement	angle
2	linear	180°
3	trigonal planar	120°
4	tetrahedral	109.5°

Lone pairs occupy a domain but are **not** drawn as part of the shape name, so they bend the visible geometry (e.g. water is "bent").

Lone pairs change the shape name

NH_3 has 4 domains (3 bonds + 1 lone pair): electron geometry tetrahedral, but the **molecular shape** is **trigonal pyramidal**, angle ≈ 107° (lone pair squeezes it).

■ **Hybridization from domain count**

2 domains → *sp*; 3 → sp^2; 4 → sp^3. For CO_2 (2 domains), carbon is *sp*; for CH_4 (4), sp^3.

2 Practice

Now apply the methods above.

2.1 How many electron domains are around C in CH_4? [1]

2.2 State the shape and bond angle of CH_4. [2]

2.3 State the hybridization of carbon in CO_2. [1]

3 Exam-style questions

3.1 A central atom with 3 electron domains and no lone pairs has the shape [1]

- **A** linear
- **B** trigonal planar
- **C** tetrahedral
- **D** bent

3.2 Consider H_2O.

(a) Count the electron domains on oxygen. [1]

(b) State the molecular shape and approximate bond angle. [2]

(c) State the hybridization of oxygen. [1]

3.3 Explain why the bond angle in NH_3 (107°) is smaller than in CH_4 (109.5°). [2]

Solutions

2.1 4.

2.2 Tetrahedral, 109.5°.

2.3 *sp*.

3.1 **B** — 3 domains with no lone pairs is trigonal planar.

3.2 (a) 4 (2 bonds + 2 lone pairs). (b) Bent, $\approx$ 104.5°. (c) sp^3.

3.3 NH_3 has one lone pair, which repels more strongly than a bonding pair and pushes the N–H bonds closer together, reducing the angle below the tetrahedral 109.5°.

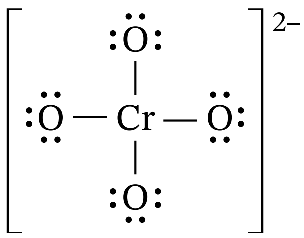
Question 2: Version J

2. Answer the following questions about the chromate ion, CrO_4^{2-}, and the dichromate ion, $Cr_2O_7^{2-}$.

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.

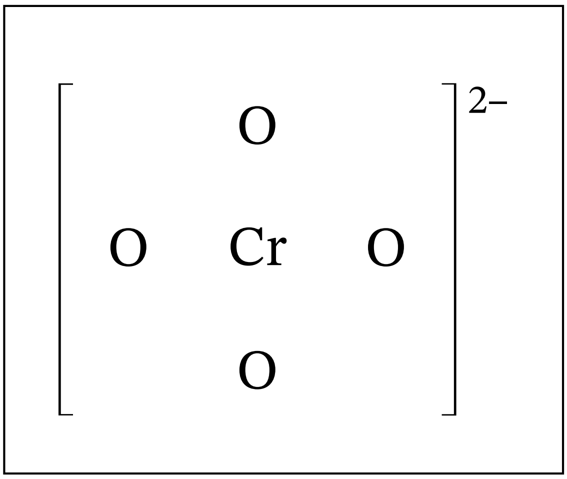
Figure 1



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 $HNO_3(aq)$, $CrO_4^{2-}(aq)$ can be converted to $Cr_2O_7^{2-}(aq)$ and $H_2O(l)$ in a reversible reaction.

i. **Write** a balanced net ionic equation for the reaction between $CrO_4^{2-}(aq)$ 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, $Cr_2O_7^{2-}(aq)$ reacts to form $CrO_3(aq)$ according to Equation 1.

$$\text{Equation 1: } Cr_2O_7^{2-}(aq) + 2\ H_3O^+(aq) \rightarrow 2\ CrO_3(aq) + 3\ H_2O(l)$$

$CrO_3(aq)$ can be electrolyzed to plate objects with a thin layer of chromium metal according to Equation 2.

$$\text{Equation 2: } CrO_3(aq) + 6\ H^+(aq) + 6\ e^- \rightarrow Cr(s) + 3\ H_2O(l) \qquad E^\circ = -1.32\ \text{V}$$

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.

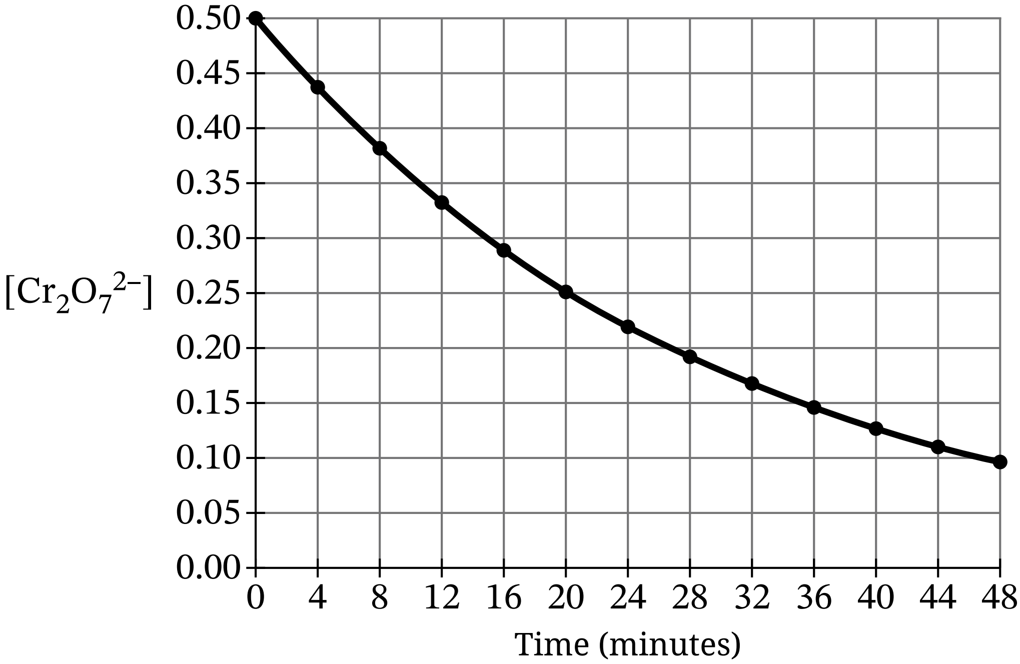
Part D

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 M $Cr_2O_7^{2-}(aq)$ with pH = 1.99. The concentration of $Cr_2O_7^{2-}(aq)$ remaining is recorded over time, and the results are presented in Figure 3.

Figure 3

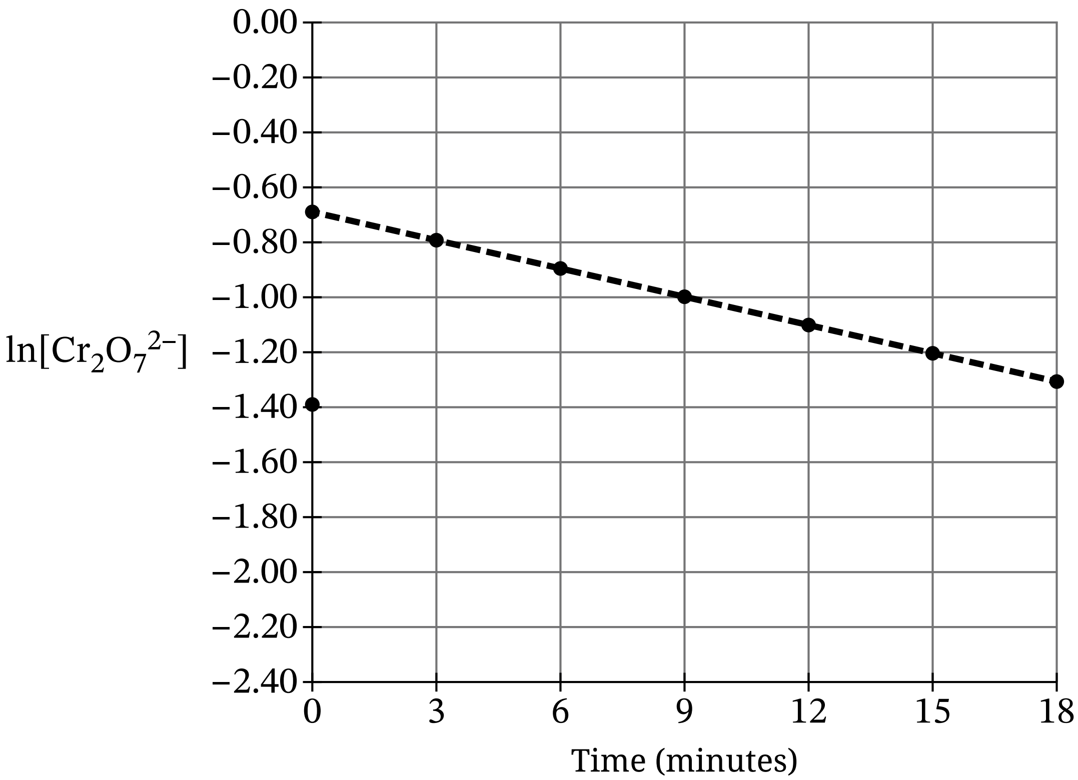


Explain how the data in Figure 3 support the conclusion that the reaction is first order with respect to $Cr_2O_7^{2-}$.

The following information applies to parts F and G.

The student creates a plot of $\ln\left[Cr_2O_7^{2-}\right]$ versus time for a trial with an initial concentration of $0.50\ M\ Cr_2O_7^{2-}(aq)$, 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 $0.25\ M\ Cr_2O_7^{2-}(aq)$ instead of $0.50\ M\ Cr_2O_7^{2-}(aq)$. On Figure 4, carefully **draw** the plot of $\ln\left[Cr_2O_7^{2-}\right]$ 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.

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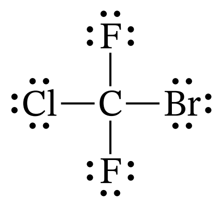
5. The Lewis diagram of $CBrClF_2$ is shown.



Part A

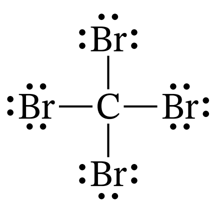
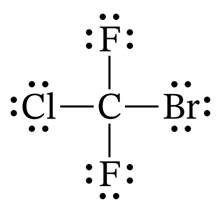
Which of the bonds in $CBrClF_2$ (C−Br, C−Cl, or C−F) is the most polar? **Justify** your answer.

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		
Boiling point	463 K	269 K

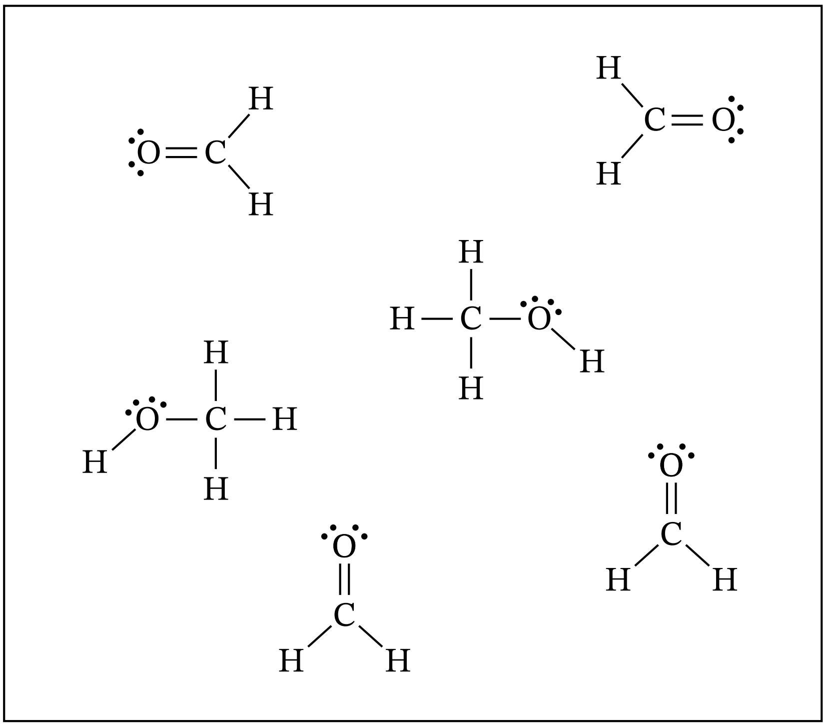
i. Clearly **identify** all the intermolecular forces in pure $CBr_4(l)$ and in pure $CBrClF_2(l)$.

$CBr_4(l)$:

$CBrClF_2(l)$:

ii. In terms of the relative strengths of all the intermolecular forces, **explain** why pure $CBr_4(l)$ has a higher boiling point than pure $CBrClF_2(l)$ 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.

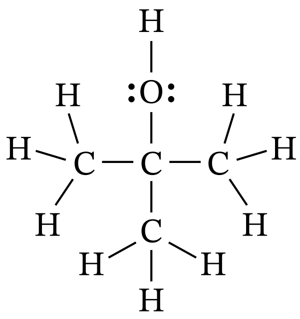
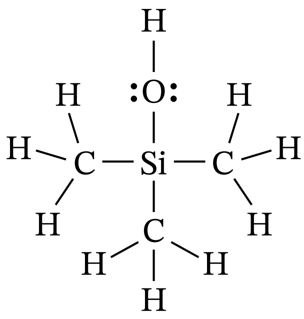
C. The scientist plans to cool a gaseous mixture of CH_3OH and H_2CO to form a liquid mixture and finds data on the two compounds. The data are summarized in the table.

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 $CH_3OH(l)$ 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.

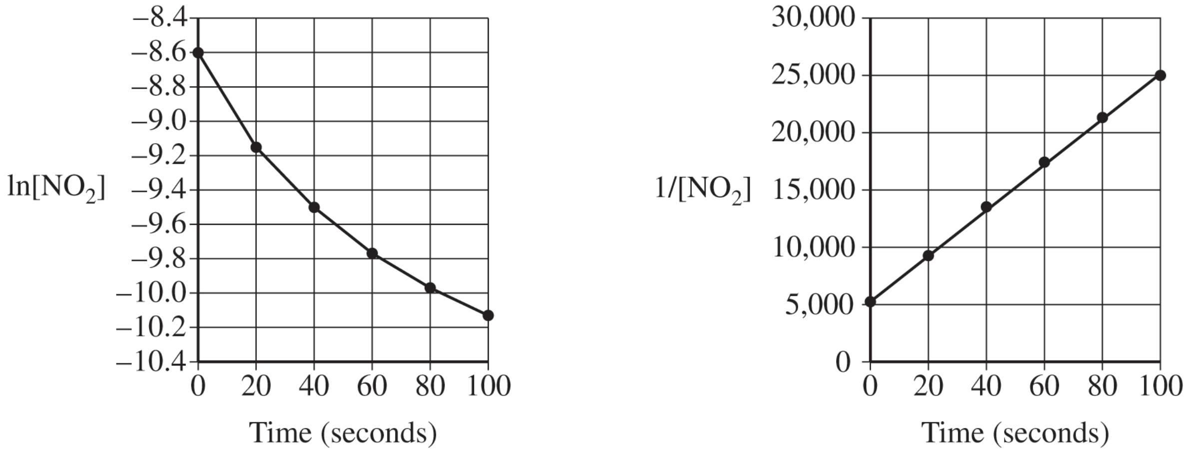
C. An equimolar mixture of the two compounds is heated. When the mixture reaches 82°C, which compound will have the higher vapor pressure? Justify your answer.

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.

$$2\ NO_2 \rightarrow 2\ NO + O_2$$

A scientist measures the change in $[NO_2]$ 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 $rate = k[NO_2]^2$.

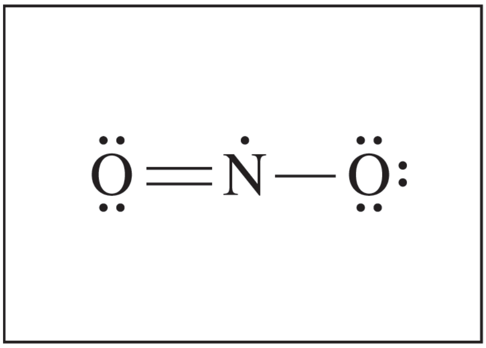
(a) Explain how the graphs indicate that the reaction is second order with respect to NO_2.

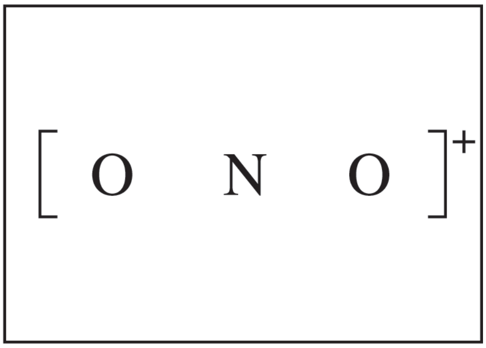
(b) At a certain point in the reaction, the rate of disappearance of NO_2 is determined to be 6.52×10^{-7} M/s. Determine the rate of appearance, in M/s, of O_2 at this same point in the reaction.

GO ON TO THE NEXT PAGE.

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.

GO ON TO THE NEXT PAGE.

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.

$$\text{Reaction 1: } AlCl_3(g) \rightarrow Al(g) + 3\,Cl(g) \quad \Delta H_1^\circ = ?$$

(a) How many grams of $Cl(g)$ can be formed from 1.25 mol of $AlCl_3(g)$?

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

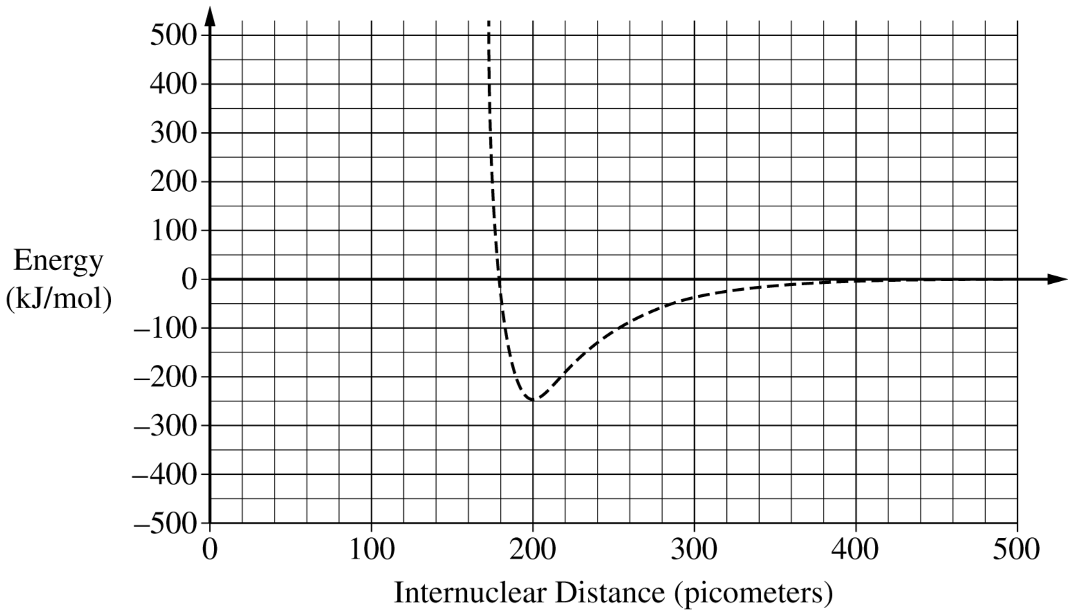
Reaction Number	Equation	ΔH_{rxn}° (kJ/mol$_{rxn}$)
2	$Al(s) + \frac{3}{2}\,Cl_2(g) \rightarrow AlCl_3(g)$	−583
3	$Al(s) \rightarrow Al(g)$	+326
4	$Cl_2(g) \rightarrow 2\,Cl(g)$	+243

(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 2** 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 Al – Cl bond length is 220 picometers and the average bond energy is 425 kJ/mol. Draw the potential energy curve for the average Al – Cl bond on the preceding graph.

(d) Three proposed Lewis diagrams for the $AlCl_3(g)$ molecule are shown.

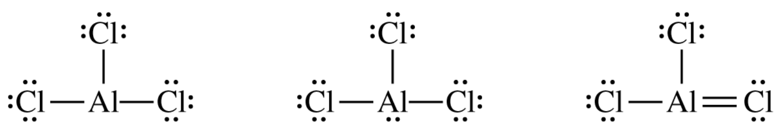


Diagram 1 Diagram 2 Diagram 3

(i) The $AlCl_3(g)$ 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.

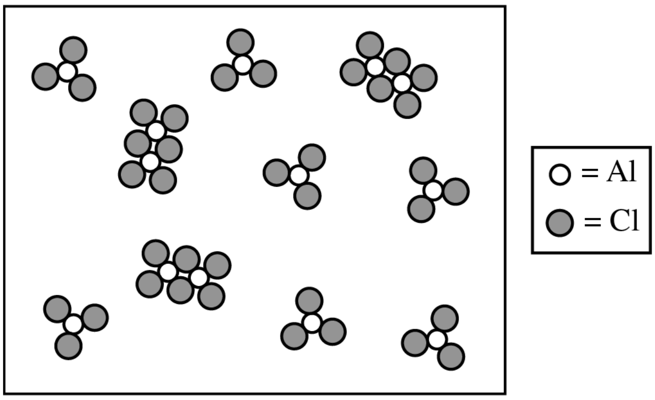
(ii) Which of the three diagrams is the best representation for the bonding in $AlCl_3$? Justify your choice based on formal charges.

$AlCl_3$ is known to dimerize reversibly in the gas phase. The dimerization equilibrium is represented by the following equation.

$$2\ AlCl_3(g) \rightleftarrows Al_2Cl_6(g)$$

(e) Write the expression for the equilibrium constant, K_p, for this reaction.

A particle-level diagram of an equilibrium mixture of $AlCl_3(g)$ and $Al_2Cl_6(g)$ 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.

GO ON TO THE NEXT PAGE.

. A Lewis electron-dot diagram of the oxalate ion, $C_2O_4{}^{2-}$, is shown.

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

(b) Silver oxalate, $Ag_2C_2O_4(s)$, is slightly soluble in water. The value of K_{sp} for $Ag_2C_2O_4$ is 5.40×10^{-12}.

(i) Write the expression for the solubility-product constant, K_{sp}, for $Ag_2C_2O_4$.

(ii) Calculate the molar solubility of $Ag_2C_2O_4$ in neutral distilled water.

(iii) The molar solubility of $Ag_2C_2O_4$ increases when it is dissolved in $0.5\,M$ $HClO_4(aq)$ 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 $Ag_2C_2O_4(aq)$ in $HClO_4(aq)$.

GO ON TO THE NEXT PAGE.

STOP

END OF EXAM

CHEMISTRY

Section II

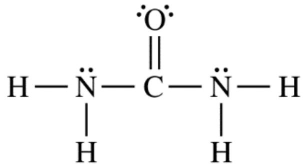
Time—1 hour and 45 minutes

7 Questions

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.

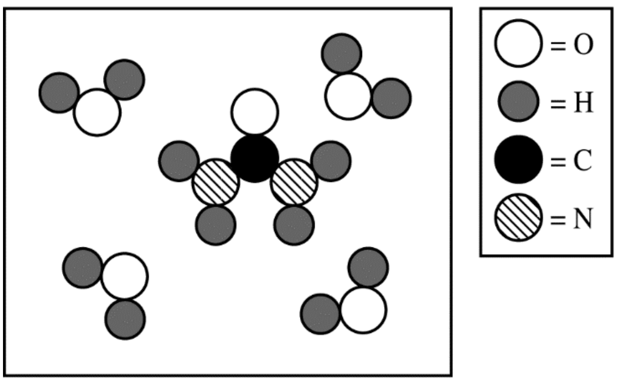
Write your response in the space provided following each question. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer.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



1. 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.

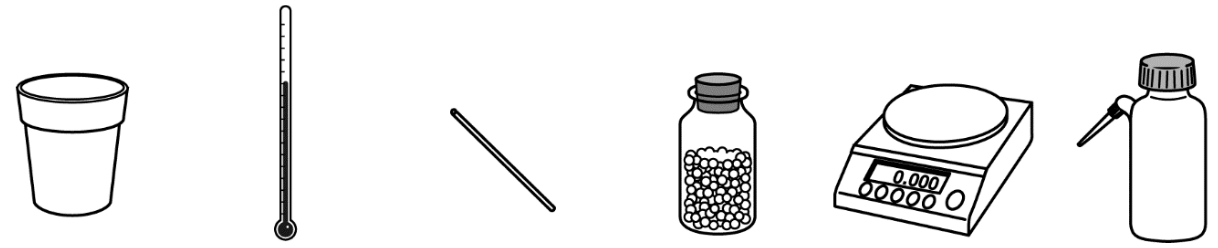


$$H_2NCONH_2(s) \rightleftarrows H_2NCONH_2(aq)$$

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.



Polystyrene Cup — Thermometer — Stirring Rod — Bottle of Urea — Balance — Distilled Water

(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))
$H_2NCONH_2(s)$	104.6
$H_2NCONH_2(aq)$	?

(f) The entropy change for the dissolution of urea, ΔS°_{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.

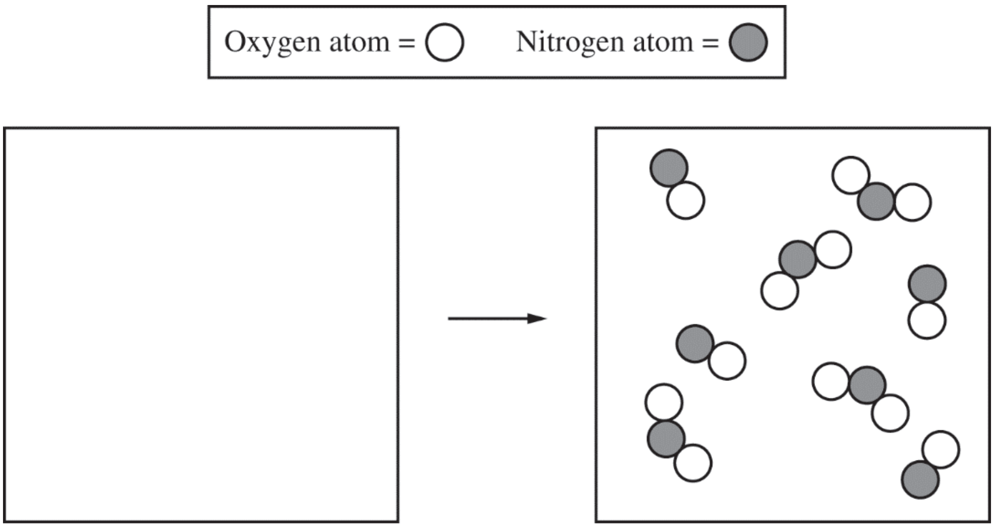
(g) Using particle-level reasoning, explain why ΔS°_{soln} is positive for the dissolution of urea in water.

(h) The student claims that $\Delta S°$ 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.

$$2\,NO(g) + O_2(g) \rightarrow 2\,NO_2(g)$$

2. A student investigates the reactions of nitrogen oxides. One of the reactions in the investigation requires an equimolar mixture of $NO(g)$ and $NO_2(g)$, which the student produces by using the reaction represented above.

   (a) The particle-level representation of the equimolar mixture of $NO(g)$ and $NO_2(g)$ in the flask at the completion of the reaction between $NO(g)$ and $O_2(g)$ 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 $NO(g)$ and $O_2(g)$ 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.



Reactant Mixture Product Mixture

The student reads in a reference text that $NO(g)$ and $NO_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.

$$NO(g) + NO_2(g) \rightleftarrows N_2O_3(g)$$

ΔH°_{298}	ΔS°_{298}	ΔG°_{298}
-40.4 kJ/mol$_{rxn}$	-138.5 J/(K·mol$_{rxn}$)	0.87 kJ/mol$_{rxn}$

   (b) The student begins with an equimolar mixture of $NO(g)$ and $NO_2(g)$ in a rigid reaction vessel and the mixture reaches equilibrium at 298 K.

      (i) Calculate the value of the equilibrium constant, K, for the reaction at 298 K.

      (ii) If both P_{NO} and P_{NO_2} in the vessel are initially 1.0 atm, will $P_{N_2O_3}$ at equilibrium be equal to 1.0 atm? Justify your answer.

   (c) The student hypothesizes that increasing the temperature will increase the amount of $N_2O_3(g)$ in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

$N_2O_3(g)$ reacts with water to form nitrous acid, $HNO_2(aq)$, a compound involved in the production of acid rain. The reaction is represented below.

$$N_2O_3(g) + H_2O(l) \rightarrow 2\ HNO_2(aq)$$

(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.

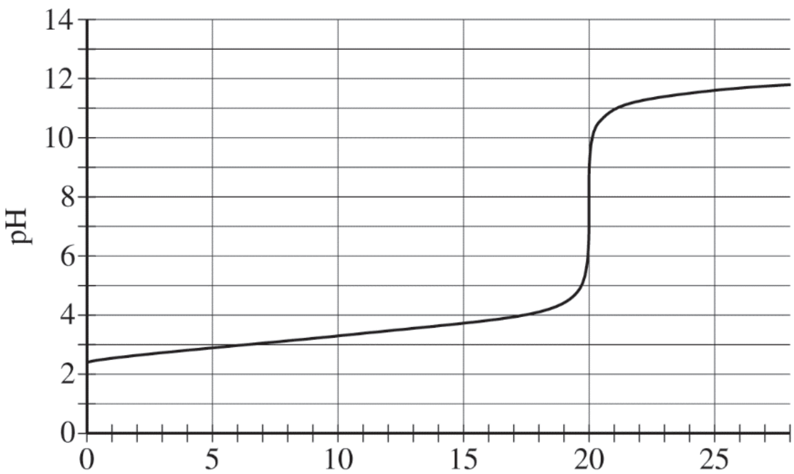
H O N O

(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 $N_2O_3(g)$ into distilled water. Assume that the reaction goes to completion and that HNO_2 is the only species produced. To determine the concentration of $HNO_2(aq)$ in the resulting solution, the student titrates a 100. mL sample of the solution with 0.100 M KOH(aq). The neutralization reaction is represented below.

$$HNO_2(aq) + OH^-(aq) \rightarrow NO_2^-(aq) + H_2O(l)$$

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



Volume of 0.100 M KOH(aq) Added (mL)

(e) Use the titration curve and the information above to

(i) determine the initial concentration of the $HNO_2(aq)$ solution

(ii) estimate the value of pK_a for $HNO_2(aq)$

(f) During the titration, after a volume of 15 mL of 0.100 M KOH(aq) has been added, which species, $HNO_2(aq)$ or $NO_2^-(aq)$, 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.

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$$CS_2(g) + 3\ Cl_2(g) \rightarrow CCl_4(g) + S_2Cl_2(g)$$

1. Carbon tetrachloride, $CCl_4(g)$, 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, $Cl_2(g)$, is initially present in the container at a pressure of 0.40 atm.

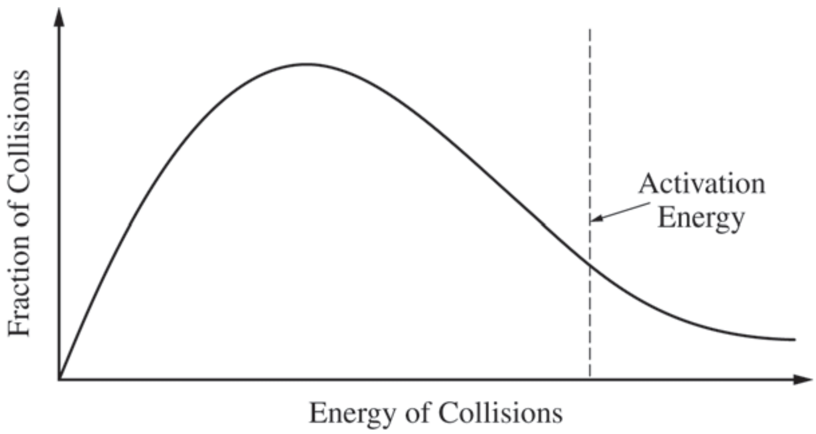
   (i) How many moles of $Cl_2(g)$ are in the container?

   (ii) How many grams of carbon disulfide, $CS_2(g)$, are needed to react completely with the $Cl_2(g)$?

   (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.

   (i) Explain how the higher temperature affects the collisions between the reactant molecules so that the reaction occurs at an observable rate at 120°C.

   (ii) 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.

Cl S S Cl

(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.)

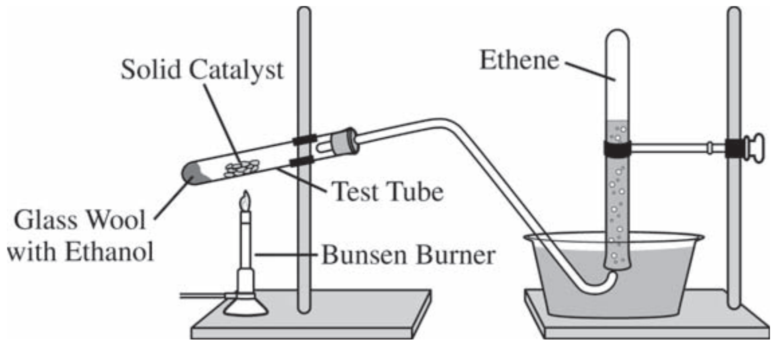
(d) $CCl_4(g)$ can also be produced by reacting $CHCl_3(g)$ with $Cl_2(g)$ at 400°C, as represented by the equation below.

$$CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$$

At the completion of the reaction a chemist successfully separates the $CCl_4(g)$ from the $HCl(g)$ by cooling the mixture to 70°C, at which temperature the $CCl_4(g)$ condenses while the $HCl(g)$ remains in the gaseous state.

(i) Identify all types of intermolecular forces present in $HCl(l)$.

(ii) What can be inferred about the relative strengths of the intermolecular forces in $CCl_4(l)$ and $HCl(l)$? Justify your answer in terms of the information above.



2. Ethene, $C_2H_4(g)$ (molar mass 28.1 g/mol), may be prepared by the dehydration of ethanol, $C_2H_5OH(g)$ (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.

$$\underset{\text{ethanol}}{C_2H_5OH(g)} \xrightarrow{\text{catalyst}} \underset{\text{ethene}}{C_2H_4(g)} + \underset{\text{water}}{H_2O(g)} \quad \Delta H^\circ_{298} = 45.5 \text{ kJ/mol}_{rxn}; \ \Delta S^\circ_{298} = 126 \text{ J/(K}\cdot\text{mol}_{rxn})$$

A student added a 0.200 g sample of $C_2H_5OH(l)$ to a test tube using the setup shown above. The student heated the test tube gently with a Bunsen burner until all of the $C_2H_5OH(l)$ 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 $C_2H_4(g)$

(i) that are actually produced in the experiment and measured in the gas collection tube and

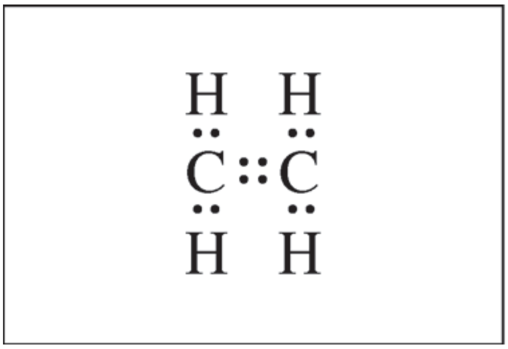
(ii) that would be produced if the dehydration reaction went to completion.

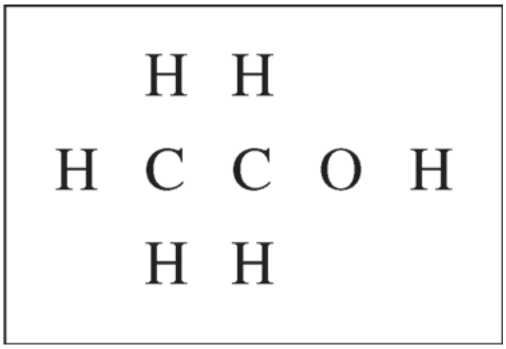
(b) Calculate the percent yield of $C_2H_4(g)$ in the experiment.

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 C_2H_5OH 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, $C_2H_4(g)$ and unreacted $C_2H_5OH(g)$ passed through the tube into the water. The C_2H_4 was quantitatively collected as a gas, but the unreacted C_2H_5OH 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 ClF_3. In the box below, draw a complete Lewis electron-dot diagram for a molecule of ClF_3.

(c) Two possible geometric shapes for the ClF_3 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 ClF_3 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 ClF_3 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.