AP Chemistry Unit 2

ADVANCED FRQ PRACTICE

APChemistryRescue.com

Molecular & Ionic Compound Structure and Properties

Difficulty: Challenging | Time: 150 minutes (15 min/question)

Master Chemical Bonding: From Lewis Structures to Intermolecular Forces!

Reference Information

- Avogadro's Number: $N_A = 6.022 \times 10^{23}\ \text{mol}^{-1}$
- Electronegativity: F (4.0) > O (3.5) > N (3.0) > Cl (3.0) > C (2.5) > H (2.1)
- Bond Energies: Provided in questions when needed
- VSEPR Theory: Predict molecular geometry from electron domains
- Coulomb's Law: $E = k(q_1q_2)/r$
- Formal Charge: FC = V - N - B/2 (V=valence, N=nonbonding, B=bonding)

⚡ **Unit 2 Focus:** Draw complete Lewis structures with all lone pairs visible, explain bonding using electronegativity differences, identify molecular geometries precisely, and connect IMF strength to physical properties. Always justify your reasoning!

1 Lewis Structures & Formal Charge Analysis

The thiocyanate ion (SCN^-) can be represented by multiple Lewis structures with different arrangements of atoms and electrons.

(a) Draw three different Lewis structures for the thiocyanate ion (SCN^-) that obey the octet rule, showing all lone pairs of electrons. The three structures should have different atomic arrangements. **(3 points)**

(b) For each Lewis structure drawn in part (a), calculate the formal charge on each atom. Show your work using the formal charge equation: $FC = V - N - B/2$, where V = valence electrons, N = non-bonding electrons, B = bonding electrons. **(6 points)**

(c) Based on formal charge analysis, determine which Lewis structure is the most stable and likely to contribute most significantly to the actual bonding in the thiocyanate ion. Justify your answer using formal charge principles. **(3 points)**

(d) Explain why the thiocyanate ion does not typically place the nitrogen atom in the center of the structure, even though nitrogen is less electronegative than carbon. Use both formal charge and molecular orbital considerations. **(3 points)**

2 VSEPR Theory & Molecular Geometry

Consider the following four molecules: NH_3, BF_3, SF_4, and XeF_4.

(a) For each molecule, determine:

- (i) The total number of valence electrons
- (ii) The Lewis structure (including all lone pairs)
- (iii) The electron domain geometry
- (iv) The molecular geometry

(8 points total, 2 per molecule)

(b) Identify which of these molecules are polar and which are nonpolar. For each molecule, justify your answer by discussing both molecular geometry and bond polarity. **(4 points)**

(c) Compare the bond angles in NH_3 and BF_3. Explain why the H-N-H bond angle in NH_3 (approximately 107°) is smaller than the ideal tetrahedral angle of 109.5°, while the F-B-F bond angle in BF_3 is exactly 120°. **(3 points)**

(d) XeF_4 is an example of a noble gas compound. Explain how xenon can form stable compounds despite being a noble gas, and why smaller noble gases (like helium and neon) do not form similar compounds under normal conditions. **(3 points)**

3 Hybridization & Bonding Theory

The acetone molecule (CH_3COCH_3) contains both single and double bonds with different carbon hybridization states.

Acetone Structure:

$H_3C—CO—CH_3$

(a) Draw the complete Lewis structure for acetone, showing all bonds and lone pairs of electrons. **(2 points)**

(b) Identify the hybridization of each carbon atom in the acetone molecule. Explain your reasoning for each carbon. **(4 points)**

(c) Describe the types of bonds (sigma and pi) present in the C=O double bond. Explain which atomic orbitals overlap to form each bond type. **(3 points)**

(d) Predict the approximate C-C-O bond angle and the C-C-H bond angle. Justify your predictions using hybridization and VSEPR theory. **(3 points)**

(e) Explain why rotation around the C=O double bond is restricted, while rotation around the C-C single bonds is relatively free. Use orbital overlap diagrams or descriptions to support your explanation. **(3 points)**

4 Intermolecular Forces & Physical Properties

Four liquids are analyzed in a laboratory: water (H_2O), methanol (CH_3OH), acetone (CH_3COCH_3), and hexane (C_6H_{14}).

SUBSTANCE	MOLECULAR FORMULA	MOLAR MASS (G/MOL)	BOILING POINT (°C)
Water	H_2O	18.0	100.0
Methanol	CH_3OH	32.0	64.7
Acetone	CH_3COCH_3	58.1	56.2
Hexane	C_6H_{14}	86.2	68.7

(a) Identify the predominant type(s) of intermolecular forces present in each substance. Be specific about hydrogen bonding, dipole-dipole interactions, and London dispersion forces. **(4 points)**

(b) Explain why water has a significantly higher boiling point than methanol, even though both molecules can form hydrogen bonds and water has a lower molar mass. **(3 points)**

(c) Compare the boiling points of acetone and hexane. Explain why hexane has a higher boiling point than acetone despite acetone having dipole-dipole interactions and hexane having only London dispersion forces. **(3 points)**

(d) Water and methanol are completely miscible (form a homogeneous solution in all proportions), but water and hexane are immiscible. Explain these observations using the principle "like dissolves like" and intermolecular force considerations. **(3 points)**

(e) Predict and explain the relative surface tensions of water and hexane.

Which substance would have higher surface tension, and why? **(2 points)**

5 Ionic Bonding & Lattice Energy

Consider the ionic compounds NaCl, MgO, and CaO.

COMPOUND	CATION CHARGE	ANION CHARGE	IONIC RADIUS (PM) CATION	IONIC RADIUS (PM) ANION	LATTICE ENERGY (KJ/MOL)
NaCl	+1	-1	102	181	-786
MgO	+2	-2	72	140	-3795
CaO	+2	-2	100	140	-3414

(a) Using Coulomb's Law ($E \propto q_1q_2/r$), explain why MgO has a much larger (more negative) lattice energy than NaCl. Consider both ionic charges and ionic radii in your explanation. **(4 points)**

(b) Compare the lattice energies of MgO and CaO. Both compounds have the same ionic charges (+2 and -2), but MgO has a larger lattice energy. Explain this difference using the relationship between lattice energy and ionic radius. **(3 points)**

(c) The melting point of MgO (2852°C) is significantly higher than that of NaCl (801°C). Explain this difference in terms of lattice energy and the strength of ionic bonding. **(3 points)**

(d) Predict whether Li_2O or Na_2O would have a larger lattice energy. Justify your prediction using ionic radii considerations. (Given: Li^+ radius = 76 pm, Na^+ radius = 102 pm, O^{2-} radius = 140 pm) **(3 points)**

(e) Explain why ionic compounds like NaCl conduct electricity when molten or dissolved in water, but not in the solid state. **(2 points)**

6 Resonance Structures & Electron Delocalization

The nitrate ion (NO_3^-) exhibits resonance, meaning its actual structure is a hybrid of multiple Lewis structures.

(a) Draw all three resonance structures for the nitrate ion (NO_3^-), showing all bonds and lone pairs. **(3 points)**

(b) Calculate the formal charge on each atom in one of your resonance structures. Show all calculations. **(2 points)**

(c) Explain why all three N-O bonds in the nitrate ion are identical in length and strength, even though the Lewis structures show one double bond and two single bonds. Use the concept of electron delocalization in your explanation. **(3 points)**

(d) Calculate the average bond order for the N-O bonds in the nitrate ion. Show your work. **(2 points)**

(e) Compare the N-O bond length in the nitrate ion to the N-O bond length in the nitrite ion (NO_2^-), which has two resonance structures. Predict which ion has shorter N-O bonds and explain your reasoning using bond order. **(3 points)**

(f) Identify the molecular geometry and bond angles in the nitrate ion. Explain whether the nitrate ion is polar or nonpolar. **(2 points)**

7 Metallic Bonding & Alloys

Metallic bonding involves the delocalization of valence electrons throughout a metallic crystal structure.

(a) Describe the "electron sea model" of metallic bonding. In your description, explain how this model accounts for the electrical conductivity of metals. **(3 points)**

(b) Compare the melting points of sodium (Na, 97.7°C) and magnesium (Mg, 650°C). Explain why magnesium has a significantly higher melting point than sodium in terms of metallic bonding strength. **(3 points)**

(c) Explain why metals are malleable (can be hammered into sheets) and ductile (can be drawn into wires), while ionic compounds are brittle and fracture when stressed. Use bonding models to support your explanation. **(4 points)**

(d) Brass is an alloy composed of copper (Cu) and zinc (Zn). Sterling silver is an alloy of silver (Ag) and copper (Cu). Explain how alloying affects the properties of pure metals, and classify these alloys as either substitutional or interstitial. Justify your classifications. **(4 points)**

(e) Explain why metals have luster (appear shiny) using the electron sea model and the interaction of light with delocalized electrons. **(2 points)**

8 Network Covalent & Molecular Solids

Different types of solids exhibit different physical properties based on their bonding and structure.

SUBSTANCE	MELTING POINT (°C)	ELECTRICAL CONDUCTIVITY	SOLUBILITY IN WATER
Diamond (C)	3550	None	Insoluble
Graphite (C)	3652	Good (in plane)	Insoluble
Iodine (I_2)	114	None	Slightly soluble
Silicon dioxide (SiO_2)	1713	None	Insoluble

(a) Classify each substance as either a network covalent solid or a molecular solid. Justify your classifications using the melting point data provided. **(4 points)**

(b) Both diamond and graphite are composed entirely of carbon atoms, yet graphite conducts electricity while diamond does not. Explain this difference in terms of bonding and structure. **(4 points)**

(c) Explain why molecular solids like iodine have much lower melting points than network covalent solids like diamond and silicon dioxide. **(3 points)**

(d) Silicon dioxide (SiO_2) and carbon dioxide (CO_2) are both composed of one central atom bonded to two oxygen atoms, yet SiO_2 forms a network solid with

> a very high melting point (1713°C) while CO_2 is a molecular solid that sublimes at -78°C. Explain this dramatic difference in properties. **(4 points)**

9 Bond Energy & Enthalpy Calculations

Bond energies can be used to estimate the enthalpy change (ΔH) for chemical reactions using the equation:

ΔH_{rxn} = Σ(bonds broken) - Σ(bonds formed)

Bond Energies (kJ/mol):

C-H: 413 | C-C: 348 | C=C: 614 | C-O: 358 | C=O: 799

O-H: 463 | O=O: 495 | H-H: 436 | N-H: 391 | N≡N: 945

Consider the combustion of methane:

$CH_4(g) + 2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(g)$

(a) Draw Lewis structures for all reactants and products, showing all bonds. **(2 points)**

(b) Calculate the total energy required to break all bonds in the reactants (CH_4 and O_2). Show all work with units. **(3 points)**

(c) Calculate the total energy released when forming all bonds in the products (CO_2 and H_2O). Show all work with units. **(3 points)**

(d) Calculate the estimated enthalpy change (ΔH_{rxn}) for this combustion reaction. Is the reaction exothermic or endothermic? **(3 points)**

(e) The actual experimental value for this reaction is ΔH_{rxn} = -802 kJ/mol. Compare your calculated value to the experimental value. Explain why bond energy calculations provide only estimates and may differ from experimental values. **(3 points)**

10 Photoelectron Spectroscopy & Bonding

Photoelectron spectroscopy (PES) can provide information about the electronic structure and bonding in molecules.

(a) The PES spectrum of N_2 shows peaks at the following approximate ionization energies (in MJ/mol): 1.5, 1.9, 15.6, and 409. Assign each peak to the appropriate molecular orbital: σ_{1s}, σ^*_{1s}, σ_{2s}, σ^*_{2s}, π_{2p}, σ_{2p}, or π^*_{2p}. Explain your reasoning. **(4 points)**

(b) Calculate the bond order of N_2 using molecular orbital theory. The electron configuration of N_2 is: $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2$. Show your calculation. **(2 points)**

(c) Compare the bond length and bond energy of N_2 (bond order = 3) to that of O_2 (bond order = 2). Which molecule would have a shorter bond length and higher bond energy? Explain your reasoning. **(3 points)**

(d) Using molecular orbital theory, explain why N_2 is diamagnetic (has no unpaired electrons) while O_2 is paramagnetic (has unpaired electrons). **(3 points)**

(e) The ionization energy from the σ_{2p} orbital of N_2 (1.5 MJ/mol) is lower than the ionization energy from the π_{2p} orbitals (1.9 MJ/mol). This is unusual because σ bonds are typically stronger than π bonds. Propose an explanation for this observation. **(3 points)**

📋 DETAILED ANSWER KEY & SCORING RUBRIC

> Complete Solutions with Step-by-Step Explanations

✓ Question 1 Solutions (15 points total)

(a) Three Lewis structures for SCN$^-$ (3 points)

```
Structure 1: [S=C=N]⁻
                 ..
             :S=C=N:
              ..   ..


Structure 2: [S-C≡N]⁻
                 ..
             :S-C≡N:
                 ..


Structure 3: [S≡C-N]⁻
                    ..
             :S≡C-N:
                    ..
```

3 points (1 point each structure with all lone pairs)

(b) Formal charge calculations (6 points)

Structure 1: [S=C=N]$^-$ S: FC = 6 - 4 - 4/2 = 6 - 4 - 2 = 0 C: FC = 4 - 0 - 8/2 = 4 - 0 - 4 = 0 N: FC = 5 - 4 - 4/2 = 5 - 4 - 2 = -1 Structure 2: [S-C≡N]$^-$ S: FC = 6 - 6 - 2/2 = 6 - 6 - 1 = -1 C: FC = 4 - 0 - 8/2 = 4 - 0 - 4 = 0 N: FC = 5 - 2 - 6/2 = 5 - 2 - 3 = 0 Structure 3: [S≡C-N]$^-$ S: FC = 6 - 2 - 6/2 = 6 - 2 - 3 = +1 C: FC = 4 - 0 - 8/2 = 4 - 0 - 4 = 0 N: FC = 5 - 6 - 2/2 = 5 - 6 - 1 = -2

6 points (2 points per structure)

(c) Most stable structure (3 points)

> ***Structure 2 [S-C≡N]⁻ is the most stable*** *for the following reasons: 1.* ***Minimal formal charges:*** *The formal charges are either 0 or ±1, which is preferred over Structure 3 which has a -2 formal charge. 2.* ***Negative charge on most electronegative atom:*** *The -1 formal charge is on sulfur (electronegativity 2.5), which is less electronegative than nitrogen (3.0). However, this structure places the negative charge furthest from the highly electronegative nitrogen, which helps stabilize the structure. 3.* ***Optimal charge distribution:*** *Structure 2 has the best balance between minimizing formal charges and placing negative charge on an appropriate atom. Structure 1 is also stable (negative charge on N), but Structure 2 is observed most commonly in thiocyanate chemistry.*

3 points (1 for identifying Structure 2, 2 for complete justification)

(d) Why nitrogen is not central (3 points)

> *If nitrogen were placed in the center (making structures like S-N-C), the formal charge distribution would be highly unfavorable. Carbon has 4 valence electrons and "wants" to make 4 bonds, while nitrogen has 5 valence electrons and typically makes 3 bonds. Placing nitrogen in the center would force it to make more bonds than optimal, creating large formal charges. Additionally, carbon is more versatile in forming multiple bonds and can accommodate different bonding arrangements more readily than nitrogen. Molecular orbital considerations also suggest that carbon's 2p orbitals are better suited for forming the strong multiple bonds required in the thiocyanate ion when carbon is centrally located. The observed [S-C≡N]⁻ structure allows carbon to utilize its full bonding capacity efficiently while keeping formal charges minimal.*

3 points (1 for formal charge reasoning, 1 for bonding preferences, 1 for MO considerations)

✓ Question 2 Solutions (18 points total)

(a) Molecular geometry analysis (8 points)

`NH₃ (Ammonia):` (i) Valence electrons: N(5) + 3×H(1) = 8 total (ii) Lewis structure: N central with 3 H atoms bonded and 1 lone pair on N (iii) Electron domain geometry: Tetrahedral (4 electron domains) (iv) Molecular geometry: Trigonal pyramidal **BF₃ (Boron trifluoride):** (i) Valence electrons: B(3) + 3×F(7) = 24 total (ii) Lewis structure: B central with 3 F atoms bonded, no lone pairs on B (iii) Electron domain geometry: Trigonal planar (3 electron domains) (iv) Molecular geometry: Trigonal planar **SF₄ (Sulfur tetrafluoride):** (i) Valence electrons: S(6) + 4×F(7) = 34 total (ii) Lewis structure: S central with 4 F atoms bonded and 1 lone pair on S (iii) Electron domain geometry: Trigonal bipyramidal (5 electron domains) (iv) Molecular geometry: Seesaw (or distorted tetrahedral) **XeF₄ (Xenon tetrafluoride):** (i) Valence electrons: Xe(8) + 4×F(7) = 36 total (ii) Lewis structure: Xe central with 4 F atoms bonded and 2 lone pairs on Xe (iii) Electron domain geometry: Octahedral (6 electron domains) (iv) Molecular geometry: Square planar

8 points (2 points per molecule: 0.5 each component)

(b) Polarity analysis (4 points)

> ***NH_3: POLAR*** *N-H bonds are polar (ΔEN = 0.9), and the trigonal pyramidal geometry is asymmetric. The lone pair on nitrogen creates a dipole moment pointing toward nitrogen, and the three N-H bond dipoles do not cancel. Net molecular dipole exists.* ***BF_3: NONPOLAR*** *B-F bonds are polar (ΔEN = 2.0), but the trigonal planar geometry is perfectly symmetric. The three B-F bond dipoles are arranged 120° apart and cancel completely. No net molecular dipole.* ***SF_4: POLAR*** *S-F bonds are polar (ΔEN = 1.5), and the seesaw geometry is asymmetric due to the lone pair on sulfur. The four S-F bond dipoles do not*

> *cancel. Net molecular dipole exists.* ***XeF_4: NONPOLAR*** *Xe-F bonds are polar (ΔEN = 1.4), but the square planar geometry is symmetric. The four Xe-F bond dipoles arranged in a square cancel completely (two pairs of opposing dipoles). No net molecular dipole despite polar bonds.*

4 points (1 point per molecule)

(c) Bond angle comparison (3 points)

> *In NH_3, the H-N-H bond angle (107°) is compressed below the ideal tetrahedral angle (109.5°) because the lone pair on nitrogen occupies more space than bonding pairs. Lone pair-bonding pair repulsion is stronger than bonding pair-bonding pair repulsion (VSEPR), forcing the three N-H bonds closer together and reducing the H-N-H angle. In BF_3, the F-B-F bond angle is exactly 120° because boron has no lone pairs and only three electron domains. The three bonding pairs arrange themselves as far apart as possible in trigonal planar geometry, creating perfect 120° angles with no distortion from lone pair repulsion. The key difference: lone pairs compress bond angles, while the absence of lone pairs allows ideal geometric angles.*

3 points (1 for NH_3 explanation, 1 for BF_3 explanation, 1 for comparison)

(d) Noble gas compounds (3 points)

> *Xenon can form stable compounds because it is a large atom (5th period) with relatively low ionization energy and available d orbitals in its valence shell. The larger atomic size means the valence electrons are farther from the nucleus and less tightly held, making them more accessible for bonding. Xenon can expand its octet by utilizing d orbitals to accommodate more than 8 electrons. Smaller noble gases like helium and neon cannot form similar compounds under normal conditions because: 1. They have very high ionization energies (electrons tightly held) 2. They are small atoms with valence electrons close to the nucleus 3. They lack accessible d orbitals for octet expansion 4. Their small size creates strong electron-electron repulsion in potential compounds Only under extreme conditions (very high pressure) can some lighter noble gas compounds be formed.*

3 points (1 for xenon explanation, 2 for comparison to lighter noble gases)

✓ Question 3 Solutions (15 points total)

(a) Lewis structure for acetone (2 points)

```
     H    O    H
      |   ‖    |
   H—C—C—C—H
     |         |
     H         H

With lone pairs on oxygen:
    H    :Ö:    H
     |    ‖     |
   H—C—C—C—H
     |          |
     H          H
```

2 points (1 for correct connectivity, 1 for lone pairs on O)

(b) Hybridization of carbon atoms (4 points)

Left CH_3 carbon: sp^3 hybridization Reasoning: This carbon has 4 electron domains (4 single bonds to 3 H and 1 C). Four electron domains require sp^3 hybridization, creating tetrahedral geometry. **Central C=O carbon:** sp^2 hybridization Reasoning: This carbon has 3 electron domains (1 double bond to O, 2 single bonds to adjacent carbons). Three electron domains require sp^2 hybridization, creating trigonal planar geometry around this carbon. **Right CH_3 carbon:** sp^3 hybridization Reasoning: Same as left carbon - 4 electron domains (4 single bonds), requiring sp^3 hybridization and tetrahedral geometry.

4 points (1 for each carbon identification, 1 for complete reasoning)

(c) Sigma and pi bonds in C=O (3 points)

> *The C=O double bond consists of: **1 sigma (σ) bond:** Formed by head-on overlap of sp^2 hybrid orbital from carbon with sp^2 hybrid orbital from oxygen. This creates electron density directly along the internuclear axis. The σ bond is strong and allows for rotation. **1 pi (π) bond:** Formed by side-by-side overlap of unhybridized p orbitals (one from carbon, one from oxygen). The p orbitals are perpendicular to the plane of the molecule and create electron density above and below the internuclear axis. The π bond is weaker than the σ bond and restricts rotation. Total: The C=O double bond = 1σ + 1π*

3 points (1 for σ bond description, 1 for π bond description, 1 for orbital identification)

(d) Bond angle predictions (3 points)

C-C-O bond angle: Approximately 120° The central carbon (with C=O) is sp^2 hybridized with 3 electron domains (trigonal planar geometry). The ideal angle for trigonal planar is 120°. The actual angle is very close to 120° because all three groups around this carbon are bonding pairs with similar repulsion. **C-C-H bond angle (in CH_3 groups):** Approximately 109.5° The CH_3 carbons are sp^3 hybridized with 4 electron domains (tetrahedral geometry). The ideal tetrahedral angle is 109.5°, and since there are no lone pairs to distort the geometry, the actual angle is very close to this ideal value.

3 points (1 for each angle prediction, 1 for justifications)

(e) Rotation restriction explanation (3 points)

> ***C=O double bond (restricted rotation):** Rotation around the C=O bond is restricted because the π bond must be broken for rotation to occur. The π bond is formed by side-by-side overlap of p orbitals perpendicular to the bond axis. If the molecule rotates around the C=O bond, the p orbitals would no longer be aligned for overlap, breaking the π bond. Since breaking the π bond requires significant energy (~264 kJ/mol for C=O π bond), rotation is effectively prevented at normal*

> > *temperatures.* ***C-C single bonds (free rotation):*** *Rotation around C-C single bonds is relatively free because only σ bonds are present. σ bonds form through head-on orbital overlap along the bond axis. When the molecule rotates around a σ bond, the orbital overlap is maintained because the overlap region is cylindrically symmetric around the bond axis. The σ bond remains intact during rotation, requiring minimal energy.* ***Key concept:*** *σ bonds allow rotation; π bonds prevent rotation.*
>
> **3 points** (1 for C=O explanation, 1 for C-C explanation, 1 for orbital overlap reasoning)

✓ Question 4 Solutions (15 points total)

(a) Intermolecular forces identification (4 points)

Water (H_2O): - Hydrogen bonding (strong dipole-dipole with H-O bonds) - London dispersion forces (present in all molecules) Primary: Hydrogen bonding **Methanol (CH_3OH):** - Hydrogen bonding (O-H group can form H-bonds) - Dipole-dipole interactions (polar molecule) - London dispersion forces Primary: Hydrogen bonding **Acetone (CH_3COCH_3):** - Dipole-dipole interactions (C=O creates molecular dipole) - London dispersion forces Primary: Dipole-dipole (no H-bonding - no H on O) **Hexane (C_6H_{14}):** - London dispersion forces only (nonpolar molecule) Primary: London dispersion

4 points (1 point per substance)

(b) Water vs methanol boiling points (3 points)

> *Water (BP = 100.0°C) has a significantly higher boiling point than methanol (BP = 64.7°C) despite both forming hydrogen bonds because:* ***1. Number of H-bonds per molecule:*** *Each water molecule can form 4 hydrogen bonds (2 as donor using its 2 H atoms, 2 as acceptor using its 2 lone pairs on oxygen). Methanol can form only 3 hydrogen bonds maximum (1 as donor from its single O-H, 2 as acceptor from oxygen's lone pairs).* ***2. H-bonding network:*** *Water forms an extensive 3D network of hydrogen bonds where each molecule is hydrogen-bonded to approximately 4 neighbors. This creates a highly interconnected structure requiring more energy to break apart. Methanol's bulky CH_3 group disrupts the H-bonding network, making it less extensive.* ***3. Molecular size efficiency:*** *Water's small size allows closer approach and stronger H-bonds. The large CH_3 group in methanol creates steric hindrance, weakening the overall H-bonding network.*

3 points (1 for H-bond number, 1 for network explanation, 1 for size consideration)

(c) Acetone vs hexane boiling points (3 points)

> *Hexane (BP = 68.7°C) has a higher boiling point than acetone (BP = 56.2°C) despite acetone having dipole-dipole interactions because:* ***Molecular size dominates:*** *Hexane (C_6H_{14}, MM = 86.2 g/mol) is significantly larger than acetone (C_3H_6O, MM = 58.1 g/mol). Larger molecules have more electrons and greater surface area, leading to stronger London dispersion forces.* ***Polarizability:*** *Hexane's larger electron cloud is more polarizable, creating stronger instantaneous and induced dipoles. The total strength of London dispersion forces in hexane exceeds the combined strength of dipole-dipole interactions plus weaker dispersion forces in acetone.* ***Molecular shape:*** *Hexane's linear shape allows extensive intermolecular contact, maximizing dispersion forces. Acetone's more compact shape limits surface contact between molecules. This demonstrates that molecular size and dispersion forces can overcome the effect of dipole-dipole interactions when the size difference is large enough.*

3 points (1 for molecular size, 1 for dispersion force strength, 1 for shape consideration)

(d) Miscibility explanation (3 points)

> ***Water and methanol (miscible):*** *Both molecules are polar and can form hydrogen bonds. When mixed, methanol molecules can hydrogen bond with water molecules, releasing energy that compensates for breaking water-water and methanol-methanol H-bonds. The similar intermolecular forces allow favorable interactions, satisfying "like dissolves like."* ***Water and hexane (immiscible):*** *Water is highly polar with extensive H-bonding, while hexane is completely nonpolar with only dispersion forces. Dissolving hexane in water would require breaking strong water-water H-bonds without forming equally strong water-hexane interactions (since only weak dipole-induced dipole forces would form). This is energetically unfavorable. Water molecules prefer to maximize H-bonding with each other, excluding nonpolar hexane molecules. Additionally, dissolving*

> *hexane would disrupt water's organized H-bonding network, decreasing entropy of water structure. The entropy decrease is not compensated by favorable enthalpic interactions, making mixing thermodynamically unfavorable.*

3 points (1 for water-methanol, 1 for water-hexane, 1 for energetic reasoning)

(e) Surface tension comparison (2 points)

> ***Water has MUCH higher surface tension than hexane.*** *Surface tension arises from the unbalanced intermolecular forces at the liquid surface. Water's strong hydrogen bonding creates powerful cohesive forces pulling surface molecules inward, resulting in high surface tension (72 mN/m at 25°C). Hexane's weak London dispersion forces create much weaker cohesive forces, resulting in low surface tension (18 mN/m at 25°C). Water's surface tension is approximately 4× greater than hexane's, allowing water to form droplets and support small objects (like insects) on its surface.*

2 points (1 for prediction, 1 for explanation)

✓ Question 5 Solutions (15 points total)

(a) MgO vs NaCl lattice energy (4 points)

Using Coulomb's Law: $E \propto (q_1 \times q_2) / r$ **Charge effect:** MgO: $q_1 = +2$, $q_2 = -2$, so $q_1 \times q_2 = +2 \times (-2) = 4$ NaCl: $q_1 = +1$, $q_2 = -1$, so $q_1 \times q_2 = +1 \times (-1) = 1$ The charge product for MgO is 4× larger than NaCl, creating much stronger electrostatic attraction (4× stronger from charge alone). **Distance effect:** MgO: $r = 72 + 140 = 212$ pm NaCl: $r = 102 + 181 = 283$ pm MgO has a smaller ionic separation (212 pm vs 283 pm), which increases the electrostatic attraction further. Since $E \propto 1/r$, smaller r means larger E. Ratio: 283/212 = 1.33× stronger attraction from distance factor **Combined effect:** MgO lattice energy is approximately 4 × 1.33 ≈ 5.3× more negative than NaCl from Coulomb's Law considerations. Experimental: $|-3795|/|-786| = 4.8\times$ (close to prediction!)

4 points (2 for charge analysis, 1 for distance analysis, 1 for combined reasoning)

(b) MgO vs CaO comparison (3 points)

> *MgO (lattice energy = -3795 kJ/mol) has a larger (more negative) lattice energy than CaO (lattice energy = -3414 kJ/mol) despite both having the same ionic charges (+2 and -2) because:* ***Ionic radius effect:*** *•* Mg^{2+} *radius = 72 pm (smaller cation) •* Ca^{2+} *radius = 100 pm (larger cation) •* O^{2-} *radius = 140 pm (same anion)* ***Calculation:*** *MgO separation: r = 72 + 140 = 212 pm CaO separation: r = 100 + 140 = 240 pm Since* $E \propto 1/r$*, the smaller distance in MgO creates stronger electrostatic attraction. The smaller* Mg^{2+} *ion allows closer approach to* O^{2-}*, increasing the lattice energy by approximately (240/212) = 1.13× or about 13% stronger from distance alone. The actual ratio:* $|-3795|/|-3414| = 1.11\times$*, confirming the prediction.*

3 points (1 for identifying ionic radius, 1 for calculation, 1 for relationship)

(c) Melting point correlation (3 points)

> *MgO's melting point (2852°C) is dramatically higher than NaCl's (801°C) because melting point correlates directly with lattice energy—the strength of ionic bonding.* ***Energy requirement:*** *To melt an ionic compound, sufficient energy must be supplied to overcome the electrostatic attractions holding ions in the crystal lattice. MgO's much larger lattice energy (|-3795| vs |-786| kJ/mol, nearly 5× greater) means significantly more energy is required to disrupt the crystal structure.* ***Bonding strength:*** *The* Mg^{2+}*-*O^{2-} *electrostatic attraction is far stronger than* Na^+*-*Cl^- *attraction due to both higher charges (2+ and 2- vs 1+ and 1-) and smaller ionic radii. These stronger ionic bonds require much higher temperatures to break. The melting point difference of over 2000°C reflects the dramatic difference in ionic bond strength between these compounds.*

3 points (1 for correlation statement, 2 for detailed explanation)

(d) Li_2O vs Na_2O prediction (3 points)

Prediction: Li_2O has LARGER lattice energy than Na_2O Reasoning using Coulomb's Law ($E \propto q_1q_2/r$): Both compounds have same charges: M^+ and O^{2-} Ionic radii: Li^+ = 76 pm (smaller) Na^+ = 102 pm (larger) O^{2-} = 140 pm (same) Distance calculations: Li_2O: r = 76 + 140 = 216 pm Na_2O: r = 102 + 140 = 242 pm Since $E \propto 1/r$ and Li_2O has smaller r, it has larger lattice energy. Ratio: 242/216 = 1.12 Li_2O lattice energy is approximately 12% more negative than Na_2O. **Conclusion:** Smaller cation (Li^+) → shorter distance → stronger electrostatic attraction → larger lattice energy

3 points (1 for correct prediction, 2 for complete justification with calculation)

(e) Electrical conductivity explanation (2 points)

> ***Solid state (no conductivity):*** *In solid ionic compounds, ions are locked in fixed positions within the crystal lattice. They cannot move freely, so they cannot conduct electricity despite being charged particles. Electrical current requires mobile charge carriers.* ***Molten or aqueous (conducts electricity):*** *When*

> *melted or dissolved in water, the rigid crystal structure breaks down and ions become mobile. These free-moving ions can carry electrical current by migrating toward oppositely charged electrodes (cations → cathode, anions → anode), allowing electrical conductivity.*

2 points (1 for solid explanation, 1 for liquid/aqueous explanation)

✓ Question 6 Solutions (15 points total)

(a) Three resonance structures for NO_3^- (3 points)

```
         ..              ..              ..
        :O:             :O              :O:
       //                |              \\
      N                 N                N
    /  \              / \\            //  \
  :O:  :O⁻          :O⁻  :O:        :O:  :O⁻
   ..   ..           ..   ..         ..   ..

Structure 1      Structure 2      Structure 3
```

3 points (1 point each structure, must show all lone pairs)

(b) Formal charge calculation (2 points)

Using Structure 1: Nitrogen (N): FC = 5 - 0 - 8/2 = 5 - 0 - 4 = +1 Doubly-bonded oxygen (top): FC = 6 - 4 - 4/2 = 6 - 4 - 2 = 0 Singly-bonded oxygen (bottom left): FC = 6 - 6 - 2/2 = 6 - 6 - 1 = -1 Singly-bonded oxygen (bottom right): FC = 6 - 6 - 2/2 = 6 - 6 - 1 = -1 Sum of formal charges: +1 + 0 + (-1) + (-1) = -1 ✓ (matches the overall charge of NO_3^-)

2 points (1 for all calculations shown, 1 for correct values)

(c) Bond length equality explanation (3 points)

> *All three N-O bonds in the nitrate ion are identical in length and strength (even though individual Lewis structures show one double bond and two single bonds) because the actual structure of NO_3^- is a **resonance hybrid**—an average of all three resonance structures. **Electron delocalization:** The electrons in the π*

> *system are not localized between specific atom pairs but are delocalized (spread out) across all four atoms (N and three O atoms). This creates a "cloud" of π electron density distributed equally over all three N-O bonds.* ***Experimental evidence:*** *X-ray crystallography shows all three N-O bonds have identical length (122 pm), which is intermediate between a typical N-O single bond (136 pm) and N=O double bond (115 pm). This intermediate bond length is consistent with electron delocalization and resonance. The resonance hybrid is more stable than any single Lewis structure would suggest, and all three N-O bonds share the "extra" electron density equally.*

3 points (1 for resonance hybrid concept, 1 for delocalization, 1 for experimental evidence)

(d) Average bond order calculation (2 points)

Bond order = (Total number of bonds) / (Number of bonding locations) In each resonance structure: - 1 double bond (bond order = 2) - 2 single bonds (bond order = 1 each) - Total bonds = 2 + 1 + 1 = 4 There are 3 N-O bonding locations Average bond order = 4 bonds / 3 locations = 4/3 = 1.33 Alternatively: Average of (2 + 1 + 1) / 3 = 4/3 = 1.33

2 points (1 for method, 1 for correct answer)

(e) NO_3^- vs NO_2^- bond length comparison (3 points)

NO_2^- (nitrite ion) resonance: Has 2 resonance structures with N-O bonds Total bonds = 1 double + 1 single = 3 bonds total Number of N-O locations = 2 Average bond order = 3/2 = 1.5 **Comparison:** NO_3^-: bond order = 1.33 NO_2^-: bond order = 1.5 **Prediction: NO_2^- has SHORTER N-O bonds than NO_3^-** Reasoning: Higher bond order = more electron density between atoms = stronger bond = shorter bond length. The bond order of 1.5 in NO_2^- indicates more double bond character per N-O bond compared to 1.33 in NO_3^-. More double bond character means shorter, stronger bonds.

3 points (1 for NO_2^- bond order, 1 for prediction, 1 for reasoning)

(f) Geometry and polarity (2 points)

Molecular geometry: Trigonal planar N has 3 electron domains (3 bonding, 0 lone pairs) Bond angles = 120° **Polarity:** NONPOLAR Despite N-O bonds being polar, the perfect trigonal planar symmetry causes the three bond dipoles to cancel completely. The three N-O bond dipoles arranged 120° apart sum to zero net dipole moment. The symmetry of the resonance hybrid ensures the molecule is nonpolar.

2 points (1 for geometry/angles, 1 for polarity with reasoning)

✓ Question 7 Solutions (16 points total)

(a) Electron sea model description (3 points)

> *The **electron sea model** describes metallic bonding as metal cations (positively charged nuclei with core electrons) fixed in a regular crystalline lattice, surrounded by a "sea" of delocalized valence electrons that are free to move throughout the entire metal structure. **Key features:** • Metal atoms lose their valence electrons to form cations • Valence electrons are no longer associated with specific atoms • These delocalized electrons move freely through the lattice • Electrostatic attraction between cations and electron sea holds the structure together **Electrical conductivity:** The free-moving electrons in the electron sea can easily carry electrical current. When a voltage is applied, electrons flow toward the positive terminal, allowing metals to conduct electricity even in solid state (unlike ionic compounds). The mobility of delocalized electrons makes metals excellent electrical conductors.*

3 points (1 for model description, 1 for delocalization, 1 for conductivity explanation)

(b) Na vs Mg melting points (3 points)

> *Magnesium (MP = 650°C) has a significantly higher melting point than sodium (MP = 97.7°C) because magnesium forms stronger metallic bonds: **1. Number of delocalized electrons:** • Na: 1 valence electron per atom ($Na \rightarrow Na^+ + 1e^-$) • Mg: 2 valence electrons per atom ($Mg \rightarrow Mg^{2+} + 2e^-$) Magnesium contributes twice as many electrons to the electron sea, creating a denser, more negatively charged electron cloud that holds the cations together more strongly. **2. Charge of metal cations:** • Na^+ (+1 charge): weaker attraction to electron sea • Mg^{2+} (+2 charge): stronger electrostatic attraction to electron sea The +2 charge on Mg^{2+} creates much stronger attraction to the delocalized electrons compared to +1 charge on Na^+. **3. Atomic size:** Mg^{2+} is smaller than Na^+, allowing tighter packing and stronger interactions. These combined factors make magnesium's*

> *metallic bonding approximately 6-7× stronger, reflected in its much higher melting point.*

3 points (1 for electron number, 1 for charge, 1 for combined effect)

(c) Malleability and ductility explanation (4 points)

> ***METALS (malleable and ductile):*** *When stress is applied to a metal, layers of metal cations can slide past each other while remaining embedded in the electron sea. The delocalized electrons instantly "flow" to maintain electrostatic attraction between layers in their new positions. Since the electron sea is not directional (electrons surround all cations equally), the metallic bond strength is maintained even after deformation. The non-directional nature of metallic bonding allows atoms to move without breaking bonds. The electron sea acts like a "cushion" that accommodates structural changes while preserving overall bonding.* ***IONIC COMPOUNDS (brittle):*** *Ionic compounds have highly directional bonding where each cation must be surrounded by anions (and vice versa) in a specific geometric arrangement. When stress causes one layer to shift, cations align with cations and anions align with anions, creating strong electrostatic repulsion (like charges repel). This repulsion causes the crystal to fracture along cleavage planes rather than deform. The rigid, directional nature of ionic bonding prevents layers from sliding past each other without breaking bonds and creating destabilizing repulsions.* ***Summary:*** *Metallic bonds are non-directional and flexible → malleable/ductile. Ionic bonds are directional and rigid → brittle.*

4 points (2 for metal explanation with electron sea, 2 for ionic explanation with repulsion)

(d) Alloy types and effects (4 points)

> ***Effects of alloying:*** *Alloys typically have different properties than pure metals because the mixed atomic sizes disrupt the regular crystal lattice, making it harder for atomic layers to slide past each other. This generally increases hardness and strength while decreasing malleability and ductility. Alloys can also have different melting points, electrical conductivity, and corrosion resistance compared to pure component metals.* ***Brass (Cu + Zn): SUBSTITUTIONAL ALLOY*** *• Copper atomic radius: 128 pm • Zinc atomic radius: 134 pm • Size*

> *difference: ~5% Classification reasoning: Zn and Cu have similar atomic sizes (within ~15% difference) and are adjacent in the periodic table with similar crystal structures (both FCC). Zinc atoms can replace copper atoms in the crystal lattice without significantly distorting the structure. This is a substitutional alloy where Zn atoms occupy regular lattice sites normally occupied by Cu atoms.* ***Sterling Silver (Ag + Cu): SUBSTITUTIONAL ALLOY*** *• Silver atomic radius: 144 pm • Copper atomic radius: 128 pm • Size difference: ~11% Classification reasoning: Ag and Cu have reasonably similar atomic sizes (within 15%) and both have FCC crystal structures. Copper atoms can substitute for silver atoms in the lattice. Sterling silver is typically 92.5% Ag and 7.5% Cu, forming a substitutional solid solution. The slightly smaller Cu atoms create lattice distortions that strengthen the alloy compared to pure silver.* ***Note:*** *Interstitial alloys involve small atoms (like C, N, H) fitting into spaces between metal atoms in the lattice, typically when atomic radius ratio is < 0.59. Both these alloys have similar-sized metal atoms, making them substitutional.*

4 points (1 for alloying effects, 1.5 for each alloy classification with reasoning)

(e) Metallic luster explanation (2 points)

> *Metals appear shiny (lustrous) because the delocalized electrons in the electron sea can absorb photons of light across a wide range of frequencies. When these electrons absorb light energy, they are excited to higher energy levels. However, they immediately re-emit this energy as photons of the same frequency in all directions as they return to lower energy states. The re-emission of light occurs at the metal surface, causing most incoming light to be reflected rather than absorbed or transmitted. This efficient reflection of light across all visible wavelengths gives metals their characteristic shiny appearance. The mobile electrons act like tiny mirrors throughout the metal surface.*

2 points (1 for absorption/emission, 1 for reflection connection)

✓ Question 8 Solutions (15 points total)

(a) Classification of solids (4 points)

`Diamond (C): NETWORK COVALENT SOLID` `MP = 3550°C (extremely high) indicates strong covalent bonds throughout entire structure. Each C atom is covalently bonded to 4 other C atoms in a continuous 3D network requiring enormous energy to break apart.` **Graphite (C): NETWORK COVALENT SOLID** MP = 3652°C (extremely high) indicates covalent bonding network. Graphite has layers of covalently bonded C atoms (hexagonal sheets). The very high MP reflects the strong C-C covalent bonds within layers that must be broken for melting (not just weak London forces between layers). **Iodine (I_2): MOLECULAR SOLID** MP = 114°C (relatively low) indicates weak intermolecular forces between discrete I_2 molecules. Only London dispersion forces hold I_2 molecules together in the solid, requiring little energy to break apart. Molecules remain intact upon melting. **Silicon dioxide (SiO_2): NETWORK COVALENT SOLID** MP = 1713°C (very high) indicates strong covalent bonding throughout. Each Si atom is covalently bonded to 4 O atoms, and each O atom bridges 2 Si atoms, creating a continuous 3D network of Si-O covalent bonds.

4 points (1 point per substance: 0.5 classification, 0.5 justification)

(b) Diamond vs graphite conductivity (4 points)

> ***DIAMOND (does NOT conduct electricity):*** *In diamond, each carbon atom forms 4 covalent bonds using all 4 valence electrons in sp^3 hybridization. All electrons are localized in σ bonds between specific carbon atoms—there are no delocalized or free electrons. Since electrical conductivity requires mobile electrons, and diamond has no mobile charge carriers, it cannot conduct electricity. Diamond structure: Tetrahedral arrangement where each C is bonded to 4 other C atoms in a rigid 3D network with all electrons tightly held in covalent bonds.* ***GRAPHITE (DOES conduct electricity, especially within planes):*** *In*

> *graphite, each carbon atom forms 3 covalent bonds using sp² hybridization, leaving one electron per carbon in an unhybridized p orbital perpendicular to the plane. These p orbitals overlap to form delocalized π bonds above and below the graphite sheets. The electrons in these π bonds are free to move throughout the entire sheet, allowing electrical conductivity along the planes. Graphite structure: Layers of hexagonal sheets where each C is bonded to 3 other C atoms. The fourth electron from each carbon is delocalized across the sheet in a "sea" of π electrons, similar to metallic bonding but confined to 2D sheets.* ***Key difference:*** *Diamond has all electrons localized (no conductivity). Graphite has delocalized π electrons (conductivity). Both are pure carbon, but different bonding and hybridization create drastically different electrical properties.*

4 points (2 for diamond explanation, 2 for graphite explanation with delocalization)

(c) Molecular vs network covalent melting points (3 points)

> ***Molecular solids have MUCH LOWER melting points*** *because only weak intermolecular forces (London dispersion, dipole-dipole, hydrogen bonding) must be overcome to melt the solid. The molecules themselves remain intact—only the attractions between molecules are broken. These intermolecular forces are typically 1-10% as strong as covalent bonds. Example: I_2 (MP = 114°C) requires breaking only London dispersion forces between I_2 molecules. The I-I covalent bond within each molecule remains intact.* ***Network covalent solids have VERY HIGH melting points*** *because strong covalent bonds throughout the entire 3D structure must be broken to melt the solid. Since covalent bonds are much stronger than intermolecular forces (typically 150-500 kJ/mol for covalent vs 1-50 kJ/mol for IMFs), enormous energy is required. Example: Diamond (MP = 3550°C) requires breaking C-C covalent bonds (347 kJ/mol) throughout the entire crystal to melt. The ratio of melting points (~30:1) reflects the dramatic difference in bond strengths between covalent bonds and intermolecular forces.*

3 points (1 for molecular explanation, 1 for network explanation, 1 for comparison/bond strength)

(d) SiO_2 vs CO_2 comparison (4 points)

> *Despite similar formulas (both are dioxide compounds), SiO_2 and CO_2 have completely different structures and properties:* ***SiO_2 (Silicon Dioxide - Network Solid, MP = 1713°C): • Bond strength:*** *Silicon forms strong single Si-O covalent bonds (452 kJ/mol). Silicon's larger size and lower electronegativity compared to carbon make Si=O double bonds unstable. •* ***Structure:*** *Each Si atom bonds to 4 O atoms tetrahedrally (sp^3), and each O atom bridges between 2 Si atoms, creating a continuous 3D network. The structure is -Si-O-Si-O-Si-O- extending in all directions. •* ***Coordination:*** *Silicon can expand its valence shell and accommodate 4 bonds easily. The large Si atom can coordinate with 4 O atoms without excessive crowding. •* ***Properties:*** *The extended network of strong covalent bonds requires enormous energy to break, resulting in very high melting point. It's a hard, rigid solid.* ***CO_2 (Carbon Dioxide - Molecular Solid, sublimes at -78°C): • Bond strength:*** *Carbon forms very strong C=O double bonds (799 kJ/mol). Carbon's small size and high electronegativity favor multiple bonding (π bonds). •* ***Structure:*** *CO_2 exists as discrete linear molecules (O=C=O) with sp hybridization on carbon. Each molecule contains 2 strong C=O double bonds but molecules are separate entities held together only by weak London dispersion forces. •* ***Coordination:*** *Carbon's small size and octet rule limitation mean it can only accommodate 4 bonds maximum (2 double bonds in CO_2). Carbon cannot form extended networks with oxygen like silicon. •* ***Properties:*** *The weak London forces between CO_2 molecules require minimal energy to overcome, causing CO_2 to sublime at very low temperature. It's a gas at room temperature.* ***KEY INSIGHT:*** *The dramatic property difference arises from: 1. Silicon's inability to form stable π bonds → single bond network 2. Carbon's preference for π bonding → discrete molecules 3. Atomic size difference: Si is much larger, changes bonding preferences 4. Network covalent (Si-O bonds throughout) vs molecular solid (London forces between molecules)*

4 points (1.5 for SiO_2 explanation, 1.5 for CO_2 explanation, 1 for direct comparison)

✓ Question 9 Solutions (14 points total)

(a) Lewis structures (2 points)

```
                 Reactants:
                       H
                       |
            H—C—H     and     O=O
                       |
                       H
          (Methane)        (Oxygen)


                  Products:
        O=C=O        and        H-O-H
      (Carbon dioxide)      (Water)
```

2 points (0.5 per structure)

(b) Energy to break bonds in reactants (3 points)

CH_4: Contains 4 C-H bonds Energy = 4 × 413 kJ/mol = 1652 kJ/mol **2 O_2: Contains 2 O=O double bonds (coefficient of 2)** Energy = 2 × 495 kJ/mol = 990 kJ/mol **Total energy required to break bonds:** Energy (bonds broken) = 1652 + 990 = 2642 kJ/mol

3 points (1 for CH_4, 1 for O_2, 1 for total)

(c) Energy released forming bonds in products (3 points)

CO_2: Contains 2 C=O double bonds Energy = 2 × 799 kJ/mol = 1598 kJ/mol **2 H_2O: Contains 4 O-H bonds total (2 per water, coefficient of 2)** Energy = 4 × 463 kJ/mol = 1852 kJ/mol **Total**

energy released when forming bonds: Energy (bonds formed) = 1598 + 1852 = 3450 kJ/mol

3 points (1 for CO_2, 1 for H_2O, 1 for total)

(d) Enthalpy change calculation (3 points)

ΔH_{rxn} = Σ(bonds broken) - Σ(bonds formed) ΔH_{rxn} = 2642 kJ/mol - 3450 kJ/mol ΔH_{rxn} = -808 kJ/mol **The reaction is EXOTHERMIC** (ΔH is negative) Explanation: More energy is released when forming bonds in the products (3450 kJ/mol) than is required to break bonds in the reactants (2642 kJ/mol). The excess energy (808 kJ/mol) is released to the surroundings as heat, making this a highly exothermic combustion reaction.

3 points (1 for calculation setup, 1 for answer, 1 for exothermic identification)

(e) Comparison to experimental value (3 points)

Calculated value: ΔH = -808 kJ/mol Experimental value: ΔH = -802 kJ/mol Difference: |-808 - (-802)| = 6 kJ/mol Percent error: (6/802) × 100 = 0.75% (excellent agreement!)

> ***Why bond energy calculations are estimates:*** *1.* ***Average values:*** *Published bond energies are average values taken from many different compounds. The actual C-H bond energy in* CH_4 *may differ slightly from the average C-H bond energy used in calculations. Bond strength varies depending on molecular environment. 2.* ***Molecular context matters:*** *A C-H bond in* CH_4 *is not exactly the same strength as a C-H bond in other molecules due to different neighboring atoms and electronic environments. Bond energies are somewhat context-dependent. 3.* ***Ignores phase changes:*** *Bond energy calculations don't account for energy associated with phase changes (gas → liquid → solid). The experimental value includes condensation of water vapor, which would release additional energy. 4.* ***Resonance and electron delocalization:*** *Some molecules have resonance structures or electron delocalization that stabilizes them beyond what simple bond energies predict (especially important for* CO_2 *which has*

> > *resonance). Despite these limitations, bond energy calculations provide reasonable estimates (within ~5% typically) and are useful for predicting whether reactions are exothermic or endothermic. The excellent agreement in this case (< 1% error) is somewhat fortunate!*
>
> **3 points** (1 for comparison, 2 for explaining why estimates differ)

✓ Question 10 Solutions (15 points total)

(a) PES peak assignments for N_2 (4 points)

Peak assignments (from lowest to highest IE): Peak at 1.5 MJ/mol → σ_{2p} (highest energy bonding orbital) Peak at 1.9 MJ/mol → π_{2p} (bonding orbitals) Peak at 15.6 MJ/mol → σ_{2s} and σ^*_{2s} (average of bonding/antibonding) Peak at 409 MJ/mol → σ_{1s} (core electrons, innermost shell) **Reasoning:** • **409 MJ/mol (σ_{1s}):** Core 1s electrons are closest to nucleus and most tightly bound, requiring enormous energy to remove. This is by far the highest IE peak. • **15.6 MJ/mol (σ_{2s}/σ^*_{2s} region):** The 2s bonding and 2s antibonding orbitals have similar energies and appear as one merged peak in PES. These are inner valence electrons, more tightly bound than 2p electrons. • **1.9 MJ/mol (π_{2p}):** The π bonding orbitals (4 electrons total, two degenerate orbitals) have moderate IE. These are valence electrons involved in the N≡N triple bond. • **1.5 MJ/mol (σ_{2p}):** The σ_{2p} bonding orbital has the LOWEST IE despite being a bonding orbital. This unusual ordering occurs because in N_2, the σ_{2p} orbital is actually higher in energy than π_{2p} orbitals due to s-p mixing. Electrons in higher energy orbitals are easier to remove (lower IE).

4 points (1 for each correct assignment: must have reasoning for full credit)

(b) Bond order calculation for N_2 (2 points)

Bond order = (bonding electrons - antibonding electrons) / 2 Electron configuration: $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2$ Bonding electrons: $\sigma_{1s}(2) + \sigma_{2s}(2) + \pi_{2p}(4) + \sigma_{2p}(2) = 10$ electrons Antibonding electrons: $\sigma^*_{1s}(2) + \sigma^*_{2s}(2) = 4$ electrons Bond order = $(10 - 4) / 2 = 6 / 2 = 3$ **N_2 has a bond order of 3 (triple bond)** This matches the Lewis structure: N≡N

2 points (1 for calculation, 1 for answer)

(c) N_2 vs O_2 bond comparison (3 points)

Bond order relationship to properties: N_2: bond order = 3 O_2: bond order = 2 Higher bond order means: • More electron density between nuclei • Stronger electrostatic attraction • Shorter bond length (atoms pulled closer) • Higher bond energy (more energy to break) **Predictions:** **Bond length:** N_2 has SHORTER bond length than O_2 • N_2: 110 pm (experimental) • O_2: 121 pm (experimental) • Triple bonds are shorter than double bonds **Bond energy:** N_2 has HIGHER bond energy than O_2 • N_2: 945 kJ/mol (experimental) • O_2: 498 kJ/mol (experimental) • N_2 bond energy is nearly 2× that of O_2! • Triple bonds are much stronger than double bonds The bond order of 3 vs 2 makes N_2 one of the strongest and most stable diatomic molecules, which is why N_2 is so unreactive (high activation energy needed to break the strong N≡N triple bond).

3 points (1 for bond length prediction, 1 for bond energy prediction, 1 for reasoning)

(d) Diamagnetic vs paramagnetic (3 points)

N_2 is DIAMAGNETIC (no unpaired electrons) MO electron configuration: $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2$ All electrons are paired: • σ_{1s}: ↑↓ • σ^*_{1s}: ↑↓ • σ_{2s}: ↑↓ • σ^*_{2s}: ↑↓ • π_{2p}: ↑↓ ↑↓ (two degenerate orbitals, each filled with paired electrons) • σ_{2p}: ↑↓ Total: 14 electrons, all paired → diamagnetic (weakly repelled by magnetic field) **O_2 is PARAMAGNETIC (has unpaired electrons)** MO electron configuration: $(\sigma_{1s})^2(\sigma^*_{1s})^2(\sigma_{2s})^2(\sigma^*_{2s})^2(\sigma_{2p})^2(\pi_{2p})^4(\pi^*_{2p})^2$ The last two electrons go into π^*_{2p} antibonding orbitals: • π^*_{2p}: ↑_ ↑_ (two degenerate orbitals, one electron each by Hund's rule) Total: 16 electrons, with 2 unpaired → paramagnetic (attracted to magnetic field) **Key insight:** Molecular orbital theory correctly predicts O_2's paramagnetism,

```
while Lewis structures (showing O=O double bond with all
electrons paired) incorrectly predict diamagnetism. This is one
of the major successes of MO theory over simple Lewis
structures!
```

3 points (1 for N_2 explanation, 1.5 for O_2 explanation, 0.5 for MO theory success)

(e) Unusual σ_2p/π_2p ordering in N_2 (3 points)

> *The unusual observation that σ_2p has lower ionization energy than π_2p (meaning σ_2p is higher in energy despite σ bonds typically being stronger) occurs due to* ***s-p orbital mixing*** *in N_2.* ***Explanation:*** *In light molecules (B_2, C_2, N_2), the 2s and 2p orbitals are close enough in energy that they interact significantly when forming molecular orbitals. This "mixing" causes the σ_2s orbital to be pushed lower in energy and the σ_2p orbital to be pushed higher in energy.* ***Energy level inversion:*** *• Normal order (O_2, F_2): σ_2p is below π_2p (σ bonds stronger) • Inverted order (B_2, C_2, N_2): π_2p is below σ_2p (due to s-p mixing) For N_2 specifically, the σ_2p orbital is pushed high enough in energy that it sits ABOVE the π_2p orbitals. Electrons in higher energy orbitals are less tightly bound and easier to remove, explaining the lower ionization energy from σ_2p (1.5 MJ/mol) compared to π_2p (1.9 MJ/mol).* ***Why s-p mixing occurs in N_2 but not O_2:*** *• Small energy gap between 2s and 2p in nitrogen (small Z) • Larger energy gap in oxygen (larger Z) prevents significant mixing • As you move right on periodic table, 2s drops in energy faster than 2p This explains why the orbital ordering "flips" between N_2 and O_2 in the periodic table, an important subtlety in molecular orbital theory.*

3 points (1 for s-p mixing concept, 1 for energy inversion, 1 for N_2 vs O_2 comparison)

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