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AP Chemistry Unit 3

ADVANCED FRQ PRACTICE

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Intermolecular Forces & Properties
Difficulty: Challenging | Time: 150 minutes (15 min/question)

> 🌡️ **Master IMFs, Gas Laws, and Properties of Matter - From Molecules to Macroscopic!**

📊 Reference Information & Constants

- Gas Constant: $R = 0.0821\ \text{L·atm/(mol·K)} = 8.314\ \text{J/(mol·K)}$
- Ideal Gas Law: $PV = nRT$
- STP: $T = 273.15\ \text{K}\ (0°\text{C})$, $P = 1\ \text{atm}$, 1 mole gas = 22.4 L
- Kinetic Energy: $KE_{avg} = (3/2)RT$
- Graham's Law: $Rate_1/Rate_2 = \sqrt{(M_2/M_1)}$
- Clausius-Clapeyron: $\ln(P_2/P_1) = (-\Delta H_{vap}/R)(1/T_2 - 1/T_1)$
- Raoult's Law: $P_{solution} = X_{solvent} \times P°_{solvent}$

⚡ **Unit 3 Success Strategy:** Connect molecular-level IMFs to macroscopic properties, use KMT to explain gas behavior, apply gas laws with proper units, analyze phase diagrams carefully, and justify all predictions with particulate-level reasoning!

1 Intermolecular Forces & Physical Properties

Four substances are analyzed in a laboratory: ethanol (C_2H_5OH), dimethyl ether (CH_3OCH_3), propane (C_3H_8), and water (H_2O).

SUBSTANCE	FORMULA	MOLAR MASS (G/MOL)	BOILING POINT (°C)	VAPOR PRESSURE AT 25°C (MMHG)
Ethanol	C_2H_5OH	46.0	78.4	59
Dimethyl ether	CH_3OCH_3	46.0	-24.8	5330
Propane	C_3H_8	44.1	-42.1	>7600
Water	H_2O	18.0	100.0	24

> **(a)** Draw Lewis structures for ethanol and dimethyl ether. Despite having identical molecular formulas (C_2H_6O), these compounds are structural isomers with dramatically different boiling points. Explain this difference in terms of intermolecular forces. **(4 points)**

> **(b)** Rank the four substances in order of increasing strength of intermolecular forces. Justify your ranking by identifying the specific types of intermolecular forces present in each substance and explaining the relationship between IMF strength and the data provided. **(4 points)**

> **(c)** Explain the inverse relationship between boiling point and vapor pressure at 25°C observed in the data. Use particulate-level reasoning about the energy required to escape from the liquid phase. **(3 points)**

(d) Water has a much higher boiling point than ethanol despite having a significantly lower molar mass. Explain this observation using hydrogen bonding principles and molecular structure analysis. **(3 points)**

(e) Predict and explain which substance would have the highest surface tension at 25°C. Relate surface tension to the strength and directionality of intermolecular forces. **(2 points)**

2 Ideal Gas Law & Gas Stoichiometry

A student conducts an experiment to determine the molar mass of an unknown volatile liquid using gas law principles.

Experimental Data:

- Mass of flask + stopper: 65.347 g
- Mass of flask + stopper + condensed vapor: 65.739 g
- Volume of flask: 250.0 mL
- Temperature of boiling water bath: 99.2°C
- Atmospheric pressure: 752 mmHg

(a) Calculate the mass of the vapor that filled the flask. **(1 point)**

(b) Convert the atmospheric pressure to atmospheres and the temperature to Kelvin. **(2 points)**

(c) Using the ideal gas law, calculate the number of moles of vapor present in the flask. Show all work with proper units. **(3 points)**

(d) Calculate the molar mass of the unknown compound. Show your work with proper significant figures. **(2 points)**

(e) The unknown compound is either hexane (C_6H_{14}, MM = 86.2 g/mol), pentane (C_5H_{12}, MM = 72.2 g/mol), or butane (C_4H_{10}, MM = 58.1 g/mol). Identify the unknown and calculate the percent error if your calculated value differs from the theoretical value. **(2 points)**

(f) List two specific experimental errors that could cause the calculated molar mass to be higher than the actual value. For each error, explain the mechanism by which it would affect the result. **(4 points)**

3 Kinetic Molecular Theory & Gas Behavior

Kinetic Molecular Theory (KMT) provides a molecular-level explanation for the macroscopic behavior of gases.

(a) State the five fundamental postulates of Kinetic Molecular Theory. **(3 points)**

(b) Using KMT, explain why increasing the temperature of a gas in a rigid container causes the pressure to increase. Your explanation should reference molecular motion and collisions with container walls. **(3 points)**

(c) Two identical containers hold equal masses of helium (He, MM = 4.0 g/mol) and argon (Ar, MM = 40.0 g/mol) at the same temperature. Compare the following properties and justify your answers using KMT:

- (i) Average kinetic energy of particles
- (ii) Average speed of particles
- (iii) Pressure exerted by each gas
- (iv) Number of moles in each container

(6 points)

(d) A mixture contains 2.0 moles of N_2 and 3.0 moles of O_2 at 300 K. Calculate the average kinetic energy per mole of gas in this mixture. Explain why this value is independent of the gas identity. **(3 points)**

4

Deviations from Ideal Behavior

Real gases deviate from ideal gas behavior under certain conditions. The van der Waals equation accounts for these deviations:

```
(P + an²/V²)(V - nb) = nRT


where: a = correction for intermolecular attractions
b = correction for molecular volume
```

GAS	A (L²·ATM/MOL²)	B (L/MOL)
He	0.0341	0.0237
Ne	0.211	0.0171
H_2	0.244	0.0266
N_2	1.39	0.0391
CO_2	3.59	0.0427
NH_3	4.17	0.0371

(a) Explain what the van der Waals constant "a" represents and why NH_3 has a much larger "a" value than He. Use intermolecular force principles in your explanation. **(3 points)**

(b) Explain what the van der Waals constant "b" represents and why CO_2 has a larger "b" value than H_2. **(2 points)**

(c) Under which conditions (temperature and pressure) do real gases deviate most significantly from ideal behavior? Explain your answer using particulate-level reasoning. **(4 points)**

(d) For 1.00 mole of CO_2 gas in a 1.00 L container at 273 K, calculate:

- (i) The pressure using the ideal gas law
- (ii) The pressure using the van der Waals equation
- (iii) The percent difference between these values

(5 points)

(e) Explain whether the ideal gas law overestimates or underestimates the pressure for CO_2 under these conditions, and why. **(2 points)**

5 Phase Diagrams & Phase Transitions

The phase diagram for water is shown below (not to scale):

```
 Pressure (atm)
      ↑
  218 |                    SOLID
      |                   /
      |                  / (sublimation curve)
      |                 /
    1 |    -----------•-------------- (Normal BP: 100°C)
      |              / |
      |             /  |
      |  LIQUID    /   | VAPOR
      |           /    |
0.006 |    ------•     | (Triple point: 0.01°C)
      |         /      |
      |        /       |
      |_______/_______|_________________→
             0.01   100          Temperature (°C)
```

(a) Identify and describe the significance of the triple point for water. Include the specific temperature and pressure values. **(2 points)**

(b) Explain why the solid-liquid equilibrium line (fusion curve) for water has a negative slope, making water unusual compared to most substances. Connect this to the molecular structure and hydrogen bonding in ice versus liquid water. **(4 points)**

(c) A sample of water at -10°C and 1 atm is gradually heated at constant pressure until it reaches 120°C. Describe the phase changes that occur and sketch a heating curve showing temperature versus time. Label all phase changes and plateau regions. **(4 points)**

(d) At the top of Mount Everest, atmospheric pressure is approximately 0.31 atm. Use the phase diagram to predict the boiling point of water at this altitude. Explain why cooking food takes longer at high altitudes. **(3 points)**

(e) Explain why solid CO_2 (dry ice) sublimes at atmospheric pressure rather than melting like water does. Reference the phase diagram concept in your explanation. **(2 points)**

6 Vapor Pressure & Clausius-Clapeyron

The vapor pressure of a substance depends on temperature and can be analyzed using the Clausius-Clapeyron equation.

Vapor Pressure Data for Ethanol (C_2H_5OH):

At 20°C: P = 44.6 mmHg

At 78.4°C: P = 760 mmHg (boiling point)

(a) Using the Clausius-Clapeyron equation, calculate the heat of vaporization (ΔH_{vap}) for ethanol in kJ/mol. Show all work with proper units. **(4 points)**

$$\ln(P_2/P_1) = (-\Delta H_{vap}/R)(1/T_2 - 1/T_1)$$

(b) Using your calculated ΔH_{vap}, predict the vapor pressure of ethanol at 60°C. Show all calculations. **(3 points)**

(c) Explain at the molecular level why vapor pressure increases exponentially with temperature rather than linearly. Use the concept of kinetic energy distribution in your explanation. **(3 points)**

(d) Compare the heat of vaporization of ethanol to that of water (ΔH_{vap} = 40.7 kJ/mol). Explain why water has a higher ΔH_{vap} than ethanol in terms of intermolecular forces. **(3 points)**

(e) At 78.4°C, ethanol boils in an open container. Explain what "boiling" means at the molecular level and why the boiling point changes with external pressure. **(3 points)**

7 Solutions & Colligative Properties

A solution is prepared by dissolving 34.2 g of sucrose ($C_{12}H_{22}O_{11}$, MM = 342 g/mol) in 250.0 g of water.

(a) Calculate the molality of the sucrose solution. Show your work. **(2 points)**

(b) Calculate the mole fraction of sucrose in the solution. **(3 points)**

(c) Using Raoult's Law, calculate the vapor pressure of the solution at 25°C. The vapor pressure of pure water at 25°C is 23.8 mmHg. **(3 points)**

$$P_{solution} = X_{water} \times P^{\circ}_{water}$$

(d) Calculate the boiling point elevation for this solution. Use K_b = 0.512 °C/m for water. **(2 points)**

(e) Calculate the freezing point depression for this solution. Use K_f = 1.86 °C/m for water. **(2 points)**

(f) Explain why the addition of sucrose lowers the vapor pressure of water using particulate-level reasoning about surface molecules and intermolecular forces. **(3 points)**

(g) A student prepares a second solution by dissolving 34.2 g of NaCl (MM = 58.5 g/mol) in 250.0 g of water. Predict whether this solution will have a greater or lesser freezing point depression than the sucrose solution. Justify your prediction. **(3 points)**

8 Gas Mixtures & Partial Pressures

A 5.00 L container holds a mixture of gases at 27°C. The mixture contains 0.500 mol of N_2, 0.300 mol of O_2, and 0.200 mol of CO_2.

(a) Calculate the total pressure in the container using the ideal gas law. **(2 points)**

(b) Calculate the mole fraction of each gas in the mixture. **(2 points)**

(c) Using Dalton's Law of Partial Pressures, calculate the partial pressure of each gas. Show that the sum equals the total pressure. **(3 points)**

(d) Explain Dalton's Law at the molecular level using KMT principles. Why can each gas be treated independently when calculating pressure? **(3 points)**

(e) If 0.100 mol of CO_2 is removed from the container while maintaining constant temperature and volume, calculate the new total pressure and the new partial pressure of N_2. **(3 points)**

(f) A gas is collected over water at 25°C, where the vapor pressure of water is 23.8 mmHg. If the total pressure is 755 mmHg, calculate the pressure of the dry gas. Explain why this correction is necessary. **(3 points)**

9 Chromatography & Separation Techniques

Paper chromatography is used to separate and identify the components in a mixture of food dyes. A student performs an experiment with three food dyes (Red, Blue, Yellow) and an unknown mixture.

Chromatography Results:

Solvent front distance: 10.0 cm
Red dye: traveled 8.5 cm
Blue dye: traveled 4.2 cm
Yellow dye: traveled 7.8 cm
Unknown spot 1: traveled 8.5 cm
Unknown spot 2: traveled 4.2 cm

(a) Calculate the R_f value (retention factor) for each known dye. Show the formula and all calculations. **(3 points)**

(b) Based on the R_f values, identify which dyes are present in the unknown mixture. Justify your answer. **(2 points)**

(c) Explain why different dyes have different R_f values in terms of intermolecular forces between:

- (i) The dye and the stationary phase (paper)
- (ii) The dye and the mobile phase (solvent)

(4 points)

(d) Predict whether using a more polar solvent would increase or decrease the R_f values for polar dyes. Explain your reasoning. **(3 points)**

(e) Distillation is another separation technique. Explain how fractional distillation separates a mixture of ethanol (BP = 78.4°C) and water (BP = 100°C). Reference vapor pressure and boiling point differences in your explanation. **(3 points)**

10 Solubility & Henry's Law

The solubility of gases in liquids is affected by temperature and pressure, following Henry's Law for gases:

$S = k_H \times P_{gas}$

where: S = solubility of gas (mol/L)

k_H = Henry's law constant

P_{gas} = partial pressure of gas

Given Information:

Henry's Law constant for CO_2 in water at 25°C: $k_H = 3.4 \times 10^{-2}$ mol/(L·atm)

Atmospheric CO_2 partial pressure: 4.0×10^{-4} atm

(a) Calculate the solubility of CO_2 in water at 25°C under normal atmospheric conditions. Express your answer in mol/L. **(2 points)**

(b) A carbonated beverage is bottled under a CO_2 pressure of 4.0 atm. Calculate the solubility of CO_2 in the beverage at 25°C. **(2 points)**

(c) When the bottle is opened, the pressure drops to atmospheric pressure. Calculate how many moles of CO_2 per liter will escape from solution. Explain why the beverage fizzes. **(3 points)**

(d) Explain at the molecular level why gas solubility increases with increasing pressure. Use Le Chatelier's principle and/or collision theory in your explanation. **(3 points)**

(e) Unlike most solids, gas solubility typically decreases with increasing temperature. Explain this observation using:

- (i) Kinetic energy and molecular motion concepts
- (ii) Thermodynamic considerations (is gas dissolution exothermic or endothermic?)

(4 points)

(f) Explain why "the bends" (decompression sickness) occurs in scuba divers who surface too quickly. Reference Henry's Law and gas solubility in blood. **(2 points)**

📋 DETAILED ANSWER KEY & SCORING RUBRIC

> Complete Solutions with Step-by-Step Explanations

✓ Question 1 Solutions (16 points total)

(a) Lewis structures and BP difference (4 points)

Ethanol (C_2H_5OH): H H | | H—C—C—O—H | | H H **Dimethyl ether (CH_3OCH_3):** H H | | H—C—O—C—H | | H H

1 point for both correct structures

> ***Boiling point difference explanation:*** *Ethanol (BP = 78.4°C) has a much higher boiling point than dimethyl ether (BP = -24.8°C) because ethanol can form* ***hydrogen bonds*** *while dimethyl ether cannot.* ***Ethanol:*** *Contains an O-H bond where hydrogen is directly bonded to oxygen (highly electronegative). This allows ethanol molecules to form strong hydrogen bonds with neighboring molecules. Hydrogen bonding is one of the strongest types of intermolecular forces.* ***Dimethyl ether:*** *Although it contains oxygen (electronegative atom), there is no O-H bond. The hydrogens are bonded to carbon, not oxygen, so hydrogen bonding is NOT possible. Dimethyl ether only experiences dipole-dipole interactions (from the polar C-O bonds) and London dispersion forces, which are much weaker than hydrogen bonding. The presence of hydrogen bonding in ethanol requires significantly more energy to overcome when vaporizing, resulting in a boiling point over 100°C higher than dimethyl ether despite identical molecular formulas and molar masses.*

3 points (1 for H-bonding in ethanol, 1 for no H-bonding in ether, 1 for comparison)

(b) Ranking by IMF strength (4 points)

Order of INCREASING IMF strength: Propane < Dimethyl ether < Ethanol < Water **Justification: Propane (C_3H_8) - WEAKEST:** • Nonpolar molecule (all C-H bonds) • Only London dispersion forces • Lowest BP (-42.1°C) and highest vapor pressure (>7600 mmHg) • Weakest IMFs **Dimethyl ether (CH_3OCH_3):** • Polar molecule (C-O bonds create dipole) • Dipole-dipole interactions + London dispersion • No hydrogen bonding (no O-H, N-H, or F-H bonds) • BP = -24.8°C, VP = 5330 mmHg • Stronger than propane but weaker than hydrogen-bonding substances **Ethanol (C_2H_5OH):** • Polar molecule with O-H bond • Hydrogen bonding + dipole-dipole + London dispersion • Can form H-bonds as donor (O-H) and acceptor (O lone pairs) • BP = 78.4°C, VP = 59 mmHg • Strong IMFs from hydrogen bonding **Water (H_2O) - STRONGEST:** • Highly polar molecule with 2 O-H bonds • Extensive hydrogen bonding network • Each molecule can form 4 H-bonds (2 as donor, 2 as acceptor) • BP = 100.0°C (highest), VP = 24 mmHg (lowest) • Strongest IMFs despite smallest molecular size

4 points (1 for correct order, 3 for complete justification of all four)

(c) BP and vapor pressure relationship (3 points)

> *Boiling point and vapor pressure at 25°C show an **inverse relationship**: substances with higher boiling points have lower vapor pressures, and vice versa. **Molecular explanation: High BP → Low VP:** Substances with strong intermolecular forces (like water and ethanol) have high boiling points because significant energy is required to separate molecules from the liquid phase. At 25°C (below their boiling points), relatively few molecules have sufficient kinetic energy to overcome these strong IMFs and escape into the vapor phase. This results in LOW vapor pressure. **Low BP → High VP:** Substances with weak intermolecular forces (like propane and dimethyl ether) have low boiling points. At 25°C (above their boiling points or close to them), many molecules have enough kinetic energy to overcome the weak IMFs and escape into the vapor phase easily. This results in HIGH vapor pressure. **Energy consideration:** Vapor pressure reflects the fraction of molecules with enough kinetic energy to overcome IMFs. Stronger IMFs (higher BP) mean fewer molecules can escape at a given temperature, producing lower vapor pressure. The inverse relationship is mathematical: substances requiring more energy to boil (high BP) release fewer molecules to vapor phase (low VP) at temperatures below their boiling point.*

3 points (1 for relationship statement, 2 for molecular-level explanation)

(d) Water vs ethanol BP comparison (3 points)

> *Water (MM = 18.0 g/mol, BP = 100.0°C) has a significantly higher boiling point than ethanol (MM = 46.0 g/mol, BP = 78.4°C) despite being much smaller because:* ***1. Number of hydrogen bonds per molecule:*** *• Water can form 4 hydrogen bonds per molecule (2 O-H bonds as H-bond donors + 2 lone pairs on O as H-bond acceptors) • Ethanol can form only 3 hydrogen bonds maximum (1 O-H as donor + 2 lone pairs as acceptors) • Water forms a more extensive 3D hydrogen bonding network* ***2. Hydrogen bonding efficiency:*** *• Water molecules are small and can pack closely, maximizing H-bond strength • Ethanol has a large nonpolar hydrocarbon tail (CH_3CH_2-) that disrupts the H-bonding network and creates steric hindrance • The bulky ethyl group reduces the efficiency of hydrogen bonding interactions* ***3. Percentage of molecule participating in H-bonding:*** *• In water, 100% of the molecule (all 3 atoms) participates in hydrogen bonding • In ethanol, only the -OH group participates; the CH_3CH_2- portion only contributes weak dispersion forces The combination of more H-bonds per molecule and greater H-bonding efficiency makes water's intermolecular forces stronger than ethanol's, despite water's much smaller size.*

3 points (1 for H-bond number, 1 for molecular structure effects, 1 for network discussion)

(e) Surface tension prediction (2 points)

> ***Water will have the highest surface tension at 25°C.*** *Surface tension arises from the unbalanced intermolecular forces experienced by molecules at the liquid surface. Surface molecules are pulled inward by attractions to molecules below them but have no molecules above to balance these forces, creating tension. Water's extensive hydrogen bonding network creates very strong cohesive forces pulling surface molecules inward, producing high surface tension (about 72 mN/m at 25°C). The strong and highly directional nature of hydrogen bonds maximizes this effect. Ethanol has lower surface tension due to fewer H-bonds and disruption by the hydrocarbon tail. Dimethyl ether and propane have very low surface tension due to weak dipole-dipole and dispersion forces only.*

2 points (1 for prediction, 1 for explanation with IMF connection)

✓ Question 2 Solutions (14 points total)

(a) Mass of vapor (1 point)

Mass of vapor = (flask + stopper + vapor) - (flask + stopper)

Mass of vapor = 65.739 g - 65.347 g = 0.392 g

1 point

(b) Unit conversions (2 points)

Pressure conversion: P = 752 mmHg × (1 atm / 760 mmHg) = 0.989 atm **Temperature conversion:** T = 99.2°C + 273.15 = 372.4 K (or 372 K)

2 points (1 for each conversion)

(c) Moles calculation using ideal gas law (3 points)

PV = nRT Solving for n: n = PV / RT Given: P = 0.989 atm V = 250.0 mL = 0.2500 L R = 0.0821 L·atm/(mol·K) T = 372.4 K n = (0.989 atm)(0.2500 L) / [(0.0821 L·atm/(mol·K))(372.4 K)] n = 0.24725 / 30.574 n = 0.00809 mol (or 8.09 × 10^{-3} mol)

3 points (1 for setup, 1 for substitution, 1 for answer with units)

(d) Molar mass calculation (2 points)

Molar Mass = mass / moles MM = 0.392 g / 0.00809 mol MM = 48.5 g/mol (or 48.4 g/mol depending on rounding)

2 points (1 for setup, 1 for answer with proper sig figs)

(e) Identification and percent error (2 points)

Comparison to known values: • Hexane: 86.2 g/mol (too high) • Pentane: 72.2 g/mol (too high) • Butane: 58.1 g/mol (closest) **The unknown is BUTANE (C_4H_{10}) Percent error:** % error = |experimental - theoretical| / theoretical × 100% % error = |48.5 - 58.1| / 58.1 × 100% % error = 9.6 / 58.1 × 100% = 16.5%

2 points (1 for identification, 1 for percent error)

(f) Experimental errors causing HIGH molar mass (4 points)

> *Since MM = mass/moles, to get a higher calculated MM, either the mass must be too HIGH or the moles must be too LOW.* ***Error 1: Incomplete vaporization (LOW moles):*** *If not all the liquid vaporized before the flask was removed from the water bath, there would be excess condensed liquid remaining in the flask. This would increase the measured mass, but the actual number of moles of gas in the flask would be lower than calculated (since some liquid didn't contribute to the gas phase). Using n = PV/RT with the full volume would overestimate moles. Wait—actually this would give HIGH mass for the calculated moles, increasing MM. Actually, let me reconsider: If the flask contained some liquid AND vapor, the mass measured includes both. But when we use PV=nRT, we assume ALL the vapor fills the flask at the given P and T. So we'd calculate moles correctly for the vapor, but the mass would be HIGH (includes liquid), giving HIGH molar mass. ✓* ***Mechanism:*** *Mass measured is too high (includes condensed liquid), but calculated moles is correct for vapor only → MM = high mass / correct moles = HIGH MM* ***Error 2: Water vapor contamination (LOW moles of unknown):*** *If water vapor from the boiling water bath entered the flask and mixed with the unknown vapor, the total mass measured would include both the unknown vapor AND water vapor. However, the water vapor contributes to the pressure in the flask. Using the total pressure with the full volume in PV=nRT would give TOTAL moles (unknown + water), not just moles of unknown. Then MM = (mass unknown + mass water) / (moles unknown + moles water) would be affected. Actually, better explanation: If we assume all the mass is from the unknown but some is actually water, then MM = (mass unknown + mass water) / moles unknown = HIGH MM* ***Mechanism:*** *The measured mass includes water vapor, but we assume it's all the unknown compound → calculated MM is too high* ***Alternative Error 2: Air not completely displaced:*** *If air remained in the*

> > *flask and wasn't completely displaced by the unknown vapor, the measured mass would include air. Using* $PV=nRT$ *assuming pure unknown vapor would give too few calculated moles of unknown, but the mass includes air → HIGH MM*
>
> **4 points** (2 for each error: 1 for identifying error, 1 for mechanism)

✓ Question 3 Solutions (15 points total)

(a) Five postulates of KMT (3 points)

The five fundamental postulates of Kinetic Molecular Theory: 1. **Gas particles are in constant, random, straight-line motion** until they collide with container walls or other particles. 2. **Gas particles are infinitely small point masses** with negligible volume compared to the volume of the container. The volume of the particles themselves is assumed to be zero. 3. **Gas particles do not attract or repel each other.** There are no intermolecular forces between particles (no attractive or repulsive forces). 4. **Collisions between gas particles and with container walls are perfectly elastic.** No kinetic energy is lost in collisions—energy is conserved. 5. **The average kinetic energy of gas particles is directly proportional to absolute temperature (Kelvin).** $KE_{avg} = (3/2)RT$, meaning all gases at the same temperature have the same average kinetic energy.

3 points (0.5-0.6 points each, need at least 4 correct for full credit)

(b) Temperature and pressure relationship (3 points)

> *When temperature increases in a rigid container (constant volume), the pressure increases because of changes in molecular motion and collisions.* ***Molecular motion:*** *According to KMT, average kinetic energy is directly proportional to temperature ($KE_{avg} = 3/2\ RT$). When temperature increases, the average kinetic energy of gas particles increases, meaning particles move faster on average.* ***Collision effects:*** *Faster-moving particles collide with container walls more frequently (more collisions per unit time) and with greater force per collision (higher momentum change). Both effects combine to increase the pressure.* ***Quantitative relationship:*** *Pressure is caused by the force of particle collisions with walls. Force depends on both the rate of collisions (how often) and the momentum change per collision (how hard). Increasing temperature increases both factors, so pressure increases proportionally with temperature ($P \propto T$ at*

> *constant V and n, from PV = nRT). In rigid container: V and n are constant, so P = (nR/V) × T, meaning P is directly proportional to T.*

3 points (1 for KE-temperature connection, 1 for collision frequency, 1 for collision force)

(c) Comparing He and Ar gases (6 points)

(i) Average kinetic energy of particles: IDENTICAL - Same average KE According to KMT postulate 5: $KE_{avg} = (3/2)RT$ Since both gases are at the same temperature, they have identical average kinetic energy per particle, regardless of mass. KE_{avg} (He) = KE_{avg} (Ar) = (3/2)RT

1.5 points (0.5 for answer, 1 for explanation)

(ii) Average speed of particles: HELIUM HAS HIGHER AVERAGE SPEED $KE = (1/2)mv^2$ Since KE is the same for both but helium has much smaller mass (4 g/mol vs 40 g/mol), helium atoms must move faster to have the same kinetic energy. Rearranging: $v = \sqrt{(2KE/m)}$ Since KE is constant and m(He) < m(Ar), then v(He) > v(Ar) Specifically, v is inversely proportional to √m, so: $v(He)/v(Ar) = \sqrt{(M(Ar)/M(He))} = \sqrt{(40/4)} = \sqrt{10} \approx 3.16$ Helium atoms move approximately 3.16× faster than argon atoms at the same temperature.

1.5 points (0.5 for answer, 1 for explanation with math)

(iii) Pressure exerted by each gas: HELIUM EXERTS HIGHER PRESSURE Given: Equal masses of He and Ar Moles of He = mass / 4.0 g/mol = mass / 4.0 Moles of Ar = mass / 40.0 g/mol = mass / 40.0 Helium has 10× more moles than argon (for equal mass) From PV = nRT at constant V and T: $P \propto n$ Since n(He) = 10 × n(Ar), then P(He) = 10 × P(Ar) Helium exerts 10× higher pressure because it contains 10× more particles colliding with the walls.

1.5 points (0.5 for answer, 1 for explanation with calculation)

(iv) Number of moles in each container: HELIUM HAS MORE MOLES (10× more) As calculated above: For equal masses, n(He) = 10 × n(Ar) Example: If mass = 40.0 g each: n(He) = 40.0 g / 4.0 g/mol = 10.0 mol n(Ar) = 40.0 g / 40.0 g/mol = 1.0 mol The container with helium has 10× more particles (moles) than the container with argon.

1.5 points (0.5 for answer, 1 for explanation)

(d) Average KE calculation for mixture (3 points)

Average kinetic energy per mole: KE_{avg} = (3/2)RT KE_{avg} = (3/2) × 8.314 J/(mol·K) × 300 K KE_{avg} = 3741 J/mol = 3.74 kJ/mol

2 points for correct calculation

> ***Why KE is independent of gas identity:*** *According to KMT, the average kinetic energy depends ONLY on temperature, not on the identity, mass, or molecular structure of the gas. The equation* $KE_{avg} = (3/2)RT$ *contains only the gas constant R and temperature T—no mass term appears. At 300 K, ALL gases (*N_2*,* O_2*, He,* CO_2*, any gas) have the same average kinetic energy per mole: 3.74 kJ/mol. This is a fundamental principle of KMT. While different gases have different average speeds (lighter gases move faster), they all have the same average kinetic energy at a given temperature because the lighter mass is compensated by higher speed in the equation* $KE = (1/2)mv^2$*.*

1 point for independence explanation

✓ Question 4 Solutions (16 points total)

(a) Van der Waals constant "a" explanation (3 points)

> *The van der Waals constant "a" represents the magnitude of* ***intermolecular attractive forces*** *between gas particles. Larger "a" values indicate stronger attractions.* NH_3 *(a = 4.17) has a much larger "a" value than He (a = 0.0341) because: •* NH_3 *is polar with strong dipole-dipole interactions and can form hydrogen bonds (N-H bonds), creating significant intermolecular attractions • He is a noble gas with only very weak London dispersion forces • The ratio (4.17/0.0341 ≈ 122) shows* NH_3 *has intermolecular forces over 100× stronger than helium The "a" term corrects pressure upward in the van der Waals equation because attractions pull particles together, reducing the force of wall collisions compared to ideal behavior.*

3 points

(b) Van der Waals constant "b" explanation (2 points)

> *The van der Waals constant "b" represents the* ***excluded volume****—the actual physical volume occupied by gas particles themselves.* CO_2 *(b = 0.0427 L/mol) has a larger "b" value than* H_2 *(b = 0.0266 L/mol) because* CO_2 *molecules are physically larger (3 atoms with molecular mass 44 g/mol vs 2 atoms with molecular mass 2 g/mol). Larger molecules occupy more space, reducing the free volume available for molecular motion.*

2 points

(c) Conditions for maximum deviation (4 points)

> *Real gases deviate most from ideal behavior under:* ***1. LOW TEMPERATURE:*** *At low temperatures, particles move slowly with low kinetic energy. Intermolecular attractive forces become significant relative to kinetic energy, causing particles to stick together more. This violates the KMT assumption of no intermolecular forces.* ***2. HIGH PRESSURE:*** *At high pressure, particles are compressed into a*

> *smaller volume, forcing them close together. The actual volume of particles becomes a significant fraction of container volume, violating the KMT assumption of negligible particle volume.* ***Combination effect:*** *At low T and high P, both factors combine—particles are close together (high P makes volume matter) and moving slowly (low T makes attractions matter). Near the condensation point, gases behave least ideally and may liquefy.* ***Ideal conditions:*** *Gases behave most ideally at high T (fast-moving particles overcome attractions) and low P (particles far apart, volume negligible).*

4 points

(d) Pressure calculations (5 points)

(i) Ideal gas law: $PV = nRT$ $P = nRT/V = (1.00\ \text{mol})(0.0821\ \text{L·atm/(mol·K)})(273\ \text{K}) / (1.00\ \text{L})$ $P = 22.4\ \text{atm}$

1.5 points

(ii) Van der Waals equation: $(P + an^2/V^2)(V - nb) = nRT$ Substitute values: $a = 3.59\ \text{L}^2\text{·atm/mol}^2$ $b = 0.0427\ \text{L/mol}$ $n = 1.00\ \text{mol}$ $V = 1.00\ \text{L}$ $T = 273\ \text{K}$ $(P + 3.59\times(1.00)^2/(1.00)^2)(1.00 - 1.00\times0.0427) = 1.00\times0.0821\times273$ $(P + 3.59)(0.9573) = 22.41$ $P + 3.59 = 22.41/0.9573 = 23.41$ $P = 23.41 - 3.59 = 19.8\ \text{atm}$

2.5 points

(iii) Percent difference: $\%\ \text{difference} = |22.4 - 19.8|/22.4 \times 100\% = 11.6\%$

1 point

(e) Ideal gas law overestimation (2 points)

> *The ideal gas law* ***OVERESTIMATES*** *the pressure for CO_2 (22.4 atm vs 19.8 atm actual). This occurs because intermolecular attractions (large "a" value for CO_2) pull particles inward, reducing the force of wall collisions. The ideal gas law*

> > *ignores these attractions and assumes all particles hit walls with full force, predicting higher pressure than actually observed. The "a" term correction in van der Waals reduces the calculated pressure to match reality.*
>
> 2 points

✓ Questions 5-10 Solutions Summary

Question 5 (Phase Diagrams): Triple point at 0.01°C and 0.006 atm where all three phases coexist; negative slope of fusion curve due to ice being less dense than water (hydrogen bonding creates open structure); heating curve shows solid→liquid→gas transitions with plateaus during phase changes; water boils at ~70°C at 0.31 atm; CO_2 triple point above 1 atm so it sublimes at atmospheric pressure.

Question 6 (Vapor Pressure): ΔH_{vap} calculation using Clausius-Clapeyron yields ~38-40 kJ/mol; vapor pressure predictions using temperature conversions; exponential increase due to Maxwell-Boltzmann distribution; water has higher ΔH_{vap} due to stronger H-bonding network; boiling occurs when vapor pressure equals external pressure.

Question 7 (Colligative Properties): Molality = 0.400 m; mole fraction calculations; Raoult's Law gives $P_{solution}$ = 23.6 mmHg; ΔT_b = 0.20°C; ΔT_f = 0.74°C; vapor pressure lowering due to solute molecules occupying surface; NaCl solution has greater effect due to dissociation (i = 2).

Question 8 (Gas Mixtures): P_{total} = 4.92 atm; mole fractions: 0.50, 0.30, 0.20; partial pressures: 2.46, 1.48, 0.98 atm; Dalton's Law works because particles don't interact; removing CO_2 reduces total pressure proportionally; water vapor pressure correction necessary for gas collected over water.

Question 9 (Chromatography): R_f = distance traveled / solvent front distance; Red = 0.85, Blue = 0.42, Yellow = 0.78; unknown contains Red and Blue; separation based on relative affinity for stationary vs mobile phase; more polar solvent increases R_f of polar compounds; distillation separates by BP differences.

Question 10 (Solubility): $S = 1.4 \times 10^{-5}$ mol/L at atmospheric pressure; S = 0.136 mol/L at 4.0 atm; 0.135 mol/L escapes when opened; gas solubility increases

> with pressure (Le Chatelier); decreases with temperature (exothermic dissolution, increased KE helps escape); the bends from rapid N_2 release.
