AP® Chemistry
2009 Scoring Guidelines

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Question 1 (10 points)

Answer the following questions that relate to the chemistry of halogen oxoacids.

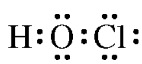
(a) Use the information in the table below to answer part (a)(i).

Acid	K_a at 298 K
$HOCl$	2.9×10^{-8}
$HOBr$	2.4×10^{-9}

(i) Which of the two acids is stronger, $HOCl$ or $HOBr$? Justify your answer in terms of K_a .

$HOCl$ is the stronger acid because its K_a value is greater than the K_a value of $HOBr$.	One point is earned for the correct answer with justification.

(ii) Draw a complete Lewis electron-dot diagram for the acid that you identified in part (a)(i).

	One point is earned for a correct diagram.

(iii) Hypoiodous acid has the formula HOI. Predict whether HOI is a stronger acid or a weaker acid than the acid that you identified in part (a)(i). Justify your prediction in terms of chemical bonding.

HOI is a weaker acid than $HOCl$ because the $O-H$ bond in HOI is stronger than the $O-H$ bond in $HOCl$. The lower electronegativity (electron-drawing ability) of I compared with that of Cl results in an electron density that is higher (hence a bond that is stronger) between the H and O atoms in HOI compared with the electron density between the H and O atoms in $HOCl$. **OR** The conjugate base OCl^- is more stable than OI^- because Cl, being more electronegative, is better able to accommodate the negative charge.	One point is earned for predicting that HOI is a weaker acid than $HOCl$ and stating that iodine has a lower electronegativity than chlorine **and EITHER** • stating that this results in a stronger $O-H$ bond in HOI **OR** • stating that this decreases the stability of the OI^- ion in solution.

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Question 1 (continued)

(b) Write the equation for the reaction that occurs between hypochlorous acid and water.

$HOCl + H_2O \rightleftarrows OCl^- + H_3O^+$ **OR** $HOCl \rightleftarrows OCl^- + H^+$	One point is earned for the correct equation.

(c) A 1.2 *M* NaOCl solution is prepared by dissolving solid NaOCl in distilled water at 298 K. The hydrolysis reaction $OCl^-(aq) + H_2O(l) \rightleftarrows HOCl(aq) + OH^-(aq)$ occurs.

(i) Write the equilibrium-constant expression for the hydrolysis reaction that occurs between $OCl^-(aq)$ and $H_2O(l)$.

$K_b = \frac{[HOCl][OH^-]}{[OCl^-]}$	One point is earned for the correct expression.

(ii) Calculate the value of the equilibrium constant at 298 K for the hydrolysis reaction.

$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-8}} = \mathbf{3.4 \times 10^{-7}}$	One point is earned for the correct value with supporting work.

(iii) Calculate the value of $[OH^-]$ in the 1.2 *M* NaOCl solution at 298 K.

	$[OCl^-]$	$[HOCl]$	$[OH^-]$
initial value	1.2	0	≈ 0
change	$-x$	x	x
equilibrium value	$1.2 - x$	x	x

One point is earned for the correct setup.

$$K_{hyd} = 3.4 \times 10^{-7} = \frac{[OH^-][HOCl]}{[OCl^-]} = \frac{(x)(x)}{(1.2 - x)} \approx \frac{x^2}{1.2}$$

$$\Rightarrow (1.2)(3.4 \times 10^{-7}) = x^2 \Rightarrow$$

$$x = [OH^-] = \mathbf{6.4 \times 10^{-4}}\ \boldsymbol{M}$$

One point is earned for the correct answer with supporting calculations.

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Question 1 (continued)

(d) A buffer solution is prepared by dissolving some solid NaOCl in a solution of HOCl at 298 K. The pH of the buffer solution is determined to be 6.48.

(i) Calculate the value of $[H_3O^+]$ in the buffer solution.

$[H^+] = 10^{-6.48} = \mathbf{3.3 \times 10^{-7}}$ ***M***	One point is earned for the correct value.

(ii) Indicate which of $HOCl(aq)$ or $OCl^-(aq)$ is present at the higher concentration in the buffer solution. Support your answer with a calculation.

$[H^+] = 3.3 \times 10^{-7}\ M$ and K_a for HOCl $= 2.9 \times 10^{-8}$ $K_a = \frac{[H^+][OCl^-]}{[HOCl]}$ $2.9 \times 10^{-8} = \frac{(3.3 \times 10^{-7})[OCl^-]}{[HOCl]}$ $\frac{[OCl^-]}{[HOCl]} = \frac{2.9 \times 10^{-8}}{3.3 \times 10^{-7}} = 0.088 \quad \Rightarrow \quad [HOCl] > [OCl^-]$	One point is earned for the correct answer with supporting buffer calculations.

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Question 2 (10 points)

A student was assigned the task of determining the molar mass of an unknown gas. The student measured the mass of a sealed 843 mL rigid flask that contained dry air. The student then flushed the flask with the unknown gas, resealed it, and measured the mass again. Both the air and the unknown gas were at 23.0°C and 750. torr. The data for the experiment are shown in the table below.

Volume of sealed flask	843 mL
Mass of sealed flask and dry air	157.70 g
Mass of sealed flask and unknown gas	158.08 g

(a) Calculate the mass, in grams, of the dry air that was in the sealed flask. (The density of dry air is 1.18 g L^{-1} at 23.0°C and 750. torr.)

$m = D \times V = (1.18 \text{ g L}^{-1})(0.843 \text{ L}) = \mathbf{0.995 \text{ g}}$	One point is earned for the correct setup and calculation of mass.

(b) Calculate the mass, in grams, of the sealed flask itself (i.e., if it had no air in it).

157.70 g – 0.995 g = **156.71 g**	One point is earned for subtracting the answer in part (a) from 157.70 g.

(c) Calculate the mass, in grams, of the unknown gas that was added to the sealed flask.

158.08 g – 156.71 g = **1.37 g**	One point is earned for subtracting the answer in part (b) from 158.08 g.

(d) Using the information above, calculate the value of the molar mass of the unknown gas.

$n = \frac{PV}{RT} = \frac{\left(\frac{750.}{760}\text{atm}\right)(0.843 \text{ L})}{(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(296 \text{ K})} = 0.0342 \text{ mol}$ molar mass $= \frac{1.37 \text{ g}}{0.0342 \text{ mol}} = \mathbf{40.1 \text{ g mol}^{-1}}$ **OR** molar mass $= \frac{DRT}{P}$ $= \frac{\left(\frac{1.37 \text{ g}}{0.843 \text{ L}}\right)(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(296 \text{ K})}{\left(\frac{750.}{760}\text{atm}\right)}$ $= \mathbf{40.0 \text{ g mol}^{-1}}$	One point is earned for the conversion of pressure (if necessary) and temperature and the use of the appropriate *R*. One point is earned for the correct setup and calculation of moles of gas. One point is earned for the correct setup and calculation of molar mass. **OR** If calculation is done in a single step, 1 point is earned for the correct *P* and *T*, 1 point is earned for the correct density, and 1 point is earned for the correct answer.

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Question 2 (continued)

After the experiment was completed, the instructor informed the student that the unknown gas was carbon dioxide (44.0 g mol^{-1}).

(e) Calculate the percent error in the value of the molar mass calculated in part (d).

percent error $= \dfrac{\lvert 44.0 \text{ g mol}^{-1} - 40.1 \text{ g mol}^{-1} \rvert}{44.0 \text{ g mol}^{-1}} \times 100 = 8.9\%$	One point is earned for the correct setup and answer.

(f) For each of the following two possible occurrences, indicate whether it by itself could have been responsible for the error in the student's experimental result. You need not include any calculations with your answer. For each of the possible occurrences, justify your answer.

<u>Occurrence 1</u>: The flask was incompletely flushed with $CO_2(g)$, resulting in some dry air remaining in the flask.

This occurrence could have been responsible. The dry air left in the flask is less dense (or has a lower molar mass) than CO_2 gas at the given T and P. This would result in a <u>lower</u> mass of gas in the flask and a <u>lower</u> result for the molar mass of the unknown gas.	One point is earned for the correct reasoning and conclusion.

<u>Occurrence 2</u>: The temperature of the air was 23.0°C, but the temperature of the $CO_2(g)$ was lower than the reported 23.0°C.

This occurrence could <u>not</u> have been responsible. The density of CO_2 is greater at the lower temperature. A larger mass of CO_2 would be in the flask than if the CO_2 had been at 23.0°C, resulting in a higher calculated molar mass for the unknown gas.	One point is earned for the correct reasoning and conclusion.

(g) Describe the steps of a laboratory method that the student could use to verify that the volume of the rigid flask is 843 mL at 23.0°C. You need not include any calculations with your answer.

Valid methods include the following: 1. Find the mass of the empty flask. Fill the flask with a liquid of known density (e.g., water at 23°C), and measure the mass of the liquid-filled flask. Subtract to find the mass of the liquid. Using the known density and mass, calculate the volume. 2. Measure 843 mL of a liquid (e.g., water) in a 1,000 mL graduated cylinder and transfer the liquid quantitatively into the flask to see if the water fills the flask completely.	One point is earned for a valid method.

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Question 2 (continued)

Note: Significant figures were checked in this problem: parts (a) and (d) were scored with ±1 significant figure needed, and parts (b) and (c) were scored with the correct number of significant figures needed for the subtraction.

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Question 3 (8 points)

$$CH_4(g) + 2\ Cl_2(g) \rightarrow CH_2Cl_2(g) + 2\ HCl(g)$$

Methane gas reacts with chlorine gas to form dichloromethane and hydrogen chloride, as represented by the equation above.

(a) A 25.0 g sample of methane gas is placed in a reaction vessel containing 2.58 mol of $Cl_2(g)$.

(i) Identify the limiting reactant when the methane and chlorine gases are combined. Justify your answer with a calculation.

Cl_2 is the limiting reactant because, in order to react with the given amount of CH_4, more moles of Cl_2 are required than the 2.58 moles of Cl_2 that are present. $25.0\text{ g } CH_4 \times \frac{1\text{ mol } CH_4}{16.04\text{ g } CH_4} \times \frac{2\text{ mol } Cl_2}{1\text{ mol } CH_4} = 3.12\text{ mol } Cl_2$	One point is earned for the correct answer with supporting calculation. (Alternative methods are acceptable.)

(ii) Calculate the total number of moles of $CH_2Cl_2(g)$ in the container after the limiting reactant has been totally consumed.

$2.58\text{ mol } Cl_2 \times \frac{1\text{ mol } CH_2Cl_2}{2\text{ mol } Cl_2} = \mathbf{1.29\ mol}\ CH_2Cl_2$	One point is earned for the correct answer.

Initiating most reactions involving chlorine gas involves breaking the Cl–Cl bond, which has a bond energy of 242 kJ mol^{-1}.

(b) Calculate the amount of energy, in joules, needed to break a single Cl–Cl bond.

$242\ \frac{\text{kJ}}{\text{mol}} \times \frac{1{,}000\text{ J}}{1\text{ kJ}} \times \frac{1\text{ mol}}{6.02 \times 10^{23}} = \mathbf{4.02 \times 10^{-19}\ J}$	One point is earned for the correct answer with appropriate setup.

(c) Calculate the longest wavelength of light, in meters, that can supply the energy per photon necessary to break the Cl–Cl bond.

For electromagnetic radiation, $c = \lambda\nu$ and $E = h\nu$. $\nu = \frac{E}{h} = \frac{4.02 \times 10^{-19}\text{ J}}{6.63 \times 10^{-34}\text{ J s}} = 6.06 \times 10^{14}\text{ s}^{-1}$ $\lambda = \frac{c}{\nu} = \frac{3.0 \times 10^{8}\text{ m s}^{-1}}{6.06 \times 10^{14}\text{ s}^{-1}} = \mathbf{4.9 \times 10^{-7}\ m}$	One point is earned for a correct setup that is consistent with part (b). (Both appropriate equations or the combined equation $E = hc/\lambda$ are required.) One point is earned for the correct answer.

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Question 3 (continued)

The following mechanism has been proposed for the reaction of methane gas with chlorine gas. All species are in the gas phase.

Step 1	$Cl_2 \rightleftarrows 2\ Cl$	*fast equilibrium*
Step 2	$CH_4 + Cl \rightarrow CH_3 + HCl$	*slow*
Step 3	$CH_3 + Cl_2 \rightarrow CH_3Cl + Cl$	*fast*
Step 4	$CH_3Cl + Cl \rightarrow CH_2Cl_2 + H$	*fast*
Step 5	$H + Cl \rightarrow HCl$	*fast*

(d) In the mechanism, is CH_3Cl a catalyst, or is it an intermediate? Justify your answer.

CH_3Cl is an intermediate because it is produced in step 3 and consumed in step 4 of the reaction mechanism.	One point is earned for identification of CH_3Cl with appropriate justification.

(e) Identify the order of the reaction with respect to each of the following according to the mechanism. In each case, justify your answer.

(i) $CH_4(g)$

The order of the reaction with respect to CH_4 is 1. The rate law for the slowest step in the reaction, step 2, is rate = $k\,[CH_4]\,[Cl]$. Because the exponent of CH_4 in the rate law is 1, the order of the reaction with respect to CH_4 is 1.	One point is earned for the correct answer with appropriate justification.

(ii) $Cl_2(g)$

The order of the reaction with respect to Cl_2 is $\frac{1}{2}$. For step 1, $K = \frac{[Cl]^2}{[Cl_2]} \Rightarrow [Cl] = K^{1/2}\,[Cl_2]^{1/2}$ Substituting into the rate law for step 2 (the slowest step in the mechanism): rate = $k\,[CH_4]\,[Cl] = k\,[CH_4](K^{1/2}\,[Cl_2]^{1/2})$ $= (k)(K^{1/2})\,[CH_4]\,[Cl_2]^{1/2}$ Because the exponent of Cl_2 in the rate law is 1/2, the order of the reaction with respect to Cl_2 is 1/2.	One point is earned for the correct answer with appropriate justification.

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Question 4 (15 points)

(a) A sample of solid iron(III) oxide is reduced completely with solid carbon.

(i) Balanced equation: $2\ Fe_2O_3 + 3\ C \rightarrow 4\ Fe + 3\ CO_2$ **OR** $Fe_2O_3 + 3\ C \rightarrow 2\ Fe + 3\ CO$	One point is earned for both correct reactants. Two points are earned for the correct products (1 point each). One point is earned for correctly balancing (mass and charge) the equation.

(ii) What is the oxidation number of carbon before the reaction, and what is the oxidation number of carbon after the reaction is complete?

The oxidation number of C before the reaction is 0, and the oxidation number of C after the reaction is +4.	One point is earned for both oxidation numbers consistent with part (i).

(b) Equal volumes of equimolar solutions of ammonia and hydrochloric acid are combined.

(i) Balanced equation: $NH_3 + H^+ \rightarrow NH_4^+$ **OR** $NH_3 + H_3O^+ \rightarrow NH_4^+ + H_2O$	Two points are earned for the correct reactants. One point is earned for the correct product(s). One point is earned for correctly balancing (mass and charge) the equation.

(ii) Indicate whether the resulting solution is acidic, basic, or neutral. Explain.

The resulting solution is acidic because of the hydrolysis of the NH_4^+ ion, which reacts with water to form NH_3 and H^+. **OR** The mixing of a strong acid and a weak base results in an acidic solution.	One point is earned for a correct answer consistent with part (i).

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Question 4 (continued)

(c) Solid mercury(II) oxide decomposes as it is heated in an open test tube in a fume hood.

(i) Balanced equation: $2\ HgO \rightarrow 2\ Hg + O_2$	One point is earned for the correct reactant. Two points are earned for the correct products (1 point each). One point is earned for correctly balancing (mass and charge) the equation.

(ii) After the reaction is complete, is the mass of the material in the test tube greater than, less than, or equal to the mass of the original sample? Explain.

The mass of the contents of the test tube will decrease owing to the loss of O_2 gas to the atmosphere.	One point is earned for a correct answer consistent with part (i).

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Question 5 (8 points)

Reaction	Equation	ΔH°_{298}	ΔS°_{298}	ΔG°_{298}
X	$C(s) + H_2O(g) \rightleftarrows CO(g) + H_2(g)$	+131 kJ mol^{-1}	+134 J mol^{-1} K^{-1}	+91 kJ mol^{-1}
Y	$CO_2(g) + H_2(g) \rightleftarrows CO(g) + H_2O(g)$	+41 kJ mol^{-1}	+42 J mol^{-1} K^{-1}	+29 kJ mol^{-1}
Z	$2\ CO(g) \rightleftarrows C(s) + CO_2(g)$	?	?	?

Answer the following questions using the information related to reactions X, Y, and Z in the table above.

(a) For reaction X, write the expression for the equilibrium constant, K_p.

$K_p = \dfrac{p_{CO} \times p_{H_2}}{p_{H_2O}}$	One point is earned for the correct expression.

(b) For reaction X, will the equilibrium constant, K_p, increase, decrease, or remain the same if the temperature rises above 298 K? Justify your answer.

K_p will increase. If the temperature is increased for an endothermic reaction (ΔH°_{298} = +131 kJ mol^{-1}), then by Le Chatelier's principle the reaction will shift toward products, thereby absorbing energy. With greater concentrations of products at equilibrium, the value of K_p will increase. **OR** Because $\Delta G^\circ = -RT \ln K_p = \Delta H^\circ_{298} - T\,\Delta S^\circ_{298}$, then $\ln K_p = -\dfrac{\Delta H^\circ_{298}}{RT} + \dfrac{\Delta S^\circ_{298}}{R}$. An increase in T for a positive ΔH°_{298} results in an increase in $\ln K_p$ and thus an increase in K_p.	One point is earned for the correct answer with appropriate justification.

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Question 5 (continued)

(c) For reaction Y at 298 K, is the value of K_p greater than 1, less than 1, or equal to 1? Justify your answer.

K_p for reaction Y is less than 1. For reaction Y, $\Delta G^\circ_{298} = +29$ kJ mol^{-1}, a positive number. Because $\Delta G^\circ = -RT \ln K$ and ΔG° is positive, then $\ln K_p$ must be negative. This is true when K_p is less than 1. **OR** A positive ΔG° results in a nonspontaneous reaction under standard conditions. This favors reactants over products as equilibrium is approached starting from standard conditions, resulting in a K_p less than 1.	One point is earned for the correct answer with appropriate justification.

(d) For reaction Y at 298 K, which is larger: the total bond energy of the reactants or the total bond energy of the products? Explain.

The total bond energy of the reactants is larger. Reaction Y is endothermic ($\Delta H^\circ_{298} = +41$ kJ mol^{-1} > 0), so there is a net input of energy as the reaction occurs. Thus, the total energy required to break the bonds in the reactants must be greater than the total energy released when the bonds are formed in the products.	One point is earned for the correct answer with appropriate explanation.

(e) Is the following statement true or false? Justify your answer.

"On the basis of the data in the table, it can be predicted that reaction Y will occur more rapidly than reaction X will occur."

The statement is false. Thermodynamic data for an overall reaction have no bearing on how slowly or rapidly the reaction occurs.	One point is earned for the correct answer with appropriate justification.

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Question 5 (continued)

(f) Consider reaction Z at 298 K.

(i) Is $\Delta S°$ for the reaction positive, negative, or zero? Justify your answer.

$\Delta S°$ for reaction Z is negative. In reaction Z, two moles of gas with relatively high entropy are converted into one mole of solid and one mole of gas, a net loss of one mole of gas and thus a net loss in entropy. **OR** Reaction Z can be obtained by reversing reactions X and Y and adding them together. Thus $\Delta S°$ for reaction Z is the sum of two negative numbers and must itself be negative.	One point is earned for the correct answer with an appropriate justification.

(ii) Determine the value of $\Delta H°$ for the reaction.

Add the values of the negatives of ΔH°_{298} for reactions X and Y : $-131 \text{ kJ mol}^{-1} + (-41 \text{ kJ mol}^{-1}) = \mathbf{-172 \text{ kJ mol}^{-}}$	One point is earned for the correct answer.

(iii) A sealed glass reaction vessel contains only $CO(g)$ and a small amount of $C(s)$. If a reaction occurs and the temperature is held constant at 298 K, will the pressure in the reaction vessel increase, decrease, or remain the same over time? Explain.

The pressure in the flask decreases. The reaction would proceed to the right, forming more $C(s)$ and $CO_2(g)$. Because two moles of $CO(g)$ would be consumed for every mole of $CO_2(g)$ that is produced, the total number of moles of gas in the flask would decrease, thereby causing the pressure in the flask to decrease.	One point is earned for the correct answer with an appropriate explanation.

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Question 6 (8 points)

Answer the following questions related to sulfur and one of its compounds.

(a) Consider the two chemical species S and S^{2-}.

(i) Write the electron configuration (e.g., $1s^2\ 2s^2 \ldots$) of each species.

S : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^4$ S^{2-} : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ Note: Replacement of $1s^2\ 2s^2\ 2p^6$ by [Ne] is acceptable.	One point is earned for the correct configuration for S. One point is earned for the correct configuration for S^{2-}.

(ii) Explain why the radius of the S^{2-} ion is larger than the radius of the S atom.

The nuclear charge is the same for both species, but the eight valence electrons in the sulfide ion experience a greater amount of electron-electron repulsion than do the six valence electrons in the neutral sulfur atom. This extra repulsion in the sulfide ion increases the average distance between the valence electrons, so the electron cloud around the sulfide ion has the greater radius.	One point is earned for a correct explanation.

(iii) Which of the two species would be attracted into a magnetic field? Explain.

The sulfur atom would be attracted into a magnetic field. Sulfur has two unpaired *p* electrons, which results in a net magnetic moment for the atom. This net magnetic moment would interact with an external magnetic field, causing a net attraction into the field. The sulfide ion would not be attracted into a magnetic field because all the electrons in the species are paired, meaning that their individual magnetic moments would cancel each other.	One point is earned for the correct answer with a correct explanation.

(b) The S^{2-} ion is isoelectronic with the Ar atom. From which species, S^{2-} or Ar, is it easier to remove an electron? Explain.

It requires less energy to remove an electron from a sulfide ion than from an argon atom. A valence electron in the sulfide ion is less attracted to the nucleus (charge +16) than is a valence electron in the argon atom (charge +18).	One point is earned for the correct answer with a correct explanation.

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Question 6 (continued)

(c) In the H_2S molecule, the H–S–H bond angle is close to 90°. On the basis of this information, which atomic orbitals of the S atom are involved in bonding with the H atoms?

The atomic orbitals involved in bonding with the H atoms in H_2S are *p* (specifically, 3*p*) orbitals. The three *p* orbitals are mutually perpendicular (i.e., at 90°) to one another.	One point is earned for the correct answer.

(d) Two types of intermolecular forces present in liquid H_2S are London (dispersion) forces and dipole-dipole forces.

(i) Compare the strength of the London (dispersion) forces in liquid H_2S to the strength of the London (dispersion) forces in liquid H_2O. Explain.

The strength of the London forces in liquid H_2S is greater than that of the London forces in liquid H_2O. The electron cloud of H_2S has more electrons and is thus more polarizable than the electron cloud of the H_2O molecule.	One point is earned for the correct answer with a correct explanation.

(ii) Compare the strength of the dipole-dipole forces in liquid H_2S to the strength of the dipole-dipole forces in liquid H_2O. Explain.

The strength of the dipole-dipole forces in liquid H_2S is weaker than that of the dipole-dipole forces in liquid H_2O. The net dipole moment of the H_2S molecule is less than that of the H_2O molecule. This results from the lesser polarity of the H–S bond compared with that of the H–O bond (S is less electronegative than O).	One point is earned for the correct answer with a correct explanation.

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