AP® Chemistry
2009 Free-Response Questions

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INFORMATION IN THE TABLE BELOW AND IN THE TABLES ON PAGES 3-5 MAY BE USEFUL IN ANSWERING THE QUESTIONS IN THIS SECTION OF THE EXAMINATION.

DO NOT DETACH FROM BOOK.

PERIODIC TABLE OF THE ELEMENTS

1 **H** 1.008																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.30											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.91	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57 ***La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.21	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.02	89 **†Ac** 227.03	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (264)	108 **Hs** (277)	109 **Mt** (268)	110 **Ds** (271)	111 **Rg** (272)							

*Lanthanide Series	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 151.97	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
†Actinide Series	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

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STANDARD REDUCTION POTENTIALS IN AQUEOUS SOLUTION AT 25°C

Half-reaction			$E°$(V)
$F_2(g) + 2e^-$	→	$2F^-$	2.87
$Co^{3+} + e^-$	→	Co^{2+}	1.82
$Au^{3+} + 3e^-$	→	$Au(s)$	1.50
$Cl_2(g) + 2e^-$	→	$2Cl^-$	1.36
$O_2(g) + 4H^+ + 4e^-$	→	$2H_2O(l)$	1.23
$Br_2(l) + 2e^-$	→	$2Br^-$	1.07
$2Hg^{2+} + 2e^-$	→	Hg_2^{2+}	0.92
$Hg^{2+} + 2e^-$	→	$Hg(l)$	0.85
$Ag^+ + e^-$	→	$Ag(s)$	0.80
$Hg_2^{2+} + 2e^-$	→	$2Hg(l)$	0.79
$Fe^{3+} + e^-$	→	Fe^{2+}	0.77
$I_2(s) + 2e^-$	→	$2I^-$	0.53
$Cu^+ + e^-$	→	$Cu(s)$	0.52
$Cu^{2+} + 2e^-$	→	$Cu(s)$	0.34
$Cu^{2+} + e^-$	→	Cu^+	0.15
$Sn^{4+} + 2e^-$	→	Sn^{2+}	0.15
$S(s) + 2H^+ + 2e^-$	→	$H_2S(g)$	0.14
$2H^+ + 2e^-$	→	$H_2(g)$	0.00
$Pb^{2+} + 2e^-$	→	$Pb(s)$	−0.13
$Sn^{2+} + 2e^-$	→	$Sn(s)$	−0.14
$Ni^{2+} + 2e^-$	→	$Ni(s)$	−0.25
$Co^{2+} + 2e^-$	→	$Co(s)$	−0.28
$Cd^{2+} + 2e^-$	→	$Cd(s)$	−0.40
$Cr^{3+} + e^-$	→	Cr^{2+}	−0.41
$Fe^{2+} + 2e^-$	→	$Fe(s)$	−0.44
$Cr^{3+} + 3e^-$	→	$Cr(s)$	−0.74
$Zn^{2+} + 2e^-$	→	$Zn(s)$	−0.76
$2H_2O(l) + 2e^-$	→	$H_2(g) + 2OH^-$	−0.83
$Mn^{2+} + 2e^-$	→	$Mn(s)$	−1.18
$Al^{3+} + 3e^-$	→	$Al(s)$	−1.66
$Be^{2+} + 2e^-$	→	$Be(s)$	−1.70
$Mg^{2+} + 2e^-$	→	$Mg(s)$	−2.37
$Na^+ + e^-$	→	$Na(s)$	−2.71
$Ca^{2+} + 2e^-$	→	$Ca(s)$	−2.87
$Sr^{2+} + 2e^-$	→	$Sr(s)$	−2.89
$Ba^{2+} + 2e^-$	→	$Ba(s)$	−2.90
$Rb^+ + e^-$	→	$Rb(s)$	−2.92
$K^+ + e^-$	→	$K(s)$	−2.92
$Cs^+ + e^-$	→	$Cs(s)$	−2.92
$Li^+ + e^-$	→	$Li(s)$	−3.05

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ATOMIC STRUCTURE

$E = h\nu \qquad c = \lambda\nu$

$\lambda = \dfrac{h}{m\upsilon} \qquad p = m\upsilon$

$E_n = \dfrac{-2.178 \times 10^{-18}}{n^2}$ joule

E = energy
ν = frequency
λ = wavelength
p = momentum
υ = velocity
n = principal quantum number
m = mass

Speed of light, $c = 3.0 \times 10^8$ m s^{-1}

Planck's constant, $h = 6.63 \times 10^{-34}$ J s

Boltzmann's constant, $k = 1.38 \times 10^{-23}$ J K^{-1}

Avogadro's number $= 6.022 \times 10^{23}$ mol^{-1}

Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

1 electron volt per atom = 96.5 kJ mol^{-1}

EQUILIBRIUM

$K_a = \dfrac{[H^+][A^-]}{[HA]}$

$K_b = \dfrac{[OH^-][HB^+]}{[B]}$

$K_w = [OH^-][H^+] = 1.0 \times 10^{-14}$ @ 25°C
$= K_a \times K_b$

$pH = -\log[H^+]$, $pOH = -\log[OH^-]$

$14 = pH + pOH$

$pH = pK_a + \log\dfrac{[A^-]}{[HA]}$

$pOH = pK_b + \log\dfrac{[HB^+]}{[B]}$

$pK_a = -\log K_a$, $pK_b = -\log K_b$

$K_p = K_c(RT)^{\Delta n}$,
where Δn = moles product gas − moles reactant gas

Equilibrium Constants
K_a (weak acid)
K_b (weak base)
K_w (water)
K_p (gas pressure)
K_c (molar concentrations)

THERMOCHEMISTRY/KINETICS

$\Delta S^\circ = \sum S^\circ$ products $-\sum S^\circ$ reactants

$\Delta H^\circ = \sum \Delta H_f^\circ$ products $-\sum \Delta H_f^\circ$ reactants

$\Delta G^\circ = \sum \Delta G_f^\circ$ products $-\sum \Delta G_f^\circ$ reactants

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
$= -RT\ln K = -2.303RT\log K$
$= -n\mathcal{F}E^\circ$

$\Delta G = \Delta G^\circ + RT\ln Q = \Delta G^\circ + 2.303RT\log Q$

$q = mc\Delta T$

$C_p = \dfrac{\Delta H}{\Delta T}$

$\ln[A]_t - \ln[A]_0 = -kt$

$\dfrac{1}{[A]_t} - \dfrac{1}{[A]_0} = kt$

$\ln k = \dfrac{-E_a}{R}\left(\dfrac{1}{T}\right) + \ln A$

S° = standard entropy
H° = standard enthalpy
G° = standard free energy
E° = standard reduction potential
T = temperature
n = moles
m = mass
q = heat
c = specific heat capacity
C_p = molar heat capacity at constant pressure
E_a = activation energy
k = rate constant
A = frequency factor

Faraday's constant, $\mathcal{F}$ = 96,500 coulombs per mole of electrons

Gas constant, R = 8.31 J mol^{-1} K^{-1}
= 0.0821 L atm mol^{-1} K^{-1}
= 62.4 L torr mol^{-1} K^{-1}
= 8.31 volt coulomb mol^{-1} K^{-1}

GO ON TO THE NEXT PAGE.

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = nRT$$

$$P_A = P_{total} \times X_A, \text{where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{total} = P_A + P_B + P_C + \ldots$$

$$n = \frac{m}{\boldsymbol{M}}$$

$$\text{K} = {}^\circ\text{C} + 273$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$D = \frac{m}{V}$$

$$u_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{\boldsymbol{M}}}$$

$$KE \text{ per molecule} = \frac{1}{2} m\upsilon^2$$

$$KE \text{ per mole} = \frac{3}{2} RT$$

$$\frac{r_1}{r_2} = \sqrt{\frac{\boldsymbol{M}_2}{\boldsymbol{M}_1}}$$

$$\text{molarity, } M = \text{ moles solute per liter solution}$$

$$\text{molality} = \text{ moles solute per kilogram solvent}$$

$$\Delta T_f = iK_f \times \text{molality}$$

$$\Delta T_b = iK_b \times \text{molality}$$

$$\pi = iMRT$$

$$A = abc$$

P = pressure
V = volume
T = temperature
n = number of moles
D = density
m = mass
υ = velocity

u_{rms} = root-mean-square speed
KE = kinetic energy
r = rate of effusion
$\boldsymbol{M}$ = molar mass
π = osmotic pressure
i = van't Hoff factor
K_f = molal freezing-point depression constant
K_b = molal boiling-point elevation constant
A = absorbance
a = molar absorptivity
b = path length
c = concentration
Q = reaction quotient
I = current (amperes)
q = charge (coulombs)
t = time (seconds)
E° = standard reduction potential
K = equilibrium constant

OXIDATION-REDUCTION; ELECTROCHEMISTRY

$$Q = \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}, \text{ where } a\,\text{A} + b\,\text{B} \rightarrow c\,\text{C} + d\,\text{D}$$

$$I = \frac{q}{t}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{n\mathcal{F}} \ln Q = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q \quad @\ 25^\circ\text{C}$$

$$\log K = \frac{nE^\circ}{0.0592}$$

Gas constant, $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$
$= 0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1}$
$= 62.4 \text{ L torr mol}^{-1} \text{ K}^{-1}$
$= 8.31 \text{ volt coulomb mol}^{-1} \text{ K}^{-1}$

Boltzmann's constant, $k = 1.38 \times 10^{-23} \text{ J K}^{-1}$

K_f for H_2O = $1.86 \text{ K kg mol}^{-1}$

K_b for H_2O = $0.512 \text{ K kg mol}^{-1}$

1 atm = 760 mm Hg
= 760 torr

STP = 0.00 °C and 1.0 atm

Faraday's constant, $\mathcal{F}$ = 96,500 coulombs per mole of electrons

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CHEMISTRY

Section II

(Total time—95 minutes)

Part A

Time—55 minutes

YOU MAY USE YOUR CALCULATOR FOR PART A.

CLEARLY SHOW THE METHOD USED AND THE STEPS INVOLVED IN ARRIVING AT YOUR ANSWERS. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not. Attention should be paid to significant figures.

Be sure to write all your answers to the questions on the lined pages following each question in the booklet with the pink cover. Do NOT write your answers on the green insert.

Answer Questions 1, 2, and 3. The Section II score weighting for each question is 20 percent.

1. 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 .

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

(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.

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

(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 $H_2O(l)$.

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

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

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(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.

(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.

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2. 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.)

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

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

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

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).

(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.

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

Occurrence 2: 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.

(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.

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

3. 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.

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

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.

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

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.

(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) $CH_4(g)$

(ii) $Cl_2(g)$

S T O P

If you finish before time is called, you may check your work on this part only.
Do not turn to the other part of the test until you are told to do so.

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CHEMISTRY

Part B

Time—40 minutes

NO CALCULATORS MAY BE USED FOR PART B.

Answer Question 4 below. The Section II score weighting for this question is 10 percent.

4. For each of the following three reactions, write a balanced equation in part (i) and answer the question in part (ii). In part (i), coefficients should be in terms of lowest whole numbers. Assume that solutions are aqueous unless otherwise indicated. Represent substances in solutions as ions if the substances are extensively ionized. Omit formulas for any ions or molecules that are unchanged by the reaction. You may use the empty space at the bottom of the next page for scratch work, but only equations that are written in the answer boxes provided will be graded.

EXAMPLE:

A strip of magnesium metal is added to a solution of silver(I) nitrate.

(i) Balanced equation:

$Mg + 2Ag^+ \longrightarrow Mg^{2+} + 2Ag$

(ii) Which substance is oxidized in the reaction?

Mg is oxidized.

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

(i) Balanced 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?

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

(i) Balanced equation:

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

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

(i) Balanced 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.

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_____

_____

YOU MAY USE THE SPACE BELOW FOR SCRATCH WORK, BUT ONLY EQUATIONS THAT ARE WRITTEN IN THE ANSWER BOXES PROVIDED WILL BE GRADED.

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Answer Question 5 and Question 6. The Section II score weighting for these questions is 15 percent each.

Your responses to these questions will be graded on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Examples and equations may be included in your responses where appropriate. Specific answers are preferable to broad, diffuse responses.

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	$2\,CO(g) \rightleftarrows C(s) + CO_2(g)$	?	?	?

5. 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.

(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.

(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.

(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.

(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."

(f) Consider reaction Z at 298 K.

(i) Is ΔS° for the reaction positive, negative, or zero? Justify your answer.

(ii) Determine the value of ΔH° for the reaction.

(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.

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6. 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.

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

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

(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.

(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?

(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.

(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.

STOP

END OF EXAM

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