2023

AP® Chemistry

Free-Response Questions

PERIODIC TABLE OF THE ELEMENTS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
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** 47.87	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** 65.38	31 **Ga** 69.72	32 **Ge** 72.63	33 **As** 74.92	34 **Se** 78.97	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** 95.95	43 **Tc**	44 **Ru** 101.07	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** 121.76	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57–71 *	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.84	75 **Re** 186.21	76 **Os** 190.23	77 **Ir** 192.22	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**	85 **At**	86 **Rn**
87 **Fr**	88 **Ra**	89–103 †	104 **Rf**	105 **Db**	106 **Sg**	107 **Bh**	108 **Hs**	109 **Mt**	110 **Ds**	111 **Rg**	112 **Cn**	113 **Nh**	114 **Fl**	115 **Mc**	116 **Lv**	117 **Ts**	118 **Og**

*Lanthanoids	57 **La** 138.91	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm**	62 **Sm** 150.36	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** 173.05	71 **Lu** 174.97
†Actinoids	89 **Ac**	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np**	94 **Pu**	95 **Am**	96 **Cm**	97 **Bk**	98 **Cf**	99 **Es**	100 **Fm**	101 **Md**	102 **No**	103 **Lr**

AP® CHEMISTRY EQUATIONS AND CONSTANTS

Throughout the exam the following symbols have the definitions specified unless otherwise noted.

L, mL	= liter(s), milliliter(s)	mm Hg	= millimeters of mercury
g	= gram(s)	J, kJ	= joule(s), kilojoule(s)
nm	= nanometer(s)	V	= volt(s)
atm	= atmosphere(s)	mol	= mole(s)

ATOMIC STRUCTURE

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

E = energy
ν = frequency
λ = wavelength

Planck's constant, $h = 6.626 \times 10^{-34}$ J s
Speed of light, $c = 2.998 \times 10^{8}$ m s^{-1}
Avogadro's number $= 6.022 \times 10^{23}$ mol^{-1}
Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

EQUILIBRIUM

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

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

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

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

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

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

$$14 = pH + pOH$$

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

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

Equilibrium Constants

K_c (molar concentrations)
K_p (gas pressures)
K_a (weak acid)
K_b (weak base)
K_w (water)

KINETICS

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

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

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

$$t_{1/2} = \frac{0.693}{k}$$

k = rate constant
t = time
$t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

$$P_{total} = P_{\text{A}} + P_{\text{B}} + P_{\text{C}} + \ldots$$

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

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

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

$$KE_{\text{molecule}} = \frac{1}{2} mv^2$$

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

$$A = \varepsilon bc$$

P = pressure
V = volume
T = temperature
n = number of moles
m = mass
$\boldsymbol{M}$ = molar mass
D = density
KE = kinetic energy
v = velocity
A = absorbance
ε = molar absorptivity
b = path length
c = concentration

Gas constant, R = 8.314 J $\text{mol}^{-1}\,\text{K}^{-1}$
= 0.08206 L atm $\text{mol}^{-1}\,\text{K}^{-1}$
= 62.36 L torr $\text{mol}^{-1}\,\text{K}^{-1}$

1 atm = 760 mm Hg = 760 torr

STP = 273.15 K and 1.0 atm

Ideal gas at STP = 22.4 L mol^{-1}

THERMODYNAMICS / ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

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

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

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -RT \ln K$$

$$= -nF E^\circ$$

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

$$E_{cell} = E_{cell}^\circ - \frac{RT}{nF} \ln Q$$

q = heat
m = mass
c = specific heat capacity
T = temperature
S° = standard entropy
H° = standard enthalpy
G° = standard Gibbs free energy
n = number of moles
E° = standard reduction potential
I = current (amperes)
q = charge (coulombs)
t = time (seconds)
Q = reaction quotient

Faraday's constant, F = 96,485 coulombs per mole of electrons

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$

Begin your response to **QUESTION 1** on this page.

CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

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

1. Answer the following questions related to manganese compounds.

(a) Manganese has several common oxidation states.

(i) Write the complete electron configuration for an Mn atom in the ground state.

(ii) When manganese forms cations, electrons are lost from which subshell first? Identify both the number and letter associated with the subshell.

A student performs an experiment to produce a manganese salt of unknown composition, $Mn_xCl_y(aq)$, and determine its empirical formula. The student places a sample of $Mn(s)$ in a beaker containing excess $HCl(aq)$, as represented by the following equation.

$$x\ Mn(s) + y\ HCl(aq) \rightarrow Mn_xCl_y(aq) + \frac{y}{2} H_2(g)$$

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Continue your response to **QUESTION 1** on this page.

The student heats the resulting mixture until only $Mn_xCl_y(s)$ remains in the beaker. The data are given in the following table.

Mass of empty beaker	60.169 g
Mass of beaker and $Mn(s)$	61.262 g
Mass of beaker and Mn_xCl_y after heating to constant mass	62.673 g

(b) Calculate the mass of Cl in the sample of $Mn_xCl_y(s)$ remaining in the beaker.

(c) Calculate the number of moles of Cl in the sample of $Mn_xCl_y(s)$ remaining in the beaker.

(d) The student determines that 0.0199 mol of Mn was used in the experiment. Use the data to determine the empirical formula of the $Mn_xCl_y(s)$.

(e) The student repeats the experiment using the same amounts of Mn and HCl and notices that some of the Mn_xCl_y splatters out of the beaker as it is heated to dryness. Will the number of moles of Cl calculated for this trial be greater than, less than, or equal to the number calculated in part (c) ? Justify your answer.

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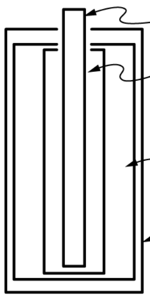
Continue your response to **QUESTION 1** on this page.

(f) Another compound of manganese, MnO_2, is used in alkaline batteries, represented by the following diagram. Some half-reactions are given in the table.



Reduction Half-Reaction	$E°$ (V)
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$ZnO(s) + H_2O(l) + 2e^- \rightarrow Zn(s) + 2OH^-(aq)$	−1.28
$2MnO_2(s) + H_2O(l) + 2e^- \rightarrow Mn_2O_3(s) + 2OH^-(aq)$	0.15

(i) Based on the half-reactions given in the table, write the balanced net ionic equation for the reaction that has the greatest thermodynamic favorability.

(ii) Calculate the value of E°_{cell} for the overall reaction.

(iii) Calculate the value of $\Delta G°$ in kJ/mol_{rxn}.

(iv) A student claims that the total mass of an alkaline battery decreases as the battery operates because the anode loses mass. Do you agree with the student's claim? Justify your answer.

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

2. In the gas phase, $AlCl_3$ is a molecular substance. A reaction of gaseous $AlCl_3$ at high temperature is represented by the following balanced equation.

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

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

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

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

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

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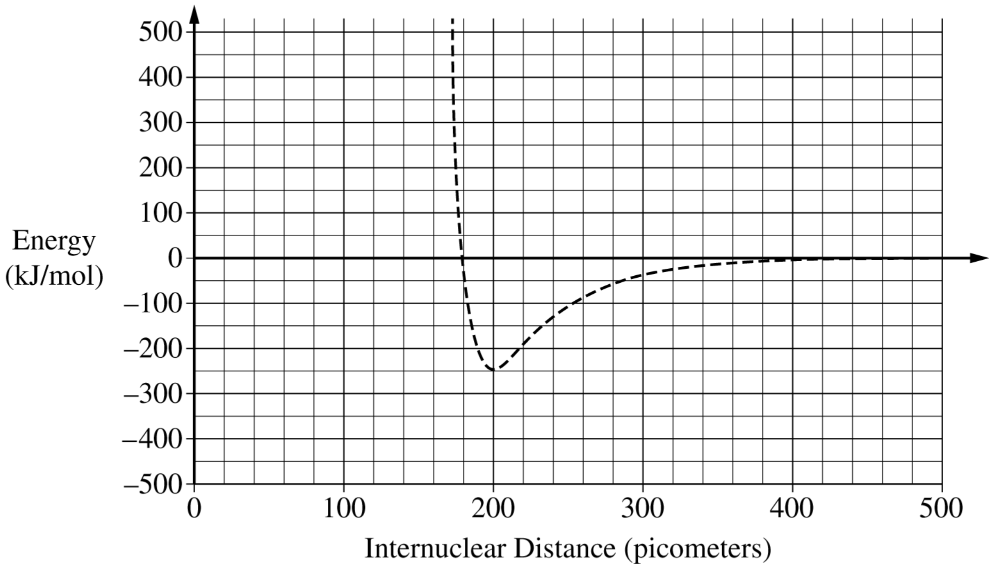
Continue your response to **QUESTION 2** on this page.

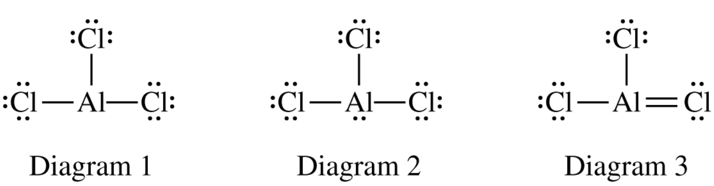
(c) A potential energy diagram for Cl_2 is shown in the following graph.



(i) Based on the graph, what is the bond length, in picometers, for Cl_2 ? __________

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

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



(i) The $AlCl_3(g)$ molecule has a trigonal planar geometry. Which diagram (1, 2, or 3) can be eliminated based on geometry? Justify your choice based on VSEPR theory.

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

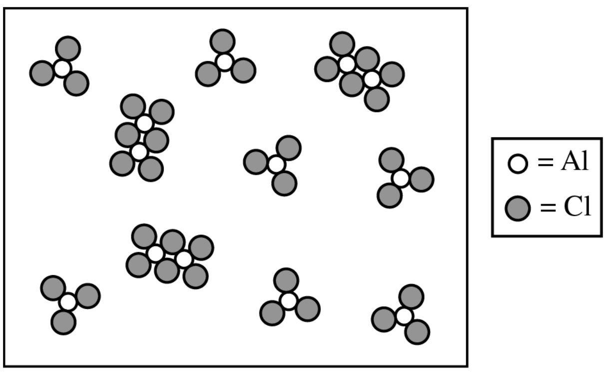
(ii) Which of the three diagrams is the best representation for the bonding in $AlCl_3$? Justify your choice based on formal charges.

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

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

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

A particle-level diagram of an equilibrium mixture of $AlCl_3(g)$ and $Al_2Cl_6(g)$ at 400°C in a 25 L closed container is shown.



(f) Using the particle-level diagram, calculate the value of K_p for the reaction if the total pressure in the container is 22.1 atm.

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

3. Answer the following questions about an experiment in which $CaCO_3(s)$ is combined with $HCl(aq)$, represented by the following balanced equation.

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

(a) Write the balanced net ionic equation for the reaction.

A student performs an investigation to study factors that affect the rate of the reaction. In each trial the student combines 50.0 mL of $HCl(aq)$ at 21.2°C with 1.00 g of $CaCO_3(s)$ and measures the time required for the reaction to go to completion. The data are given in the following table.

Trial	Concentration of $HCl(aq)$ (M)	Particle Size of $CaCO_3(s)$	Time of Reaction (s)
1	1.00	Fine powder	67
2	1.00	Small chunks	112
3	1.00	Large chunk	342
4	3.00	Fine powder	22
5	3.00	Small chunks	227
6	3.00	Large chunk	114

(b) The student correctly identifies that trial 5 is inconsistent with the other trials. Explain why the student's claim is correct using the data in the table.

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

(c) Based on the reaction conditions and the collisions that occur between particles, explain the reason for the difference in the reaction times for trial 2 and trial 3.

(d) The student claims that the reaction is zero order with respect to HCl(*aq*). Do you agree or disagree with the student's claim? Justify your answer using the student's data.

(e) The HCl(*aq*) was present in excess in all trials of the experiment. Determine the molarity of the HCl(*aq*) in the beaker after the reaction is complete in trial 2. Assume that the volume of the mixture remains constant at 50.0 mL throughout the trial. (The molar mass of $CaCO_3$ is 100.09 g/mol.)

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

$$CaCO_3(s) + 2\,HCl(aq) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

In order to measure the enthalpy of the reaction shown, the student repeats trial 1 by mixing 50.0 mL of $HCl(aq)$ with 1.00 g of $CaCO_3(s)$ using a coffee cup calorimeter. The student records the temperature of the system every 20 seconds. The data are given in the following table.

Time (s)	Measured Temperature of Solution (°C)
0	21.20
20	21.51
40	21.70
60	21.85
80	21.90
100	21.90

(f) Is the reaction endothermic or exothermic? Justify your answer using the information in the table.

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

(g) Based on the experimental data, the mass of the system is 51.0 g, and the specific heat of the reaction mixture is 4.0 J / (g · °C).

(i) Calculate the magnitude of heat transfer, q, in joules.

(ii) Calculate the enthalpy of reaction in units of kJ/mol_{rxn}. Include the algebraic sign on your answer.

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Begin your response to **QUESTION 4** on this page.

4. A student is asked to prepare a buffer solution made with equimolar amounts of $CH_3NH_2(aq)$ and $CH_3NH_3Cl(s)$. The student uses 25.00 mL of 0.100 *M* $CH_3NH_2(aq)$, which contains 0.00250 mol of CH_3NH_2, to make the buffer.

(a) Calculate the mass of $CH_3NH_3Cl(s)$ that contains 0.00250 mol of CH_3NH_3Cl.

The student has the following materials and equipment available.

- Distilled water
- 0.100 *M* $CH_3NH_2(aq)$
- Solid CH_3NH_3Cl
- Electronic balance
- Weighing paper
- 50.00 mL buret
- 50 mL beaker
- 10.0 mL graduated cylinder
- Small spatula
- Pipets
- pH meter

(b) The following table contains a partial procedure for making the buffer solution. Fill in steps 1 and 4 to complete the procedure using only materials and equipment selected from the choices given. (Not all materials listed will be used. Assume that all appropriate safety measures are already in place.)

Step	Procedure
1	
2	Place the solid in the 50 mL beaker.
3	Clean the buret and rinse with distilled water.
4	
5	Use the buret to add 25.00 mL of 0.100 *M* $CH_3NH_2(aq)$ to the beaker.
6	Mix well.
7	Check the pH with the pH meter.

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Continue your response to **QUESTION 4** on this page.

The value of K_b for $CH_3NH_2(aq)$ is 4.4×10^{-4}, and the pH of the buffer the student prepared is 10.64.

(c) The student prepares a second buffer solution. The student uses 25.00 mL of 0.050 M $CH_3NH_2(aq)$ instead of 25.00 mL of 0.100 M $CH_3NH_2(aq)$, and half the mass of $CH_3NH_3Cl(s)$ that was used in the first buffer. Is the pH of the second buffer greater than, less than, or equal to the pH of the first buffer? Justify your answer.

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Begin your response to **QUESTION 5** on this page.

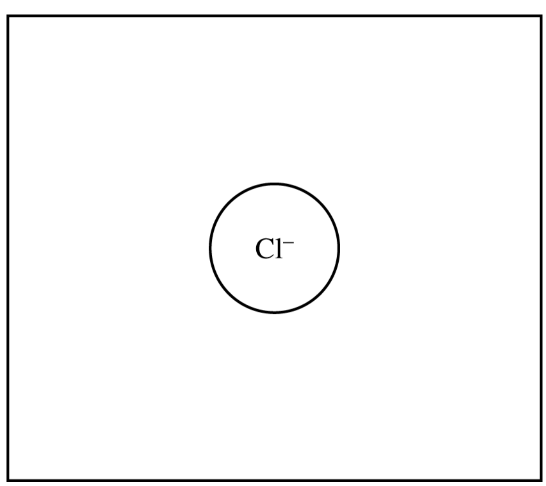
5. HCl is a molecular gas as a pure substance but acts as an acid in aqueous solution.

(a) A sample of HCl(g) is stored in a rigid 6.00 L container at 7.45 atm and 296 K.

(i) Calculate the number of moles of HCl(g) in the container.

(ii) The rigid 6.00 L container of HCl(g) is cooled to a temperature of 271 K. Calculate the new pressure, in atm, of the HCl(g).

(b) When HCl ionizes in aqueous solution, $Cl^-(aq)$ ions are formed. In the following box, draw three water molecules with proper orientation around the Cl^- ion. Use  to represent water molecules.



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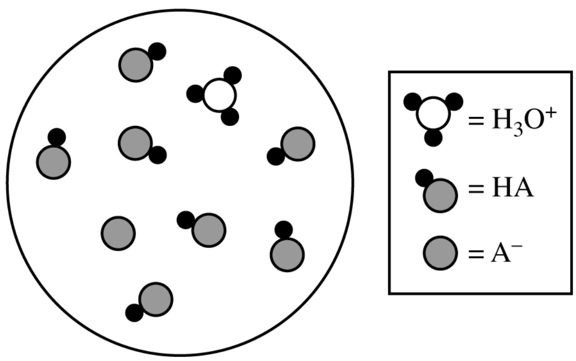
Continue your response to **QUESTION 5** on this page.

Acid (HA)	Anion (A^-)	K_a Value
HNO_2	NO_2^-	5.6×10^{-4}
HCl	Cl^-	2.0×10^7
$HClO_4$	ClO_4^-	1.6×10^{15}

The K_a values for three acids are shown in the preceding table.

(c) The following particulate diagram represents the ionization of one of the acids in the data table. Water molecules have been omitted for clarity. Which acid (HNO_2, HCl, or $HClO_4$) is represented in the diagram? Justify your answer using the information in the table.



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

6. Answer the following questions related to $HBr(l)$ and $HF(l)$.

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

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

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

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

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

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

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

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

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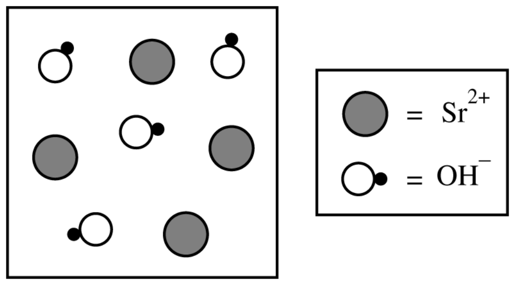
Begin your response to **QUESTION 7** on this page.

7. Strontium hydroxide dissolves in water according to the following equation. The K_{sp} expression for strontium hydroxide is provided.

$$Sr(OH)_2(s) \rightleftarrows Sr^{2+}(aq) + 2\,OH^-(aq) \qquad K_{sp} = [Sr^{2+}][OH^-]^2$$



(a) A student draws the particulate diagram shown to represent the ions present in an aqueous solution of $Sr(OH)_2$. (Water molecules are intentionally omitted.) Identify the error in the student's drawing.

(b) The student prepares a saturated solution by adding excess $Sr(OH)_2(s)$ to distilled water and stirring until no more solid dissolves. The student then determines that $[Sr^{2+}] = 0.043\ M$ in the solution.

(i) Calculate the value of $[OH^-]$ in the solution.

(ii) Calculate the value of K_{sp} for $Sr(OH)_2$.

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Continue your response to **QUESTION 7** on this page.

(c) The student prepares a second saturated solution of $Sr(OH)_2$ in aqueous $0.10\ M$ $Sr(NO_3)_2$ instead of water. Will the value of $[OH^-]$ in the second solution be greater than, less than, or equal to the value in the first solution? Justify your answer. (Assume constant temperature.)

STOP

END OF EXAM