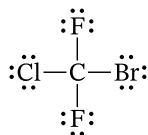


Question 5

The following information applies to parts A and B.

5. The Lewis diagram of CBrClF_2 is shown.

**Part A**

Which of the bonds in CBrClF_2 (C–Br, C–Cl, or C–F) is the most polar? **Justify** your answer.

Part B

In a molecule of CBrClF_2 , the F–C–F bond angle is 106.8° and the Br–C–Cl bond angle is 112.3° . **Explain** the difference in bond angles using principles of atomic structure and VSEPR theory.

Part C

Lewis diagrams and boiling points for CBr_4 and CBrClF_2 are given in the following table.

Formula	CBr_4	CBrClF_2
Lewis diagram	<pre> :Br: :Br—C—Br: :Br: </pre>	<pre> :F: :Cl—C—Br: :F: </pre>
Boiling point	463 K	269 K

i. Clearly **identify** all the intermolecular forces in pure $\text{CBr}_4(l)$ and in pure $\text{CBrClF}_2(l)$.

$\text{CBr}_4(l)$:

$\text{CBrClF}_2(l)$:

ii. In terms of the relative strengths of all the intermolecular forces, **explain** why pure $\text{CBr}_4(l)$ has a higher boiling point than pure $\text{CBrClF}_2(l)$ does.

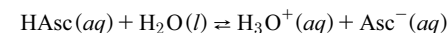
2. Answer the following questions about ascorbic acid (vitamin C).

A. A student combusts a sample of ascorbic acid, $\text{C}_x\text{H}_y\text{O}_x$, to determine its chemical composition. The only products of the reaction are 0.2400 mol of CO_2 and 2.883 g of H_2O .

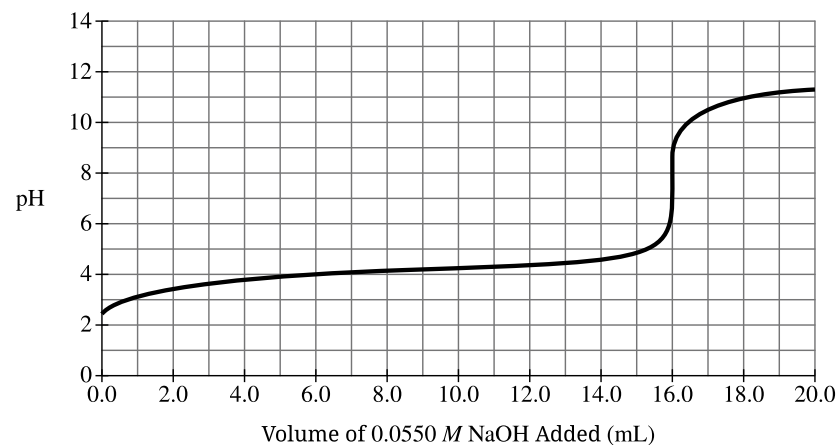
i. Calculate the number of moles of H_2O produced.

ii. The mole ratio of carbon (C) to oxygen (O) is 1:1 in ascorbic acid. Based on this information and your answer to part A (i), determine the empirical formula of ascorbic acid.

B. Ascorbic acid, $\text{HAsc}(aq)$, acts as a weak acid, as shown in the equation.



The following titration curve was produced when a 10.0 mL sample of $\text{HAsc}(aq)$ was titrated using 0.0550 M $\text{NaOH}(aq)$.



i. Calculate the molar concentration of the ascorbic acid solution.

ii. From the titration curve, determine the approximate $\text{p}K_a$ of ascorbic acid.

iii. What is the value of the ratio $\frac{[\text{Asc}^-]}{[\text{HAsc}]}$ when the pH of the solution is 4.7?

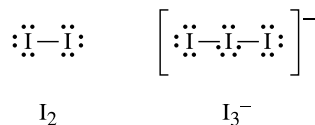
C. Dehydroascorbic acid (DHAsc) can be produced by reacting ascorbic acid with the triiodide ion, I_3^- , as represented by the following equation.



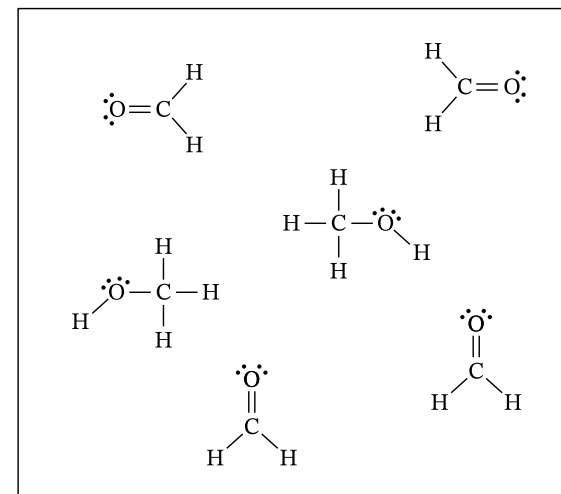
The student runs three trials of the reaction with different initial concentrations of HAsc and I_3^- , producing the following data.

Trial	[HAsc] (M)	$[\text{I}_3^-]$ (M)	Initial Rate of DHAsc Formation (M/s)
1	0.450	1.200	2.457×10^{-4}
2	0.450	0.600	1.229×10^{-4}
3	0.900	1.200	4.914×10^{-4}

- The rate law for the reaction is $\text{rate} = k[\text{HAsc}][\text{I}_3^-]$. Explain how the data in the table support the conclusion that the reaction is first order with respect to $[\text{HAsc}]$.
 - Calculate the value of the rate constant, k , for the reaction. Include units with your answer.
- D. The triiodide ion, I_3^- , is significantly more soluble in water than elemental iodine, I_2 , is. Identify an intermolecular force between I_3^- and water that is **not** present between I_2 and water, which could explain the difference in solubility. Lewis diagrams for I_2 and I_3^- are provided.



4. A scientist is investigating the properties of a mixture of CH_3OH and H_2CO . The scientist generates the following diagram to represent the mixture.



- Identify the hybridization of the valence orbitals of the C atom in the H_2CO molecule.
- In the diagram provided, draw a SINGLE dashed line (---) to represent a strong hydrogen-bonding attraction between one CH_3OH molecule and one H_2CO molecule in the mixture.
- The scientist plans to cool a gaseous mixture of CH_3OH and H_2CO to form a liquid mixture and finds data on the two compounds. The data are summarized in the table.

Substance	Melting Point (K)	Boiling Point (K)	Enthalpy of Vaporization (kJ/mol)
CH_3OH	176	338	37.6
H_2CO	181	254	24.2

- Propose a temperature to which the mixture should be cooled such that CH_3OH and H_2CO will both be liquids.
- The scientist analyzes the mixture after it is cooled and determines that 8.59 g of $\text{CH}_3\text{OH}(l)$ is present. Calculate the amount of thermal energy, in kJ, that was removed to condense the 8.59 g of CH_3OH (molar mass 32.04 g/mol) at its boiling point.

5. Complete Lewis diagrams and some physical properties for compounds X and Y are given.

Compound	X	Y
Lewis diagram		
Molar mass	74.1 g/mol	90.2 g/mol
Boiling point	82°C	98°C

- A. Based on VSEPR theory, predict the geometry around the Si atom in compound Y.
- B. A student claims that compound Y has a higher boiling point than that of compound X because compound Y has stronger London dispersion forces. Do you agree or disagree? Justify your answer.
- C. An equimolar mixture of the two compounds is heated. When the mixture reaches 82°C, which compound will have the higher vapor pressure? Justify your answer.
- D. The mixture is heated to 198°C in a sealed, rigid 12.5 L container, at which point both substances are gases and the total pressure in the container is 2.30 atm. Calculate the number of moles of gas particles in the container.

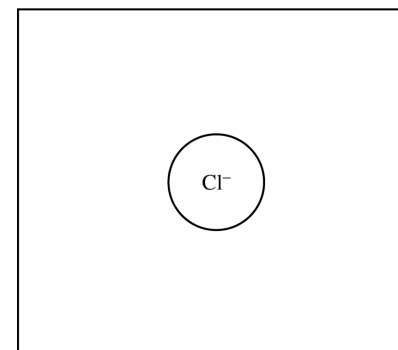
HCl is a molecular gas as a pure substance but acts as an acid in aqueous solution.

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

(i) Calculate the number of moles of $\text{HCl}(g)$ in the container.

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

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



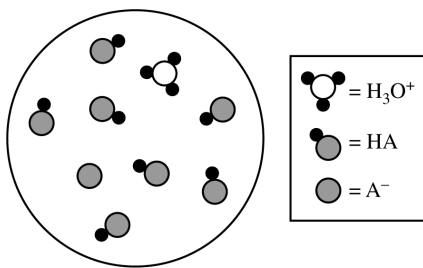
GO ON TO THE NEXT PAGE.

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.



GO ON TO THE NEXT PAGE.

Answer the following questions related to $\text{HBr}(l)$ and $\text{HF}(l)$.

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

Liquid	$\text{HBr}(l)$	$\text{HF}(l)$
Intermolecular forces present		

- (b) The enthalpy of vaporization, $\Delta H_{\text{vap}}^\circ$, for each liquid is provided in the following table.

Liquid	$\text{HBr}(l)$	$\text{HF}(l)$
$\Delta H_{\text{vap}}^\circ$	17.3 kJ/mol	25.2 kJ/mol

- (i) Based on the types and relative strengths of intermolecular forces, explain why $\Delta H_{\text{vap}}^\circ$ of $\text{HF}(l)$ is greater than that of $\text{HBr}(l)$.

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

GO ON TO THE NEXT PAGE.

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.

GO ON TO THE NEXT PAGE.

CHEMISTRY**SECTION II****Time—1 hour and 45 minutes****7 Questions****YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.**

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.

4. A student reacts 0.300 g of methyl salicylate ($\text{C}_8\text{H}_8\text{O}_3$) with a stoichiometric amount of a strong base. This product is then acidified to produce salicylic acid crystals ($\text{HC}_7\text{H}_5\text{O}_3$).

- (a) For every 1 mole of $\text{C}_8\text{H}_8\text{O}_3$ (molar mass 152.15 g/mol) reactant used, 1 mole of salicylic acid crystals ($\text{HC}_7\text{H}_5\text{O}_3$, molar mass 138.12 g/mol) is produced. Calculate the maximum mass, in grams, of $\text{HC}_7\text{H}_5\text{O}_3$ that could be produced in this reaction.

GO ON TO THE NEXT PAGE.

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

As part of the experimental procedure to purify the $\text{HC}_7\text{H}_5\text{O}_3$ crystals after the reaction is complete, the crystals are filtered from the reaction mixture, rinsed with distilled water, and dried. Some physical properties of $\text{HC}_7\text{H}_5\text{O}_3$ are given in the following table.

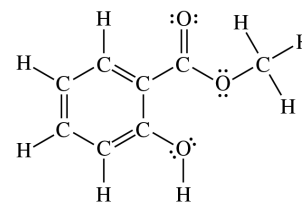
Properties of Salicylic Acid ($\text{HC}_7\text{H}_5\text{O}_3$)	
Melting point	159°C
Solubility in H_2O at 25°C	2.2 g/L
Specific heat capacity	1.17 J/(g·°C)
Heat of fusion	27.1 kJ/mol

(b) The student's experiment results in an 87% yield of dry $\text{HC}_7\text{H}_5\text{O}_3$. The student suggests that some of the $\text{HC}_7\text{H}_5\text{O}_3$ crystals dissolved in the distilled water during the rinsing step. Is the student's claim consistent with the calculated percent yield value? Justify your answer.

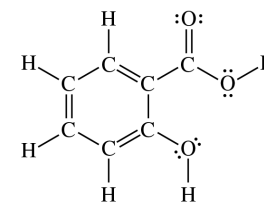
(c) Given the physical properties in the table, calculate the quantity of heat that must be absorbed to increase the temperature of a 0.105 g sample of dry $\text{HC}_7\text{H}_5\text{O}_3$ (molar mass 138.12 g/mol) crystals from 25°C to the melting point of 159°C and melt the crystals completely.

GO ON TO THE NEXT PAGE.Continue your response to **QUESTION 1** on this page.

The structures and melting points for methyl salicylate and salicylic acid are shown.



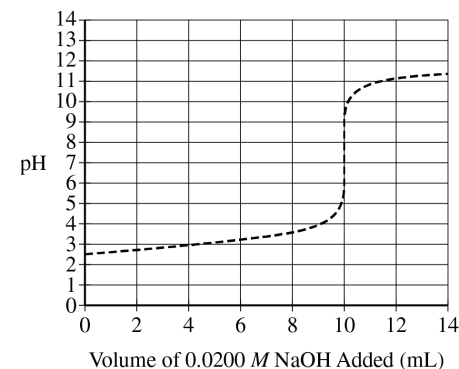
Methyl Salicylate
Melting Point: -9°C



Salicylic Acid
Melting Point: 159°C

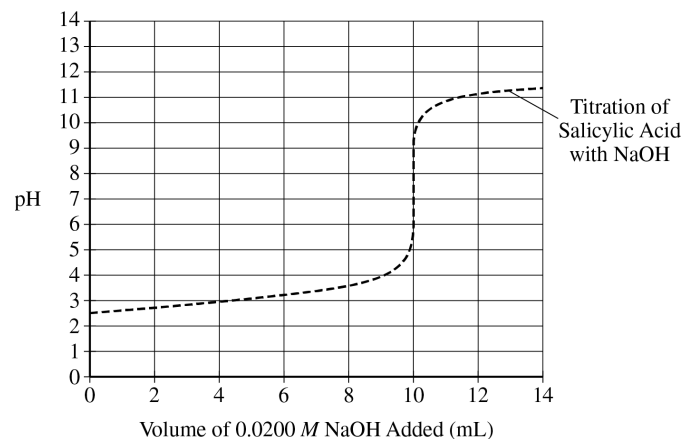
(d) The same three types of intermolecular forces (London dispersion forces, dipole-dipole interactions, and hydrogen bonding) exist among molecules of each substance. Explain why the melting point of salicylic acid is higher than that of methyl salicylate.

The student titrates 20.0 mL of 0.0100 M $\text{HC}_7\text{H}_5\text{O}_3(aq)$ with 0.0200 M NaOH, using a probe to monitor the pH of the solution. The data are plotted producing the following titration curve.

**GO ON TO THE NEXT PAGE.**

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

- (e) Using the information in the graph, estimate the pK_a of $HC_7H_5O_3$. _____
- (f) When the pH of the titration mixture is 4.00, is there a higher concentration of the weak acid, $HC_7H_5O_3$, or its conjugate base, $C_7H_5O_3^-$, in the flask? Justify your answer.
- (g) The student researches benzoic acid ($HC_7H_5O_2$) and finds that it has similar properties to salicylic acid ($HC_7H_5O_3$). The K_a for benzoic acid is 6.3×10^{-5} . Calculate the value of pK_a for benzoic acid.
- (h) The student performs a second titration, this time titrating 20.0 mL of a 0.0100 *M* benzoic acid solution with 0.0200 *M* NaOH. Sketch the curve that would result from this titration of benzoic acid on the following graph, which already shows the original curve from the titration of 20.0 mL of 0.0100 *M* salicylic acid. The initial pH of the benzoic acid solution is 3.11.

**GO ON TO THE NEXT PAGE.**

Answer the following questions about the compounds NH_2Cl and NCl_3 . The Lewis electron-dot diagrams of the two compounds are shown.



- (a) Calculate the number of moles of NH_2Cl (molar mass 51.48 g/mol) present in 1.0 L of a solution in which the concentration of NH_2Cl is 0.0016 g/L.
- (b) NH_2Cl is highly soluble in water, whereas NCl_3 is nearly insoluble. Explain this observation in terms of the types and relative strengths of the intermolecular forces between each of the solutes and water.

GO ON TO THE NEXT PAGE.

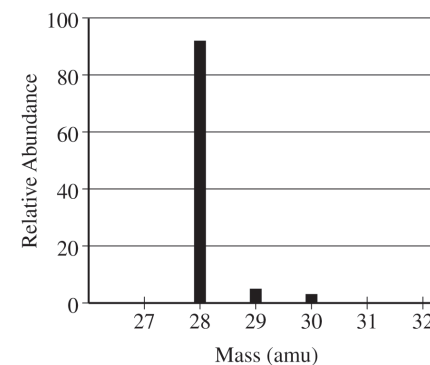
Continue your response to **QUESTION 4** on this page.

- (c) The value of $\Delta H_{\text{vaporization}}^\circ$ for $\text{NCl}_3(l)$ is 32.9 kJ/mol. Calculate the amount of energy required to vaporize a 15.0 g sample of NCl_3 (molar mass 120.36 g/mol).

GO ON TO THE NEXT PAGE.

2. Answer the following questions about the element Si and some of its compounds.

- (a) The mass spectrum of a pure sample of Si is shown below.



- (i) How many protons and how many neutrons are in the nucleus of an atom of the most abundant isotope of Si ?
- (ii) Write the ground-state electron configuration of Si.

Two compounds that contain Si are SiO_2 and SiH_4 .

- (b) At 161 K, SiH_4 boils but SiO_2 remains as a solid. Using principles of interparticle forces, explain the difference in boiling points.

GO ON TO THE NEXT PAGE.

Use a pencil or pen with black or dark blue ink only. Do NOT write your name. Do NOT write outside the box.

At high temperatures, SiH_4 decomposes to form solid silicon and hydrogen gas.

(c) Write a balanced equation for the reaction.

A table of absolute entropies of some substances is given below.

Substance	S° ($\text{J}/(\text{mol} \cdot \text{K})$)
$\text{H}_2(g)$	131
$\text{Si}(s)$	18
$\text{SiH}_4(g)$	205

(d) Explain why the absolute molar entropy of $\text{Si}(s)$ is less than that of $\text{H}_2(g)$.

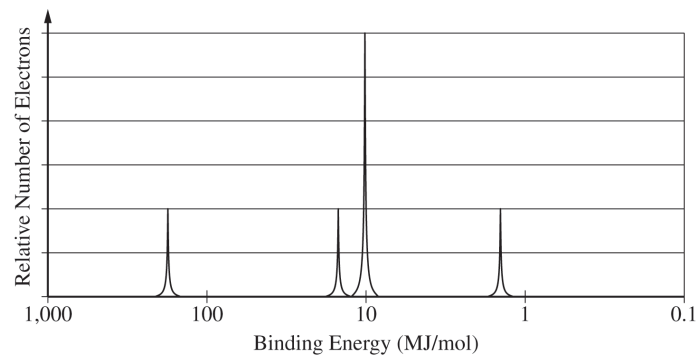
(e) Calculate the value, in $\text{J}/(\text{mol} \cdot \text{K})$, of ΔS° for the reaction.

(f) The reaction is thermodynamically favorable at all temperatures. Explain why the reaction occurs only at high temperatures.

GO ON TO THE NEXT PAGE.

Use a pencil or pen with black or dark blue ink only. Do NOT write your name. Do NOT write outside the box.

(g) A partial photoelectron spectrum of pure Si is shown below. On the spectrum, draw the missing peak that corresponds to the electrons in the $3p$ sublevel.



(h) Using principles of atomic structure, explain why the first ionization energy of Ge is lower than that of Si.

(i) A single photon with a wavelength of $4.00 \times 10^{-7} \text{ m}$ is absorbed by the Si sample. Calculate the energy of the photon in joules.

GO ON TO THE NEXT PAGE.

Use a pencil or pen with black or dark blue ink only. Do NOT write your name. Do NOT write outside the box.

CHEMISTRY

Section II

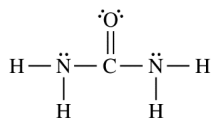
Time—1 hour and 45 minutes

7 Questions

YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

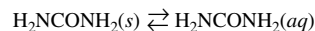
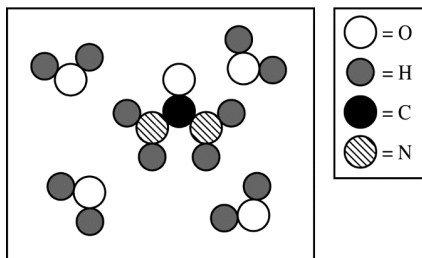
Directions: Questions 1–3 are long free-response questions that require about 23 minutes each to answer and are worth 10 points each. Questions 4–7 are short free-response questions that require about 9 minutes each to answer and are worth 4 points each.

Write your response in the space provided following each question. 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.



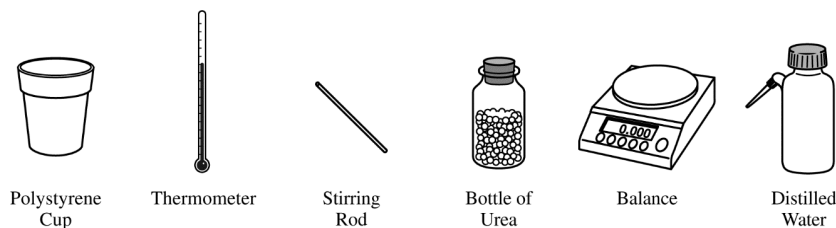
1. The compound urea, H_2NCONH_2 , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.

- (a) Identify the hybridization of the valence orbitals of the carbon atom in the urea molecule.
- (b) Urea has a high solubility in water, due in part to its ability to form hydrogen bonds. A urea molecule and four water molecules are represented in the box below. Draw ONE dashed line (----) to indicate a possible location of a hydrogen bond between a water molecule and the urea molecule.



The dissolution of urea is represented by the equation above. A student determines that 5.39 grams of H_2NCONH_2 (molar mass 60.06 g/mol) can dissolve in water to make 5.00 mL of a saturated solution at 20.°C.

- (c) Calculate the concentration of urea, in mol/L, in the saturated solution at 20.°C.
- (d) The student also determines that the concentration of urea in a saturated solution at 25°C is 19.8 M. Based on this information, is the dissolution of urea endothermic or exothermic? Justify your answer in terms of Le Chatelier's principle.



- (e) The equipment shown above is provided so that the student can determine the value of the molar heat of solution for urea. Knowing that the specific heat of the solution is 4.18 J/(g·°C), list the specific measurements that are required to be made during the experiment.

	S° (J/(mol·K))
$\text{H}_2\text{NCONH}_2(s)$	104.6
$\text{H}_2\text{NCONH}_2(aq)$	?

- (f) The entropy change for the dissolution of urea, $\Delta S^\circ_{\text{soln}}$, is 70.1 J/(mol·K) at 25°C. Using the information in the table above, calculate the absolute molar entropy, S° , of aqueous urea.
- (g) Using particle-level reasoning, explain why $\Delta S^\circ_{\text{soln}}$ is positive for the dissolution of urea in water.
- (h) The student claims that ΔS° for the process contributes to the thermodynamic favorability of the dissolution of urea at 25°C. Use the thermodynamic information above to support the student's claim.

2. Answer the following questions relating to the chemistry of the halogens.

- (a) The molecular formulas of diatomic bromine, chlorine, fluorine, and iodine are written below. Circle the formula of the molecule that has the longest bond length. Justify your choice in terms of atomic structure.



A chemistry teacher wants to prepare Br_2 . The teacher has access to the following three reagents: $\text{NaBr}(aq)$, $\text{Cl}_2(g)$, and $\text{I}_2(s)$.

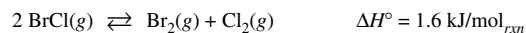
Half-Reaction	E° at 25°C (V)
$\text{Br}_2 + 2 e^- \rightarrow 2 \text{Br}^-$	1.07
$\text{Cl}_2 + 2 e^- \rightarrow 2 \text{Cl}^-$	1.36
$\text{I}_2 + 2 e^- \rightarrow 2 \text{I}^-$	0.53

- (b) Using the data in the table above, write the balanced equation for the thermodynamically favorable reaction that will produce Br_2 when the teacher combines two of the reagents. Justify that the reaction is thermodynamically favorable by calculating the value of E° for the reaction.

Br_2 and Cl_2 can react to form the compound BrCl .

- (c) The boiling point of Br_2 is 332 K, whereas the boiling point of BrCl is 278 K. Explain this difference in boiling point in terms of all the intermolecular forces present between molecules of each substance.

The compound BrCl can decompose into Br_2 and Cl_2 , as represented by the balanced chemical equation below.



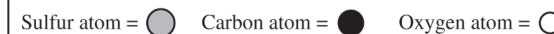
A 0.100 mole sample of pure $\text{BrCl}(g)$ is placed in a previously evacuated, rigid 2.00 L container at 298 K. Eventually the system reaches equilibrium according to the equation above.

- (d) Calculate the pressure in the container before equilibrium is established.
 (e) Write the expression for the equilibrium constant, K_{eq} , for the decomposition of BrCl .

After the system has reached equilibrium, 42 percent of the original BrCl sample has decomposed.

- (f) Determine the value of K_{eq} for the decomposition reaction of BrCl at 298 K.
 (g) Calculate the bond energy of the Br-Cl bond, in kJ/mol, using ΔH° for the reaction (1.6 kJ/mol_{rxn}) and the information in the following table.

Bond	Bond Energy (kJ/mol)
Br – Br	193
Cl – Cl	243
Br – Cl	?



Compound	Molecular Structure	Boiling Point at 1 atm (K)
CS_2		319
COS		223

4. The table above gives the molecular structures and boiling points for the compounds CS_2 and COS .

- (a) In terms of the types and relative strengths of all the intermolecular forces in each compound, explain why the boiling point of $\text{CS}_2(l)$ is higher than that of $\text{COS}(l)$.
 (b) A 10.0 g sample of $\text{CS}_2(l)$ is put in an evacuated 5.0 L rigid container. The container is sealed and heated to 325 K, at which temperature all of the $\text{CS}_2(l)$ has vaporized. What is the pressure in the container once all of the $\text{CS}_2(l)$ has vaporized?