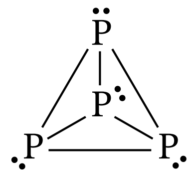
Question 4

4. White phosphorus, $P_4(g)$, can decompose into $P_2(g)$ at elevated temperatures. A balanced chemical equation, K_p expression, and Lewis diagrams for the chemical species involved in the reaction are given.

$$P_4(g) \rightleftarrows 2\ P_2(g) \qquad K_p = \frac{(P_{P_2})^2}{P_{P_4}} = \ ?$$

Compound	P_4	P_2
Lewis diagram		$:P{\equiv}P:$

Part A

The average bond length in P_4 molecules is 221 pm, whereas the average bond length in P_2 molecules is 189 pm. **Explain** why the average bond length in P_4 is greater than the average bond length in P_2.

Part B

A sample of $P_4(s)$ is placed in a sealed rigid container and heated to 1600. K, at which point the initial partial pressure of $P_4(g)$ is 0.470 atm. Some of the $P_4(g)$ decomposes into $P_2(g)$ as the system reaches equilibrium. At equilibrium, the partial pressure of $P_2(g)$ is determined to be 0.630 atm.

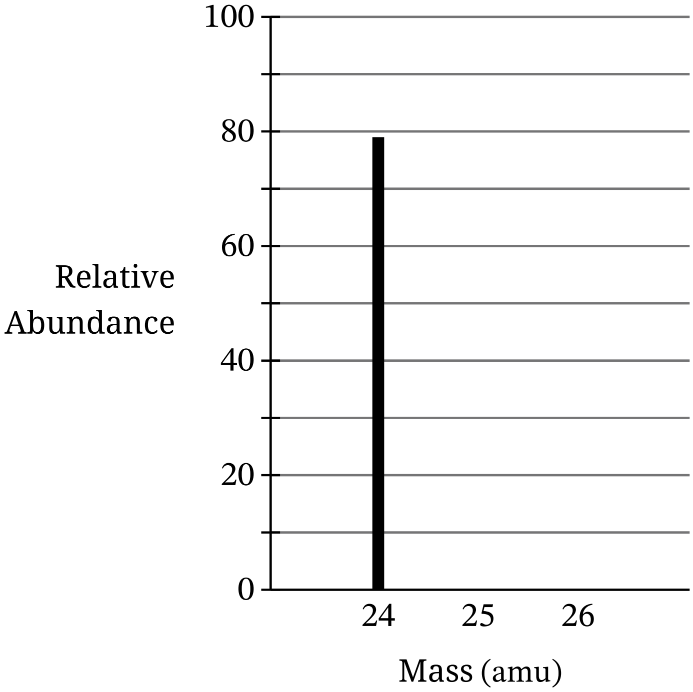
Calculate the value of the equilibrium constant, K_p, for the reaction at 1600. K. Show the work that leads to your answer.

Part C

The reaction is thermodynamically favorable under standard conditions only at temperatures above 1500 K. A student claims that the reaction must be endothermic because it is favorable only at high temperatures. Do you agree or disagree? **Justify** your answer using ΔS°_{rxn} and ΔG°_{rxn}.

1. Answer the following questions about magnesium.

A. An incomplete mass spectrum for magnesium is shown in the diagram.

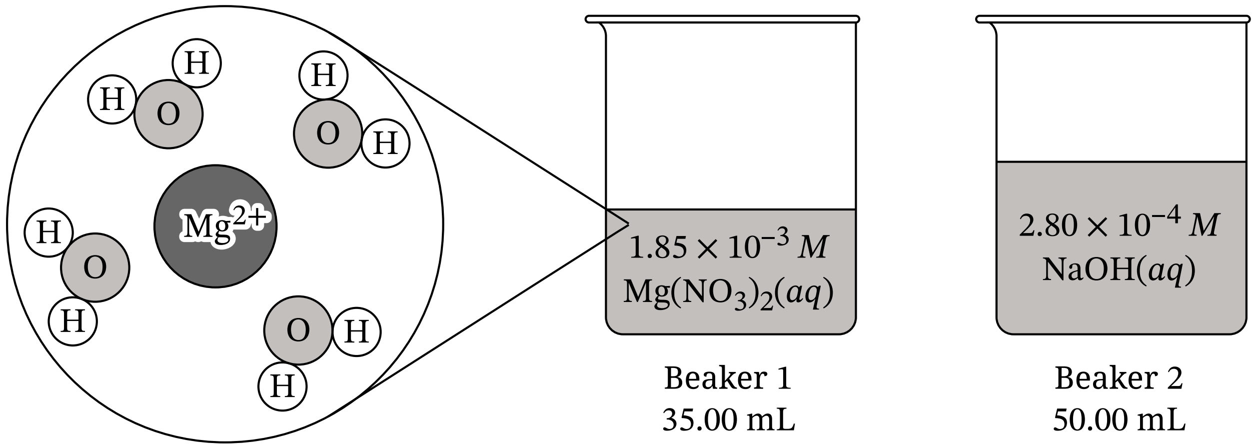


The percent abundance of magnesium-24 is 79%. The percent abundances of the other two natural isotopes of magnesium, magnesium-25 and magnesium-26, are approximately equal.

i. Complete the mass spectrum in part A by drawing thick lines in the appropriate locations to represent the percent abundance of magnesium-25 and magnesium-26.

ii. Describe the difference in atomic structure that accounts for the difference in mass between magnesium-25 and magnesium-26.

A student prepares a 1.85×10^{-3} M solution of $Mg(NO_3)_2(aq)$ in beaker 1 and a 2.80×10^{-4} M solution of $NaOH(aq)$ in beaker 2, as shown.



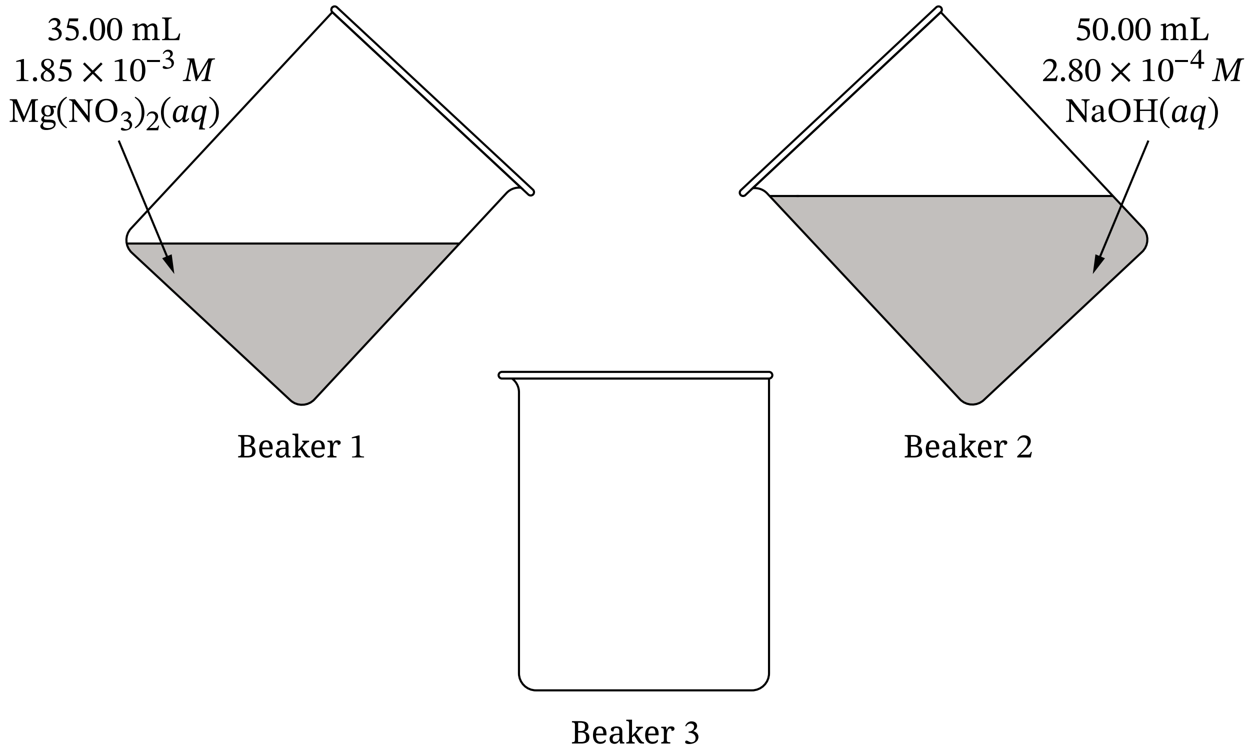
B. The particle diagram shown represents a magnesium ion, Mg^{2+}, in beaker 1. A sodium ion, Na^{+}, in beaker 2 has a weaker attraction to water than the Mg^{2+} does. Explain this phenomenon using Coulomb's law and each of the following.

i. The relative charge of the ions

ii. The relative radii of the ions

C. Calculate the pH of the solution in beaker 2.

D. A student combines 35.00 mL of 1.85×10^{-3} M $Mg(NO_3)_2(aq)$ with 50.00 mL of 2.80×10^{-4} M $NaOH(aq)$, as shown in the diagram. Calculate $[Mg^{2+}]$ after the two solutions are combined but before any reaction takes place. (Assume that volumes are additive.)



E. The dissolution of magnesium hydroxide is represented by the following equation.

$$Mg(OH)_2(s) \rightleftarrows Mg^{2+}(aq) + 2\ OH^-(aq) \quad K_{sp} = 5.61\times10^{-12}$$

i. Write the expression for the solubility product constant, K_{sp}.

ii. After the two solutions are combined in beaker 3 as described in part D, but before any reaction takes place, $[OH^-] = 1.65\times10^{-4}$ M. Using your answer to part D, calculate the value of the reaction quotient, Q.

iii. Using the reaction quotient, Q, predict whether a precipitate should form as the mixture in beaker 3 approaches equilibrium. Justify your answer.

F. In a separate experiment, the student adds $HNO_3(aq)$ to decrease the pH of a saturated solution containing undissolved $Mg(OH)_2(s)$. Does the amount of undissolved $Mg(OH)_2(s)$ increase, decrease, or remain the same as the $HNO_3(aq)$ is added? Justify your answer.

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.

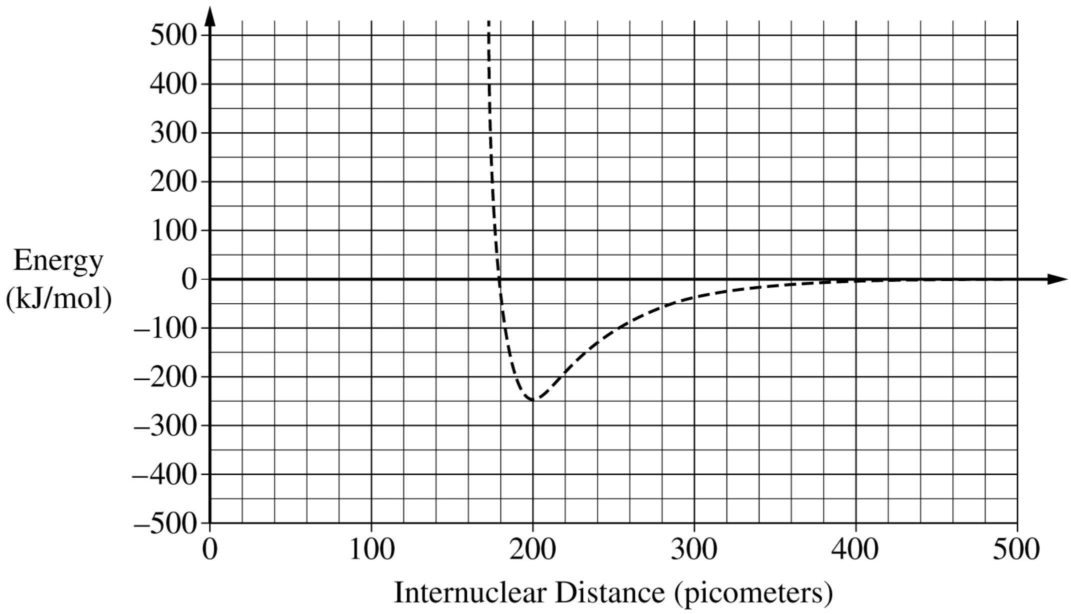
Reaction Number	Equation	ΔH_{rxn}° (kJ/mol$_{rxn}$)
2	$Al(s) + \frac{3}{2}\,Cl_2(g) \rightarrow AlCl_3(g)$	−583
3	$Al(s) \rightarrow Al(g)$	+326
4	$Cl_2(g) \rightarrow 2\,Cl(g)$	+243

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

GO ON TO THE NEXT PAGE.

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.

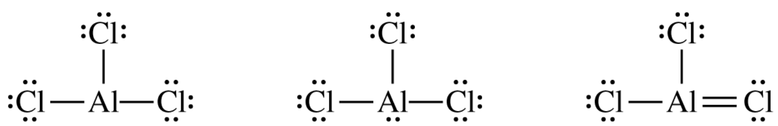


Diagram 1 Diagram 2 Diagram 3

(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.

GO ON TO THE NEXT PAGE.

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

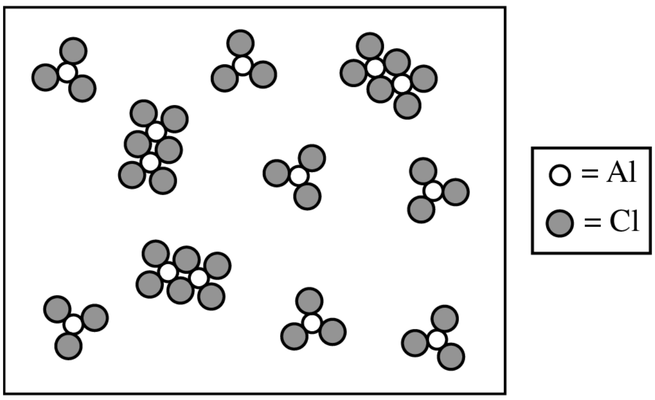
(ii) Which of the three diagrams is the best representation for the bonding in $AlCl_3$? Justify your choice based on formal charges.

$AlCl_3$ 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.

GO ON TO THE NEXT PAGE.

. 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 $HF(l)$.

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.

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.

Br_2 Cl_2 F_2 I_2

A chemistry teacher wants to prepare Br_2. The teacher has access to the following three reagents: $NaBr(aq)$, $Cl_2(g)$, and $I_2(s)$.

Half-Reaction	$E°$ at 25°C (V)
$Br_2 + 2e^- \rightarrow 2Br^-$	1.07
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$I_2 + 2e^- \rightarrow 2I^-$	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 <u>each</u> substance.

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

$$2\,BrCl(g) \rightleftarrows Br_2(g) + Cl_2(g) \qquad \Delta H° = 1.6 \text{ kJ/mol}_{rxn}$$

A 0.100 mole sample of pure $BrCl(g)$ 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 $\Delta H°$ 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	?

3. Answer the following questions relating to Fe and its ions, Fe^{2+} and Fe^{3+}.

(a) Write the ground-state electron configuration of the Fe^{2+} ion.

Ion	Ionic Radius (pm)
Fe^{2+}	92
Fe^{3+}	79

(b) The radii of the ions are given in the table above. Using principles of atomic structure, explain why the radius of the Fe^{2+} ion is larger than the radius of the Fe^{3+} ion.

(c) Fe^{3+} ions interact more strongly with water molecules in aqueous solution than Fe^{2+} ions do. Give one reason for this stronger interaction, and justify your answer using Coulomb's law.

A student obtains a solution that contains an unknown concentration of $Fe^{2+}(aq)$. To determine the concentration of $Fe^{2+}(aq)$ in the solution, the student titrates a sample of the solution with $MnO_4^-(aq)$, which converts $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$, as represented by the following equation.

$$5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) \rightarrow 5\ Fe^{3+}(aq) + Mn^{2+}(aq) + 4\ H_2O(l)$$

(d) Write the balanced equation for the half-reaction for the oxidation of $Fe^{2+}(aq)$ to $Fe^{3+}(aq)$.

(e) The student titrates a 10.0 mL sample of the $Fe^{2+}(aq)$ solution. Calculate the value of $[Fe^{2+}]$ in the solution if it takes 17.48 mL of added 0.0350 M $KMnO_4(aq)$ to reach the equivalence point of the titration.

To deliver the 10.0 mL sample of the $Fe^{2+}(aq)$ solution in part (e), the student has the choice of using one of the pieces of glassware listed below.

- 25 mL buret
- 25 mL graduated cylinder
- 25 mL beaker
- 25 mL volumetric flask

(f) Explain why the 25 mL volumetric flask would be a poor choice to use for delivering the required volume of the $Fe^{2+}(aq)$ solution.

In a separate experiment, the student is given a sample of powdered $Fe(s)$ that contains an inert impurity. The student uses a procedure to oxidize the $Fe(s)$ in the sample to $Fe_2O_3(s)$. The student collects the following data during the experiment.

Mass of $Fe(s)$ with inert impurity	6.724 g
Mass of $Fe_2O_3(s)$ produced	7.531 g

(g) Calculate the number of moles of Fe in the $Fe_2O_3(s)$ produced.

(h) Calculate the percent by mass of Fe in the original sample of powdered $Fe(s)$ with the inert impurity.

(i) If the oxidation of the $Fe(s)$ in the original sample was incomplete so that some of the 7.531 g of product was $FeO(s)$ instead of $Fe_2O_3(s)$, would the calculated mass percent of $Fe(s)$ in the original sample be higher, lower, or the same as the actual mass percent of $Fe(s)$? Justify your answer.