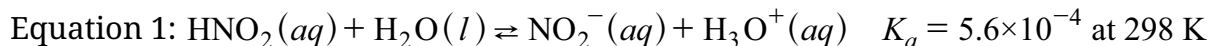


Question 3: Version J

The following information applies to all parts.

3. Nitrous acid, HNO_2 , is a weak acid that ionizes according to Equation 1.

**Part A**

Identify a conjugate acid-base pair in the equation. Be sure to clearly label which is the acid and which is the base.

Part B

A solution of $\text{HNO}_2(aq)$ with an initial concentration of 0.125 M has a pH of 2.09.

- i. **Calculate** the value of $[\text{H}_3\text{O}^+]$ in the solution. Show the work that leads to your answer.
- ii. **Calculate** $[\text{HNO}_2]$ at equilibrium. Show the work that leads to your answer.

Part C

In an experiment, the solution of 0.125 M $\text{HNO}_2(aq)$ is heated to 333 K . The new equilibrium concentrations are determined to be $[\text{HNO}_2] = 0.114 \text{ M}$, $[\text{NO}_2^-] = 0.0109 \text{ M}$, and $[\text{H}_3\text{O}^+] = 0.0109 \text{ M}$.

- i. **Calculate** the value of K_a for HNO_2 at 333 K . Show the work that leads to your answer.
- ii. Is the reaction represented by Equation 1 endothermic or exothermic? **Justify** your answer by comparing K_a values at 298 K and 333 K .

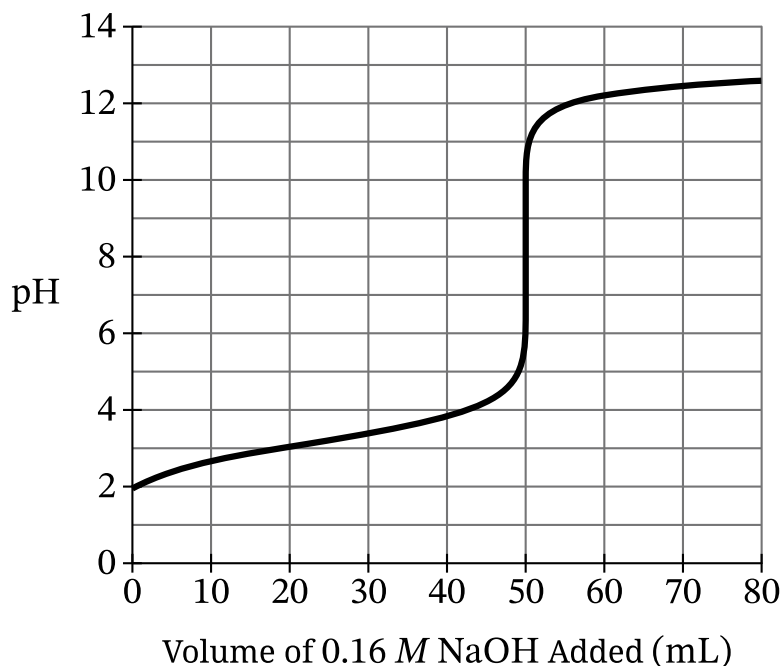
The following information applies to parts D, E, and F.

In a second experiment, a student is given a bottle containing HNO_2 with an unknown molarity. To determine the concentration of the $\text{HNO}_2(aq)$ in the bottle, the student titrates 35.0 mL of the $\text{HNO}_2(aq)$ with 0.16 M $\text{NaOH}(aq)$ at 298 K, which reacts according to Equation 2.



The results of the titration are summarized in Figure 1.

Figure 1



Part D

Using Figure 1, **identify** the pH at the equivalence point.

Part E

Using Figure 1, **calculate** the molarity $\text{HNO}_2(aq)$ of in the bottle. Show the work that leads to your answer.

Part F

Draw an X on Figure 1 to represent a point in the titration where $[\text{HNO}_2] > [\text{NO}_2^-]$ in the reaction mixture.

Part G

Equilibrium constants at 298 K are shown in Table 1 for the acid ionization reaction represented by Equation 1, K_a ; the autoionization of water, K_w ; and the neutralization reaction represented by Equation 2, K_2 .

Table 1

Chemical Equation	Equilibrium Constant
$\text{HNO}_2(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NO}_2^-(aq) + \text{H}_3\text{O}^+(aq)$	$K_a = 5.6 \times 10^{-4}$
$\text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$	$K_w = 1.0 \times 10^{-14}$
$\text{HNO}_2(aq) + \text{OH}^-(aq) \rightarrow \text{NO}_2^-(aq) + \text{H}_2\text{O}(l)$	$K_2 = ?$

Calculate the value of K_2 for Equation 2 at 298 K. Show the work that leads to your answer.

Part H

The student decides to repeat the experiment, this time using an indicator, and has access to the indicators in Table 2.

Table 2

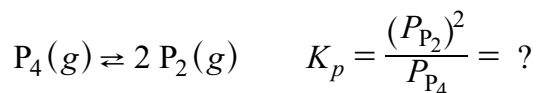
Indicator Name	Acid Color	pH Range of Color Change	Base Color
Methyl orange	Red	3.1–4.4	Yellow
Thymol blue	Yellow	8.0–9.6	Blue
Clayton yellow	Yellow	12.2–13.2	Orange

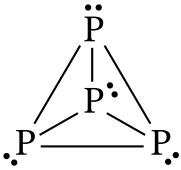
The student conducts a second titration by adding two drops of methyl orange indicator to 35.0 mL of the $\text{HNO}_2(aq)$ solution and titrating the solution with 0.16 M $\text{NaOH}(aq)$ until a color change from red to yellow occurs.

The student claims that methyl orange was the best choice for the indicator. Do you agree or disagree? **Justify** your answer.

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.



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

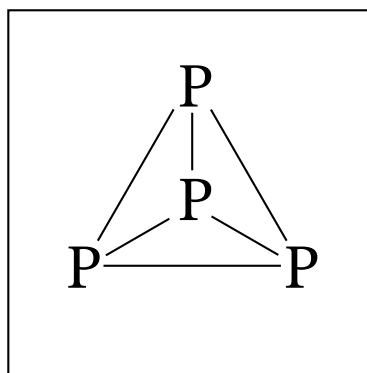
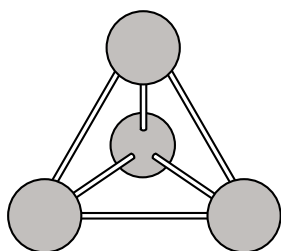
A sample of $P_4(s)$ is placed in a sealed rigid container and heated to 1600. K, at which point the initial partial pressure of $P_4(g)$ is 0.470 atm. Some of the $P_4(g)$ decomposes into $P_2(g)$ as the system reaches equilibrium. At equilibrium, the partial pressure of $P_2(g)$ is determined to be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

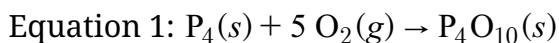
Part C

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}° .

3. White phosphorus is composed of P_4 molecules with a tetrahedral structure, as shown in the diagram on the left. Each P atom is bonded to the other three P atoms by single bonds, as shown in the incomplete Lewis diagram on the right.

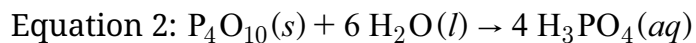


- A. In the box in part A, complete the Lewis diagram for P_4 by drawing the nonbonding electrons.
- B. The reaction of white phosphorus with oxygen to form $P_4O_{10}(s)$ is thermodynamically favorable at 298 K. The reaction is represented by equation 1.

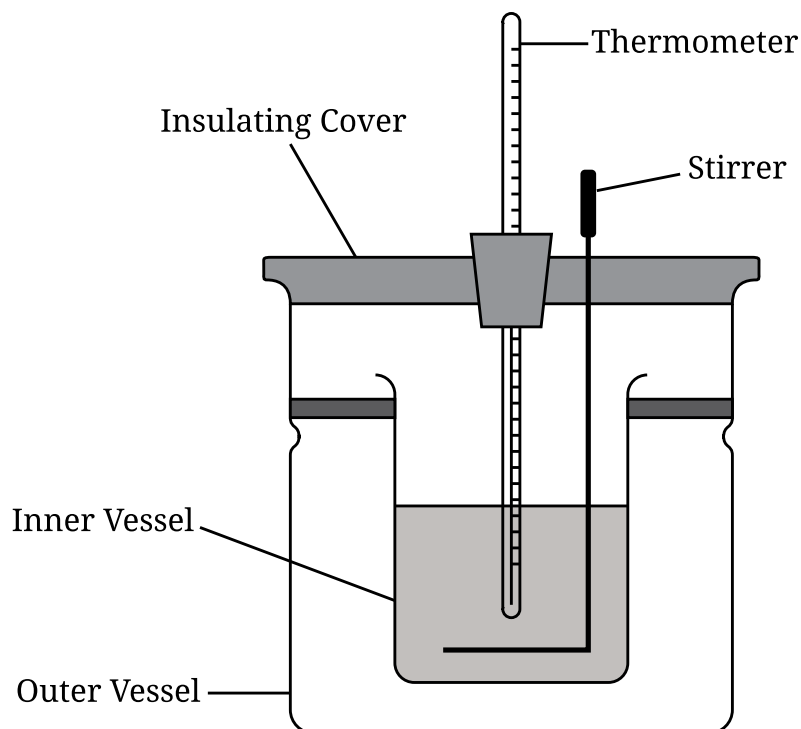


- i. The entropy change of the reaction, ΔS° , is negative. Using particle-level reasoning, explain why the entropy decreases as the reaction progresses.
- ii. The enthalpy change of the reaction, ΔH° , is also negative. A student claims that the favorability of the reaction is driven by enthalpy and **not** by entropy. Is the student's claim correct? Justify your answer by using the relationship between ΔG° , ΔH° , and ΔS° .

$\text{P}_4\text{O}_{10}(s)$ reacts exothermically with water to form phosphoric acid, as represented by equation 2.



A chemist uses a calorimetry experiment to determine the enthalpy change for the reaction, as represented by the following diagram.



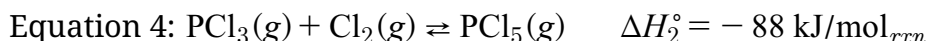
C. The chemist carries out the calorimetry experiment and records the following information.

Mass of P_4O_{10}	0.100 g
Mass of H_2O	100.0 g
Initial temperature	22.00° C
Final temperature	22.38° C
Molar mass of P_4O_{10}	283.9 g/mol
Specific heat of H_2O	4.18 J/(g·°C)

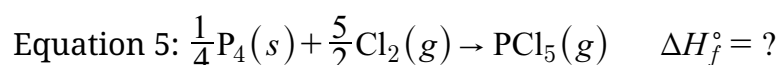
- Calculate the amount of heat, q , released during the experiment, in kJ. Assume that the specific heat of the solution is the same as that of water.
- Calculate the value of $\Delta H^\circ_{\text{rxn}}$ for equation 2 in kJ/mol_{rxn}. Include the sign in your answer.

- D. The chemist weighed out 0.100 g P_4O_{10} of and 100.0 g of H_2O to perform a second trial. In the second trial, some of the solid P_4O_{10} stuck to the weighing paper and was not transferred to the calorimeter. Given that P_4O_{10} is the limiting reactant, would ΔT for the second trial be greater than, less than, or equal to the value in the first trial? Justify your answer.

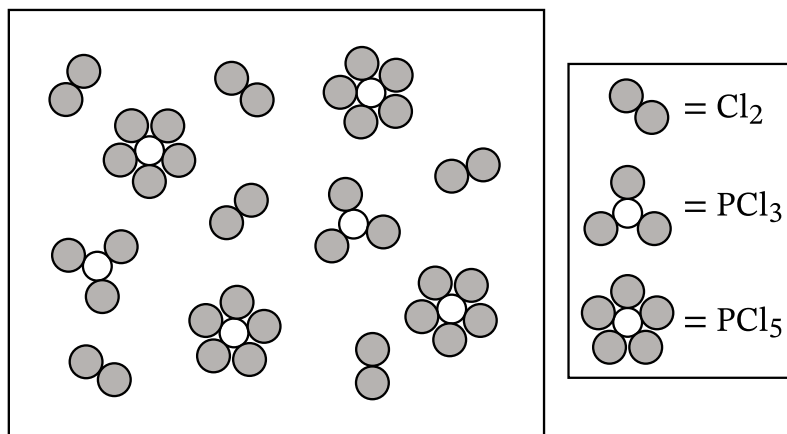
$\text{P}_4(s)$ also reacts readily with $\text{Cl}_2(g)$ to produce phosphorus trichloride, $\text{PCl}_3(g)$, which in turn reacts with $\text{Cl}_2(g)$ in an equilibrium process to produce $\text{PCl}_5(g)$. The reactions are represented by equations 3 and 4.



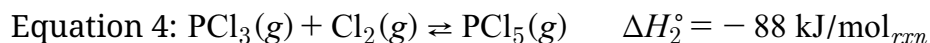
- E. Calculate the standard enthalpy of formation of $\text{PCl}_5(g)$ represented by equation 5.



The following particle-level diagram represents the contents of the vessel in an equilibrium mixture at 546 K involving equation 4.



- F. Equation 4 for the reaction that occurs is shown.



- If each particle in the diagram represents a partial pressure of 1.00 atm, what is the value of K_p for the equilibrium mixture at 546 K?
- Does the value of K_p increase, decrease, or remain the same when the temperature is increased to 596 K? Justify your answer based on ΔH_2° .

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.



- (a) How many grams of $\text{Cl}(g)$ can be formed from 1.25 mol of $\text{AlCl}_3(g)$?

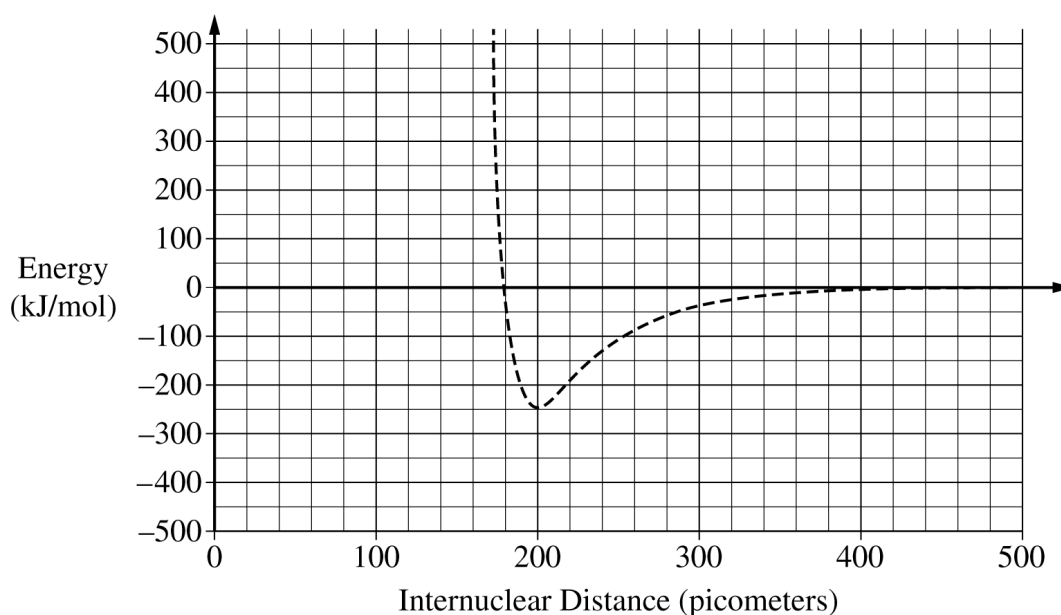
Additional reactions that involve Al or Cl are shown in the following table.

Reaction Number	Equation	ΔH_{rxn}° (kJ/mol _{rxn})
2	$\text{Al}(s) + \frac{3}{2} \text{Cl}_2(g) \rightarrow \text{AlCl}_3(g)$	-583
3	$\text{Al}(s) \rightarrow \text{Al}(g)$	+326
4	$\text{Cl}_2(g) \rightarrow 2 \text{Cl}(g)$	+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.

(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 $\text{Al} - \text{Cl}$ bond length is 220 picometers and the average bond energy is 425 kJ/mol. Draw the potential energy curve for the average $\text{Al} - \text{Cl}$ bond on the preceding graph.

(d) Three proposed Lewis diagrams for the $\text{AlCl}_3(g)$ molecule are shown.

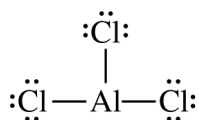


Diagram 1

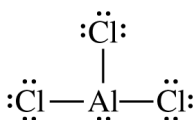


Diagram 2

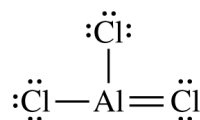


Diagram 3

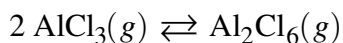
(i) The $\text{AlCl}_3(g)$ molecule has a trigonal planar geometry. Which diagram (1, 2, or 3) can be eliminated based on geometry? Justify your choice based on VSEPR theory.

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

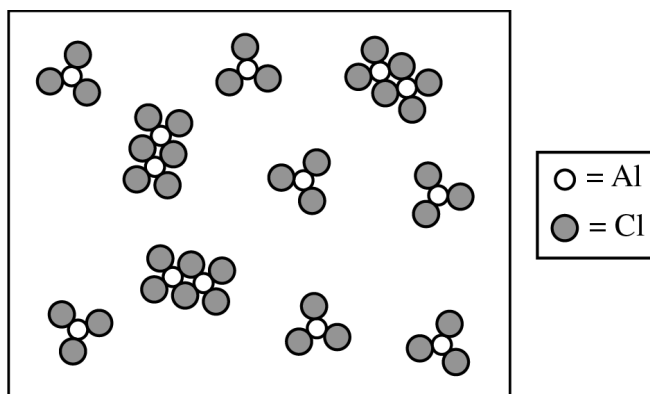
- (ii) Which of the three diagrams is the best representation for the bonding in AlCl_3 ? Justify your choice based on formal charges.

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



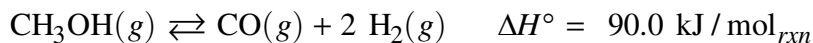
- (e) Write the expression for the equilibrium constant, K_p , for this reaction.

A particle-level diagram of an equilibrium mixture of $\text{AlCl}_3(g)$ and $\text{Al}_2\text{Cl}_6(g)$ 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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Methanol vapor decomposes to form carbon monoxide gas and hydrogen gas at high temperatures in the presence of a platinum catalyst, as represented by the balanced chemical equation given.

(a) Are the hydrogen atoms oxidized or are they reduced in the forward reaction? Justify your answer in terms of oxidation numbers.

(b) In the following box, draw the complete Lewis electron-dot diagram for the carbon monoxide molecule in which every atom obeys the octet rule. Show all bonding and nonbonding valence electrons.



(c) The values of the standard molar entropies of the compounds involved in the reaction are given in the following table.

Substance	S° (J/(K·mol))
$\text{CH}_3\text{OH}(g)$	240.
$\text{CO}(g)$	198
$\text{H}_2(g)$	131

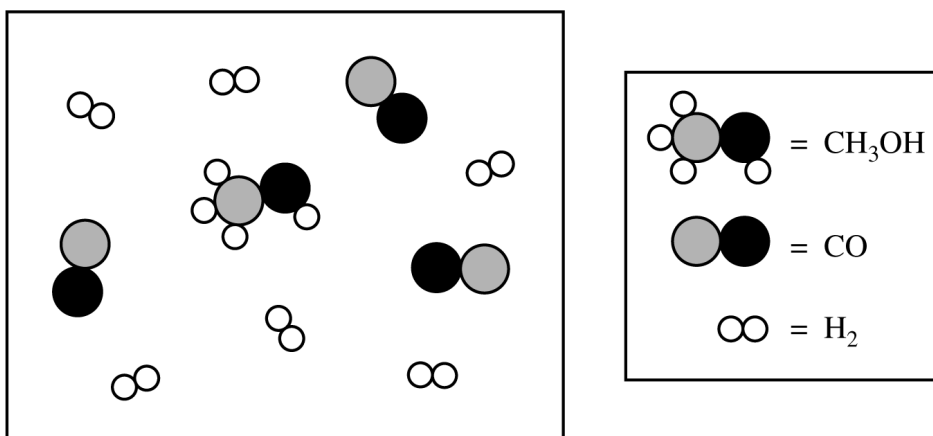
(i) Use the data in the table to calculate the value of the standard entropy change, ΔS° , in J/(K·mol_{rxn}), for the reaction.

GO ON TO THE NEXT PAGE.

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

- (ii) Calculate the value of ΔG° , in $\text{kJ/mol}_{\text{rxn}}$, for the reaction at 375 K. Assume that ΔH° and ΔS° are independent of temperature.

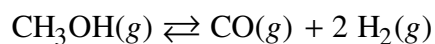
The following particle-level diagram shows a representative sample of the equilibrium mixture represented by the equation given.



- (d) Use information from the particle diagram to calculate the partial pressure of CO at equilibrium when the total pressure of the equilibrium mixture is 12.0 atm.

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

GO ON TO THE NEXT PAGE.



The reaction system represented by the equation is allowed to achieve equilibrium at a different temperature. The following table gives the partial pressure of each species in the equilibrium mixture.

Substance	Partial Pressure at Different Temperature
$\text{CH}_3\text{OH}(g)$	2.7 atm
$\text{CO}(g)$	4.2 atm
$\text{H}_2(g)$	8.4 atm

(f) Use the information in the table to calculate the value of the equilibrium constant, K_p , at the new temperature.

(g) The volume of the container is rapidly doubled with no change in temperature. As equilibrium is re-established, does the number of moles of $\text{CH}_3\text{OH}(g)$ increase, decrease, or remain the same? Justify your answer by comparing the value of the reaction quotient, Q , with the value of the equilibrium constant, K_p .

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.



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 $\text{I}_2(s)$.

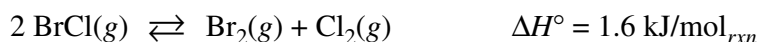
Half-Reaction	E° at 25°C (V)
$\text{Br}_2 + 2 e^- \rightarrow 2 \text{Br}^-$	1.07
$\text{Cl}_2 + 2 e^- \rightarrow 2 \text{Cl}^-$	1.36
$\text{I}_2 + 2 e^- \rightarrow 2 \text{I}^-$	0.53

- (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.



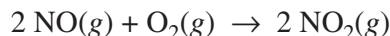
A 0.100 mole sample of pure $\text{BrCl}(g)$ is placed in a previously evacuated, rigid 2.00 L container at 298 K. Eventually the system reaches equilibrium according to the equation above.

- (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 .

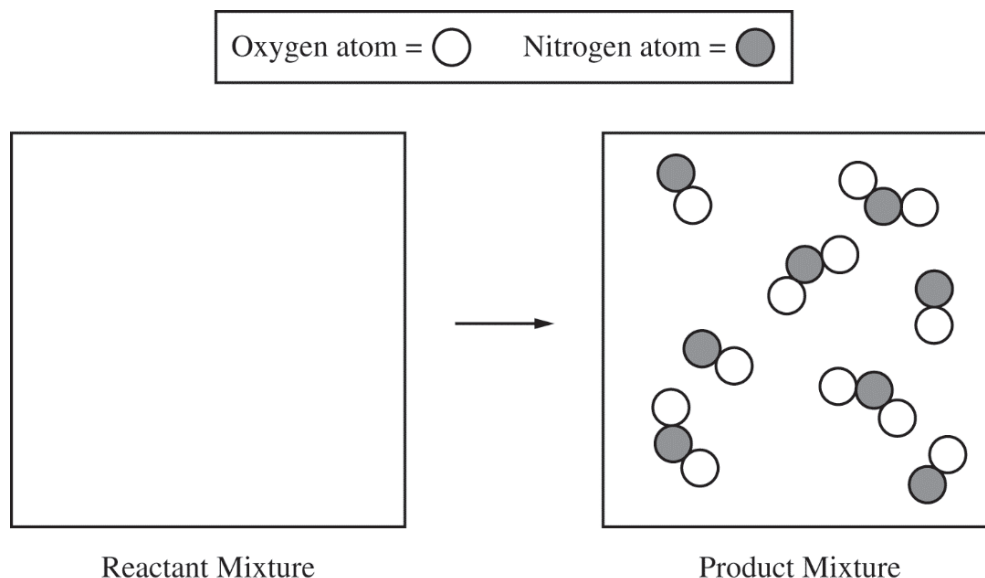
After the system has reached equilibrium, 42 percent of the original BrCl sample has decomposed.

- (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.

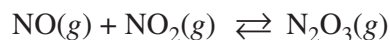
Bond	Bond Energy (kJ/mol)
Br – Br	193
Cl – Cl	243
Br – Cl	?



2. A student investigates the reactions of nitrogen oxides. One of the reactions in the investigation requires an equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$, which the student produces by using the reaction represented above.
- (a) The particle-level representation of the equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$ in the flask at the completion of the reaction between $\text{NO}(g)$ and $\text{O}_2(g)$ is shown below in the box on the right. In the box below on the left, draw the particle-level representation of the reactant mixture of $\text{NO}(g)$ and $\text{O}_2(g)$ that would yield the product mixture shown in the box on the right. In your drawing, represent oxygen atoms and nitrogen atoms as indicated below.



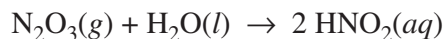
The student reads in a reference text that $\text{NO}(g)$ and $\text{NO}_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.



ΔH_{298}°	ΔS_{298}°	ΔG_{298}°
$-40.4 \text{ kJ/mol}_{\text{rxn}}$	$-138.5 \text{ J/(K} \cdot \text{mol}_{\text{rxn}})$	$0.87 \text{ kJ/mol}_{\text{rxn}}$

- (b) The student begins with an equimolar mixture of $\text{NO}(g)$ and $\text{NO}_2(g)$ in a rigid reaction vessel and the mixture reaches equilibrium at 298 K.
- Calculate the value of the equilibrium constant, K , for the reaction at 298 K.
 - If both P_{NO} and P_{NO_2} in the vessel are initially 1.0 atm, will $P_{\text{N}_2\text{O}_3}$ at equilibrium be equal to 1.0 atm? Justify your answer.
- (c) The student hypothesizes that increasing the temperature will increase the amount of $\text{N}_2\text{O}_3(g)$ in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

$\text{N}_2\text{O}_3(g)$ reacts with water to form nitrous acid, $\text{HNO}_2(aq)$, a compound involved in the production of acid rain. The reaction is represented below.



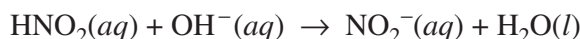
(d) The skeletal structure of the HNO_2 molecule is shown in the box below.

- (i) Complete the Lewis electron-dot diagram of the HNO_2 molecule in the box below, including any lone pairs of electrons.

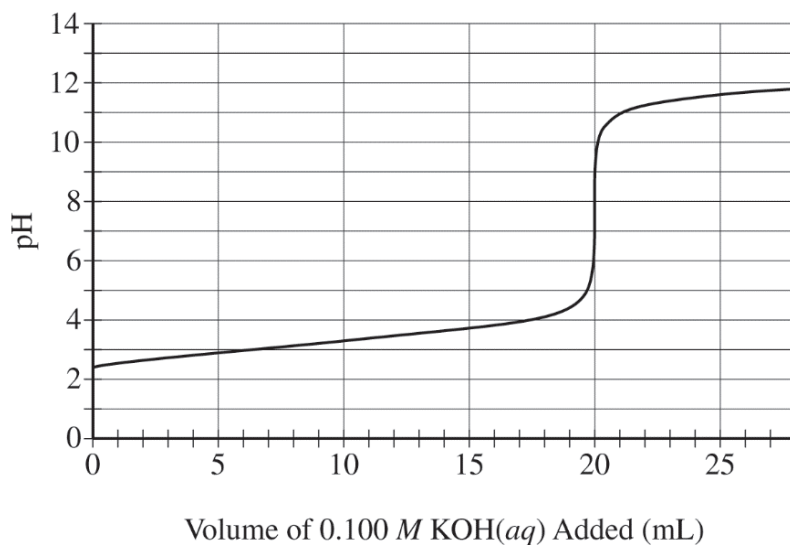


- (ii) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the HNO_2 molecule.

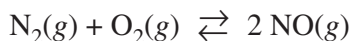
To produce an aqueous solution of HNO_2 , the student bubbles $\text{N}_2\text{O}_3(g)$ into distilled water. Assume that the reaction goes to completion and that HNO_2 is the only species produced. To determine the concentration of $\text{HNO}_2(aq)$ in the resulting solution, the student titrates a 100. mL sample of the solution with 0.100 M $\text{KOH}(aq)$. The neutralization reaction is represented below.



The following titration curve shows the change in pH of the solution during the titration.



- (e) Use the titration curve and the information above to
- determine the initial concentration of the $\text{HNO}_2(aq)$ solution
 - estimate the value of $\text{p}K_a$ for $\text{HNO}_2(aq)$
- (f) During the titration, after a volume of 15 mL of 0.100 M $\text{KOH}(aq)$ has been added, which species, $\text{HNO}_2(aq)$ or $\text{NO}_2^-(aq)$, is present at a higher concentration in the solution? Justify your answer.

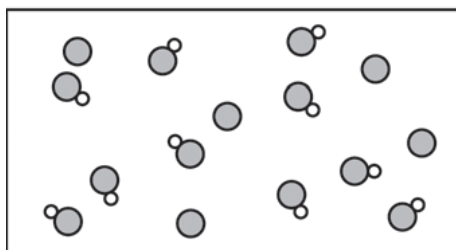
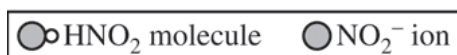


3. At high temperatures, $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ can react to produce nitrogen monoxide, $\text{NO}(\text{g})$, as represented by the equation above.

- (a) Write the expression for the equilibrium constant, K_p , for the forward reaction.
- (b) A student injects $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ into a previously evacuated, rigid vessel and raises the temperature of the vessel to 2000°C . At this temperature the initial partial pressures of $\text{N}_2(\text{g})$ and $\text{O}_2(\text{g})$ are 6.01 atm and 1.61 atm, respectively. The system is allowed to reach equilibrium. The partial pressure of $\text{NO}(\text{g})$ at equilibrium is 0.122 atm. Calculate the value of K_p .

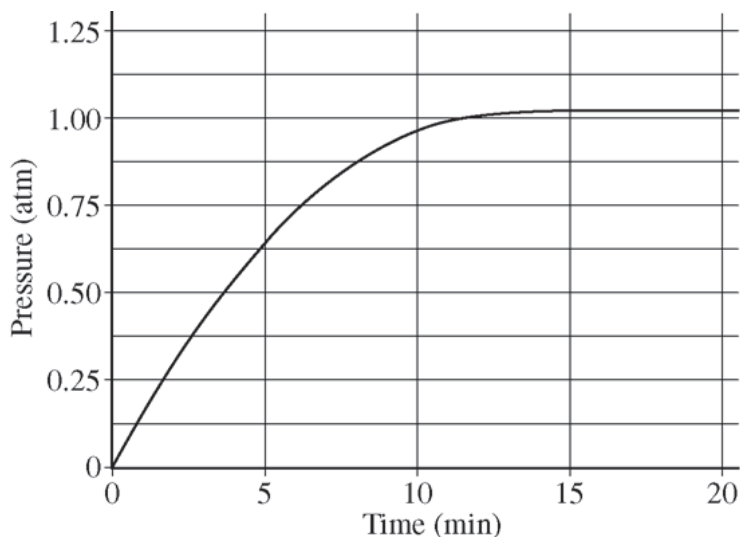
Nitrogen monoxide, $\text{NO}(\text{g})$, can undergo further reactions to produce acids such as HNO_2 , a weak acid with a K_a of 4.0×10^{-4} and a $\text{p}K_a$ of 3.40.

- (c) A student is asked to make a buffer solution with a pH of 3.40 by using 0.100 M $\text{HNO}_2(\text{aq})$ and 0.100 M $\text{NaOH}(\text{aq})$.
- (i) Explain why the addition of 0.100 M $\text{NaOH}(\text{aq})$ to 0.100 M $\text{HNO}_2(\text{aq})$ can result in the formation of a buffer solution. Include the net ionic equation for the reaction that occurs when the student adds the $\text{NaOH}(\text{aq})$ to the $\text{HNO}_2(\text{aq})$.
- (ii) Determine the volume, in mL, of 0.100 M $\text{NaOH}(\text{aq})$ the student should add to 100. mL of 0.100 M $\text{HNO}_2(\text{aq})$ to make a buffer solution with a pH of 3.40. Justify your answer.
- (d) A second student makes a buffer by dissolving 0.100 mol of $\text{NaNO}_2(\text{s})$ in 100. mL of 1.00 M $\text{HNO}_2(\text{aq})$. Which is more resistant to changes in pH when a strong acid or a strong base is added, the buffer made by the second student or the buffer made by the first student in part (c)? Justify your answer.
- (e) A new buffer is made using $\text{HNO}_2(\text{aq})$ as one of the ingredients. A particulate representation of a small representative portion of the buffer solution is shown below. (Cations and water molecules are not shown.) Is the pH of the buffer represented in the diagram greater than, less than, or equal to 3.40? Justify your answer.





4. When heated, calcium carbonate decomposes according to the equation above. In a study of the decomposition of calcium carbonate, a student added a 50.0 g sample of powdered $\text{CaCO}_3(s)$ to a 1.00 L rigid container. The student sealed the container, pumped out all the gases, then heated the container in an oven at 1100 K. As the container was heated, the total pressure of the $\text{CO}_2(g)$ in the container was measured over time. The data are plotted in the graph below.



The student repeated the experiment, but this time the student used a 100.0 g sample of powdered $\text{CaCO}_3(s)$. In this experiment, the final pressure in the container was 1.04 atm, which was the same final pressure as in the first experiment.

- Calculate the number of moles of $\text{CO}_2(g)$ present in the container after 20 minutes of heating.
- The student claimed that the final pressure in the container in each experiment became constant because all of the $\text{CaCO}_3(s)$ had decomposed. Based on the data in the experiments, do you agree with this claim? Explain.
- After 20 minutes some $\text{CO}_2(g)$ was injected into the container, initially raising the pressure to 1.5 atm. Would the final pressure inside the container be less than, greater than, or equal to 1.04 atm? Explain your reasoning.
- Are there sufficient data obtained in the experiments to determine the value of the equilibrium constant, K_p , for the decomposition of $\text{CaCO}_3(s)$ at 1100 K? Justify your answer.