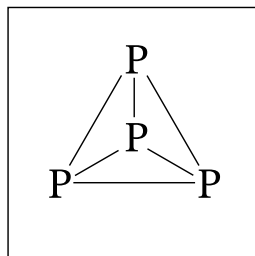
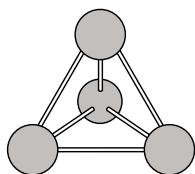
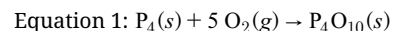


3. White phosphorus is composed of P_4 molecules with a tetrahedral structure, as shown in the diagram on the left. Each P atom is bonded to the other three P atoms by single bonds, as shown in the incomplete Lewis diagram on the right.

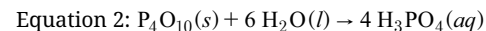


- A. In the box in part A, complete the Lewis diagram for P_4 by drawing the nonbonding electrons.
- B. The reaction of white phosphorus with oxygen to form $P_4O_{10}(s)$ is thermodynamically favorable at 298 K. The reaction is represented by equation 1.

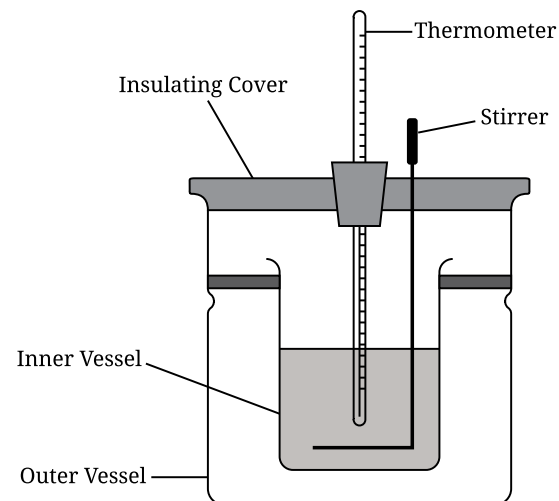


- The entropy change of the reaction, ΔS° , is negative. Using particle-level reasoning, explain why the entropy decreases as the reaction progresses.
- The enthalpy change of the reaction, ΔH° , is also negative. A student claims that the favorability of the reaction is driven by enthalpy and **not**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

$P_4O_{10}(s)$ 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.



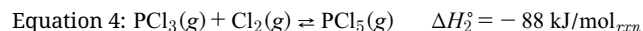
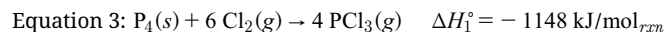
- C. The chemist carries out the calorimetry experiment and records the following information.

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)

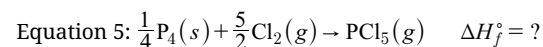
- Calculate the amount of heat, q , released during the experiment, in kJ. Assume that the specific heat of the solution is the same as that of water.
- Calculate the value of ΔH°_{rxn} for equation 2 in kJ/mol_{rxn}. Include the sign in your answer.

D. The chemist weighed out 0.100 g P_4O_{10} 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.

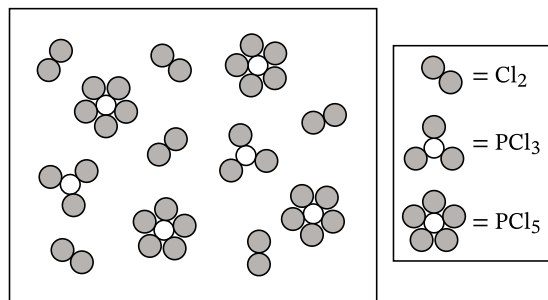
$\text{P}_4(\text{s})$ also reacts readily with $\text{Cl}_2(\text{g})$ to produce phosphorus trichloride, $\text{PCl}_3(\text{g})$, which in turn reacts with $\text{Cl}_2(\text{g})$ in an equilibrium process to produce $\text{PCl}_5(\text{g})$. The reactions are represented by equations 3 and 4.



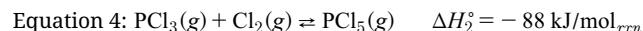
E. Calculate the standard enthalpy of formation of $\text{PCl}_5(\text{g})$ represented by equation 5.



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

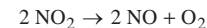


F. Equation 4 for the reaction that occurs is shown.

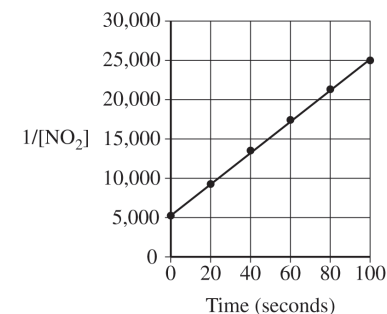
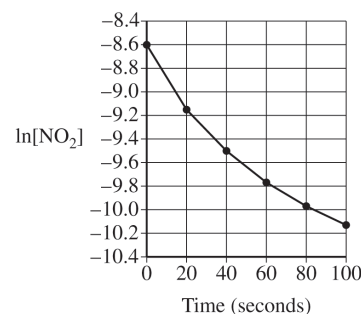


- If each particle in the diagram represents a partial pressure of 1.00 atm, what is the value of K_p for the equilibrium mixture at 546 K?
- Does the value of K_p increase, decrease, or remain the same when the temperature is increased to 596 K? Justify your answer based on ΔH_2° .

6. At elevated temperatures, NO_2 undergoes decomposition in the gas phase, forming NO and O_2 as represented by the following equation.



A scientist measures the change in $[\text{NO}_2]$ over the first 100. s of the reaction at 546°C. The scientist uses the data collected from the experiment to generate the following two graphs.



Based on these data, the scientist makes the claim that the rate law for the reaction is $\text{rate} = k[\text{NO}_2]^2$.

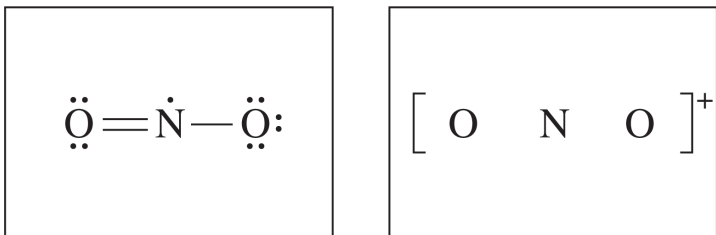
(a) Explain how the graphs indicate that the reaction is second order with respect to NO_2 .

- (b) At a certain point in the reaction, the rate of disappearance of NO_2 is determined to be $6.52 \times 10^{-7} \text{ M/s}$. Determine the rate of appearance, in M/s , of O_2 at this same point in the reaction.

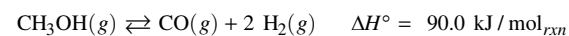
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Continue your response to **QUESTION 6** on this page.

- (c) NO_2 is a molecule that contains an odd number of electrons and can be oxidized to form the NO_2^+ ion. In NO_2 , the unpaired electron is presumed to be localized on the nitrogen atom, as shown in the Lewis diagram in the box on the left.



- (i) In the box on the right, complete the Lewis diagram for NO_2^+ . Be sure to show all bonding and nonbonding electrons.
- (ii) A student makes the claim that the bond angles in NO_2 and NO_2^+ are different from each other. Do you agree or disagree with the student's claim? Justify your answer.

GO ON TO THE NEXT PAGE.

- 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

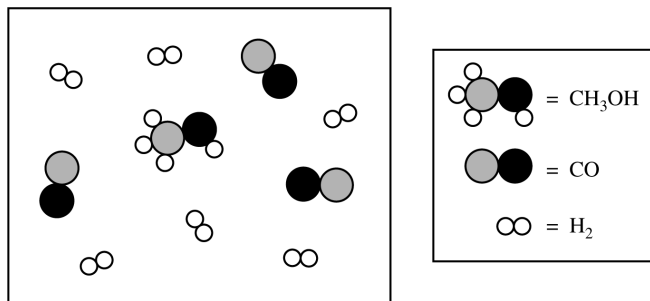
- (i) Use the data in the table to calculate the value of the standard entropy change, ΔS° , in J/(K·mol_{rxn}), for the reaction.

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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.

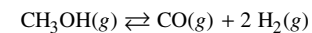
The following particle-level diagram shows a representative sample of the equilibrium mixture represented by the equation given.



- (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.

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

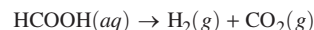
- (f) Use the information in the table to calculate the value of the equilibrium constant, K_p , at the new temperature.

- (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 .

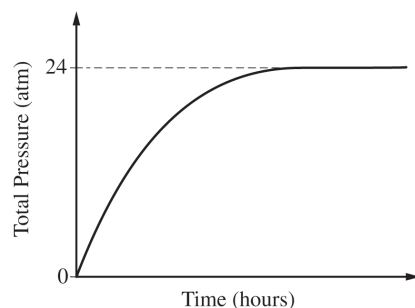
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7 Questions

When a catalyst is added to a solution of $\text{HCOOH}(aq)$, the reaction represented by the following equation occurs.



(e) Is the reaction a redox reaction? Justify your answer.

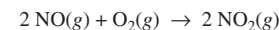


(f) The reaction occurs in a rigid 4.3 L vessel at 25°C , and the total pressure is monitored, as shown in the graph above. The vessel originally did not contain any gas. Calculate the number of moles of $\text{CO}_2(g)$ produced in the reaction. (Assume that the amount of $\text{CO}_2(g)$ dissolved in the solution is negligible.)

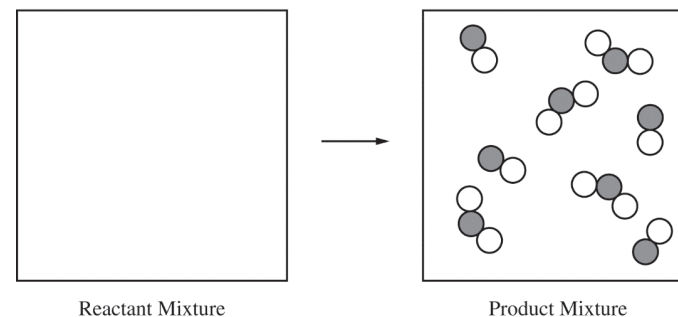
(g) After the reaction has proceeded for several minutes, does the amount of catalyst increase, decrease, or remain the same? Justify your answer.

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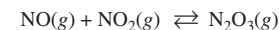
Use a pencil or pen with black or dark blue ink only. Do NOT write your name. Do NOT write outside the box.



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.



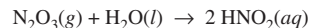
The student reads in a reference text that $\text{NO}(g)$ and $\text{NO}_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.



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.
- (i) Calculate the value of the equilibrium constant, K , for the reaction at 298 K.
- (ii) 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.



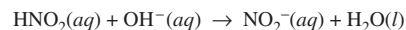
(d) The skeletal structure of the HNO_2 molecule is shown in the box below.

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

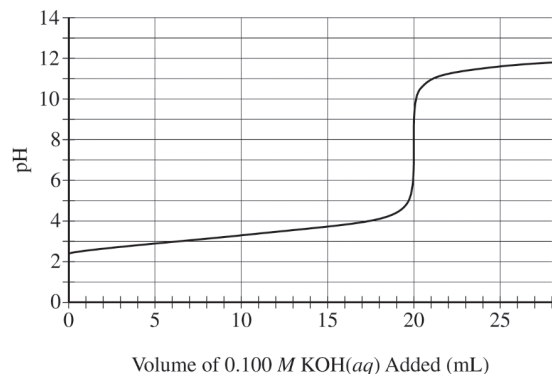


- (ii) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the HNO_2 molecule.

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.

CHEMISTRY

Section II

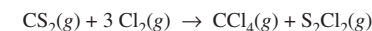
7 Questions

Time—1 hour and 45 minutes

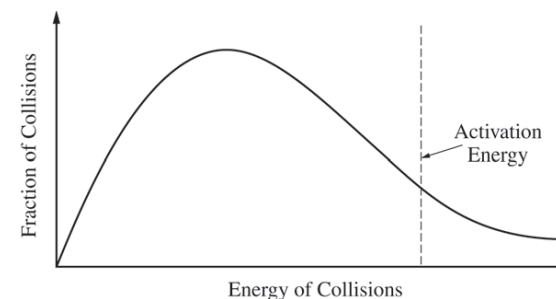
YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.

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.



- Carbon tetrachloride, $\text{CCl}_4(g)$, can be synthesized according to the reaction represented above. A chemist runs the reaction at a constant temperature of 120°C in a rigid 25.0 L container.
 - Chlorine gas, $\text{Cl}_2(g)$, is initially present in the container at a pressure of 0.40 atm.
 - How many moles of $\text{Cl}_2(g)$ are in the container?
 - How many grams of carbon disulfide, $\text{CS}_2(g)$, are needed to react completely with the $\text{Cl}_2(g)$?
 - At 30°C the reaction is thermodynamically favorable, but no reaction is observed to occur. However, at 120°C , the reaction occurs at an observable rate.
 - Explain how the higher temperature affects the collisions between the reactant molecules so that the reaction occurs at an observable rate at 120°C .
 - The graph below shows a distribution for the collision energies of reactant molecules at 120°C . Draw a second curve on the graph that shows the distribution for the collision energies of reactant molecules at 30°C .



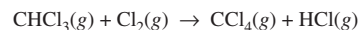
(c) S_2Cl_2 is a product of the reaction.

- (i) In the box below, complete the Lewis electron-dot diagram for the S_2Cl_2 molecule by drawing in all of the electron pairs.



- (ii) What is the approximate value of the Cl–S–S bond angle in the S_2Cl_2 molecule that you drew in part (c)(i) ? (If the two Cl–S–S bond angles are not equal, include both angles.)

(d) $\text{CCl}_4(g)$ can also be produced by reacting $\text{CHCl}_3(g)$ with $\text{Cl}_2(g)$ at 400°C , as represented by the equation below.



At the completion of the reaction a chemist successfully separates the $\text{CCl}_4(g)$ from the $\text{HCl}(g)$ by cooling the mixture to 70°C , at which temperature the $\text{CCl}_4(g)$ condenses while the $\text{HCl}(g)$ remains in the gaseous state.

- (i) Identify all types of intermolecular forces present in $\text{HCl}(l)$.
- (ii) What can be inferred about the relative strengths of the intermolecular forces in $\text{CCl}_4(l)$ and $\text{HCl}(l)$? Justify your answer in terms of the information above.



2. A student designs an experiment to study the reaction between NaHCO_3 and $\text{HC}_2\text{H}_3\text{O}_2$. The reaction is represented by the equation above. The student places 2.24 g of NaHCO_3 in a flask and adds 60.0 mL of 0.875 M $\text{HC}_2\text{H}_3\text{O}_2$. The student observes the formation of bubbles and that the flask gets cooler as the reaction proceeds.

- (a) Identify the reaction represented above as an acid-base reaction, precipitation reaction, or redox reaction. Justify your answer.
- (b) Based on the information above, identify the limiting reactant. Justify your answer with calculations.
- (c) The student observes that the bubbling is rapid at the beginning of the reaction and gradually slows as the reaction continues. Explain this change in the reaction rate in terms of the collisions between reactant particles.
- (d) In thermodynamic terms, a reaction can be driven by enthalpy, entropy, or both.
- (i) Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between $\text{NaHCO}_3(s)$ and $\text{HC}_2\text{H}_3\text{O}_2(aq)$? Answer by drawing a circle around one of the choices below.

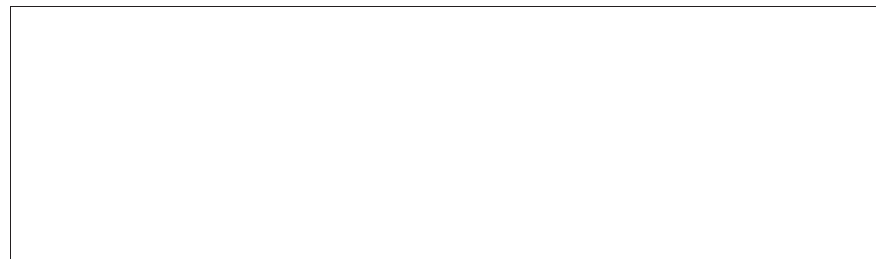
Enthalpy only

Entropy only

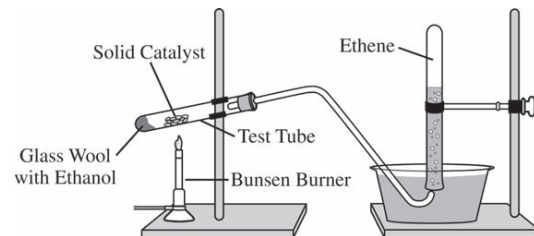
Both enthalpy and entropy

- (ii) Justify your selection in part (d)(i) in terms of ΔG° .

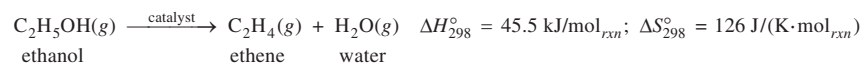
(e) The HCO_3^- ion has three carbon-to-oxygen bonds. Two of the carbon-to-oxygen bonds have the same length and the third carbon-to-oxygen bond is longer than the other two. The hydrogen atom is bonded to one of the oxygen atoms. In the box below, draw a Lewis electron-dot diagram (or diagrams) for the HCO_3^- ion that is (are) consistent with the given information.



(f) A student prepares a solution containing equimolar amounts of $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{NaC}_2\text{H}_3\text{O}_2$. The pH of the solution is measured to be 4.7. The student adds two drops of 3.0 M $\text{HNO}_3(aq)$ and stirs the sample, observing that the pH remains at 4.7. Write a balanced, net-ionic equation for the reaction between $\text{HNO}_3(aq)$ and the chemical species in the sample that is responsible for the pH remaining at 4.7.



2. Ethene, $\text{C}_2\text{H}_4(g)$ (molar mass 28.1 g/mol), may be prepared by the dehydration of ethanol, $\text{C}_2\text{H}_5\text{OH}(g)$ (molar mass 46.1 g/mol), using a solid catalyst. A setup for the lab synthesis is shown in the diagram above. The equation for the dehydration reaction is given below.



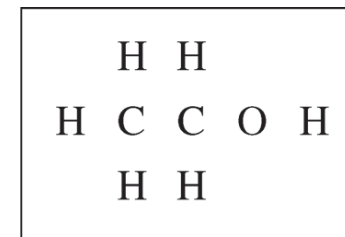
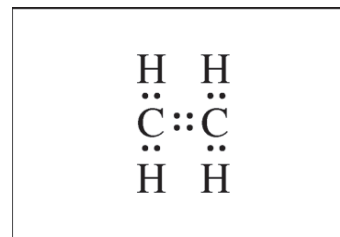
A student added a 0.200 g sample of $\text{C}_2\text{H}_5\text{OH}(l)$ to a test tube using the setup shown above. The student heated the test tube gently with a Bunsen burner until all of the $\text{C}_2\text{H}_5\text{OH}(l)$ evaporated and gas generation stopped. When the reaction stopped, the volume of collected gas was 0.0854 L at 0.822 atm and 305 K. (The vapor pressure of water at 305 K is 35.7 torr.)

- (a) Calculate the number of moles of $\text{C}_2\text{H}_4(g)$
- that are actually produced in the experiment and measured in the gas collection tube and
 - that would be produced if the dehydration reaction went to completion.
- (b) Calculate the percent yield of $\text{C}_2\text{H}_4(g)$ in the experiment.

Because the dehydration reaction is not observed to occur at 298 K, the student claims that the reaction has an equilibrium constant less than 1.00 at 298 K.

- (c) Do the thermodynamic data for the reaction support the student's claim? Justify your answer, including a calculation of ΔG_{298}° for the reaction.

- (d) The Lewis electron-dot diagram for C_2H_4 is shown below in the box on the left. In the box on the right, complete the Lewis electron-dot diagram for $\text{C}_2\text{H}_5\text{OH}$ by drawing in all of the electron pairs.



- (e) What is the approximate value of the C–O–H bond angle in the ethanol molecule?
- (f) During the dehydration experiment, $\text{C}_2\text{H}_4(g)$ and unreacted $\text{C}_2\text{H}_5\text{OH}(g)$ passed through the tube into the water. The C_2H_4 was quantitatively collected as a gas, but the unreacted $\text{C}_2\text{H}_5\text{OH}$ was not. Explain this observation in terms of the intermolecular forces between water and each of the two gases.

Nonmetal	C	N	O	Ne	Si	P	S	Ar
Formula of Compound	CF ₄	NF ₃	OF ₂	No compound	SiF ₄	PF ₃	SF ₂	No compound

5. Some binary compounds that form between fluorine and various nonmetals are listed in the table above. A student examines the data in the table and poses the following hypothesis: the number of F atoms that will bond to a nonmetal is always equal to 8 minus the number of valence electrons in the nonmetal atom.

- (a) Based on the student's hypothesis, what should be the formula of the compound that forms between chlorine and fluorine?
- (b) In an attempt to verify the hypothesis, the student researches the fluoride compounds of the other halogens and finds the formula ClF₃. In the box below, draw a complete Lewis electron-dot diagram for a molecule of ClF₃.

- (c) Two possible geometric shapes for the ClF₃ molecule are trigonal planar and T-shaped. The student does some research and learns that the molecule has a dipole moment. Which of the two shapes is consistent with the fact that the ClF₃ molecule has a dipole moment? Justify your answer in terms of bond polarity and molecular structure.

In an attempt to resolve the existence of the ClF₃ molecule with the hypothesis stated above, the student researches the compounds that form between halogens and fluorine, and assembles the following list.

Halogen	Formula(s)
F	F ₂
Cl	
Br	BrF, BrF ₃ , BrF ₅
I	IF, IF ₃ , IF ₅ , IF ₇

- (d) Based on concepts of atomic structure and periodicity, propose a modification to the student's previous hypothesis to account for the compounds that form between halogens and fluorine.