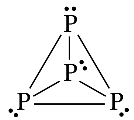
Question 4

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

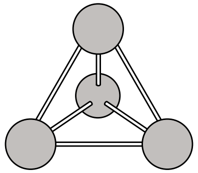
A sample of $P_4(s)$ is placed in a sealed rigid container and heated to 1600. K, at which point the initial partial pressure of $P_4(g)$ is 0.470 atm. Some of the $P_4(g)$ decomposes into $P_2(g)$ as the system reaches equilibrium. At equilibrium, the partial pressure of $P_2(g)$ is determined to be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

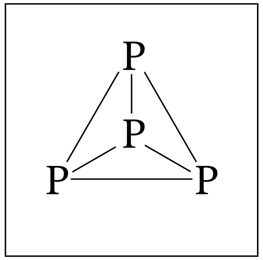
Calculate the value of the equilibrium constant, K_p, for the reaction at 1600. K. Show the work that leads to your answer.

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}.

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.

$$\text{Equation 1: } P_4(s) + 5\,O_2(g) \rightarrow P_4O_{10}(s)$$

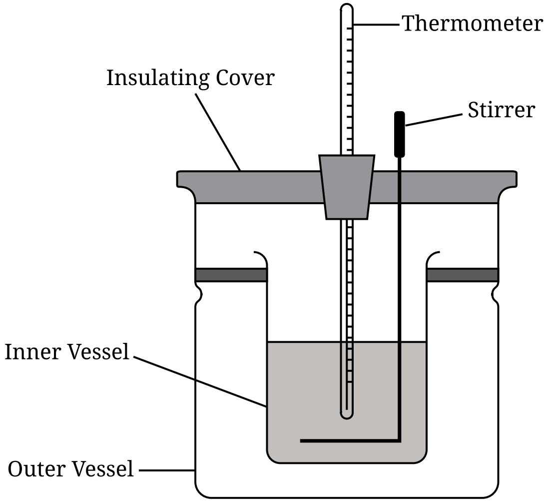
i. The entropy change of the reaction, ΔS°, is negative. Using particle-level reasoning, explain why the entropy decreases as the reaction progresses.

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°.

$P_4O_{10}(s)$ reacts exothermically with water to form phosphoric acid, as represented by equation 2.

$$\text{Equation 2: } P_4O_{10}(s) + 6\ H_2O(l) \rightarrow 4\ H_3PO_4(aq)$$

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)

i. 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.

ii. 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} 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.

$P_4(s)$ also reacts readily with $Cl_2(g)$ to produce phosphorus trichloride, $PCl_3(g)$, which in turn reacts with $Cl_2(g)$ in an equilibrium process to produce $PCl_5(g)$. The reactions are represented by equations 3 and 4.

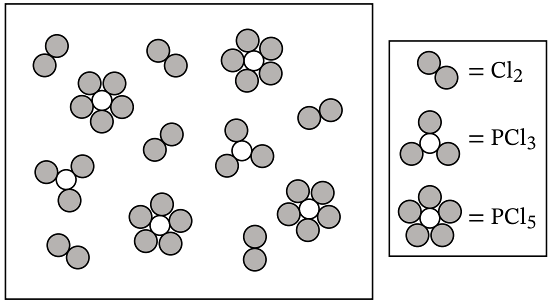
$$\text{Equation 3: } P_4(s) + 6\ Cl_2(g) \rightarrow 4\ PCl_3(g) \qquad \Delta H_1^\circ = -\ 1148\ \text{kJ/mol}_{rxn}$$

$$\text{Equation 4: } PCl_3(g) + Cl_2(g) \rightleftarrows PCl_5(g) \qquad \Delta H_2^\circ = -\ 88\ \text{kJ/mol}_{rxn}$$

E. Calculate the standard enthalpy of formation of $PCl_5(g)$ represented by equation 5.

$$\text{Equation 5: } \frac{1}{4}P_4(s) + \frac{5}{2}Cl_2(g) \rightarrow PCl_5(g) \qquad \Delta H_f^\circ = ?$$

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.

$$\text{Equation 4: } PCl_3(g) + Cl_2(g) \rightleftarrows PCl_5(g) \qquad \Delta H_2^\circ = -\ 88\ \text{kJ/mol}_{rxn}$$

i. 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?

ii. 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. A chemical reaction between maleic acid ($H_2C_4H_2O_4$) and sodium bicarbonate ($NaHCO_3$) occurs in the presence of water to produce carbon dioxide and sodium maleate ($Na_2C_4H_2O_4$), as represented by the following equation.

$$H_2C_4H_2O_4(aq) + 2\,NaHCO_3(aq) \rightarrow 2\,CO_2(g) + 2\,H_2O(l) + Na_2C_4H_2O_4(aq)$$

(a) A student combines equal masses of $H_2C_4H_2O_4(s)$ chunks and $NaHCO_3(s)$ chunks with sufficient water at 20.0°C. The student determines that 0.0114 mol of $CO_2(g)$ is produced after the reaction goes to completion.

(i) Calculate the number of grams of $CO_2(g)$ produced.

(ii) The $CO_2(g)$ produced from the reaction at 20.0°C was collected and found to have a pressure of 1.25 atm. Calculate the volume of $CO_2(g)$, in liters.

(b) The student performs a second experiment that is identical to the first except that the student grinds the chunks of $H_2C_4H_2O_4(s)$ and $NaHCO_3(s)$ into powder before combining the powder with water.

(i) What happens to the surface area of the reactants when the student grinds the chunks into powder?

(ii) The rate-determining step for the overall reaction is the dissolving of the solids. Would the time required for the dissolving of the solids in the second experiment be longer than, shorter than, or the same as the time required in the first experiment? Justify your answer based on the collisions between particles.

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

(iii) When the reaction is complete, will the volume of $CO_2(g)$ at the end of the second experiment be greater than, less than, or equal to the volume at the end of the first experiment? Justify your answer.

The student conducts additional trials of the experiment and produces the following data table.

Trial	Mass of $H_2C_4H_2O_4$ (grams)	Mass of $NaHCO_3$ (grams)	Moles of CO_2 Produced (mol)
3	1.543	1.251	0.01489
4	1.543	1.686	0.02007

(c) Based on the student's data, identify the limiting reactant in trial 3. Justify your answer.

(d) The reaction has a value of $\Delta S°$ greater than zero. Using particle-level reasoning, explain why the entropy increases as the reaction progresses.

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

The student notices that the temperature of the reaction mixture decreases as the reaction takes place and correctly determines that the reaction is endothermic.

(e) The student claims that the reaction is thermodynamically favorable at all temperatures because $\Delta S^\circ_{rxn} > 0$ and the reaction is endothermic. Do you agree or disagree with the student's claim? Justify your answer.

Next, the student investigates the acid-base behavior of maleic acid. The student notes that maleic acid is a diprotic acid. The two acid dissociation processes that occur are represented by the following equations.

$$H_2C_4H_2O_4 + H_2O \rightleftarrows HC_4H_2O_4^- + H_3O^+ \qquad K_{a_1} = 1.5 \times 10^{-2}$$

$$HC_4H_2O_4^- + H_2O \rightleftarrows C_4H_2O_4^{2-} + H_3O^+ \qquad K_{a_2} = 8.5 \times 10^{-7}$$

(f) Calculate the pK_{a_2} value for the $HC_4H_2O_4^-$ ion.

(g) A buffer solution with a pH of 7.00 is prepared using $C_4H_2O_4^{2-}$ and $HC_4H_2O_4^-$. Calculate the ratio $\dfrac{[C_4H_2O_4^{2-}]}{[HC_4H_2O_4^-]}$ in this solution.

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CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

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

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

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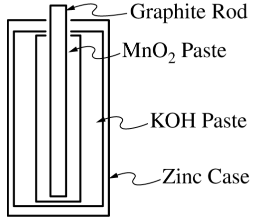
Continue your response to **QUESTION 1** on this page.

(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)
$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$	−0.76
$ZnO(s) + H_2O(l) + 2\,e^- \rightarrow Zn(s) + 2\,OH^-(aq)$	−1.28
$2\,MnO_2(s) + H_2O(l) + 2\,e^- \rightarrow Mn_2O_3(s) + 2\,OH^-(aq)$	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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$$CH_3OH(g) \rightleftarrows CO(g) + 2\ H_2(g) \qquad \Delta H° = \ 90.0\ \text{kJ / mol}_{rxn}$$

. 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 O

(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))
$CH_3OH(g)$	240.
$CO(g)$	198
$H_2(g)$	131

(i) Use the data in the table to calculate the value of the standard entropy change, $\Delta S°$, in J/(K·mol$_{rxn}$), for the reaction.

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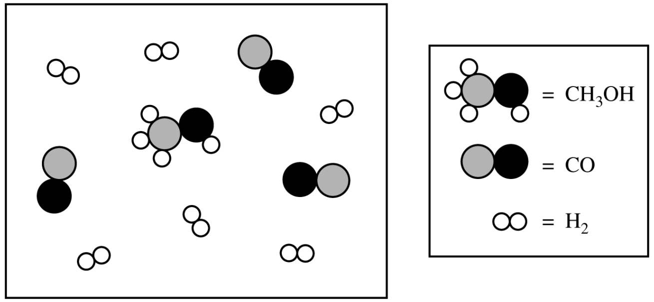
Continue your response to **QUESTION 2** on this page.

(ii) Calculate the value of $\Delta G°$, in kJ/mol$_{rxn}$, for the reaction at 375 K. Assume that $\Delta H°$ and $\Delta S°$ 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.

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

$$CH_3OH(g) \rightleftarrows CO(g) + 2\ H_2(g)$$

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
$CH_3OH(g)$	2.7 atm
$CO(g)$	4.2 atm
$H_2(g)$	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 $CH_3OH(g)$ 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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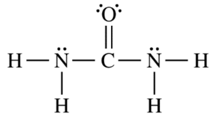
CHEMISTRY
Section II
Time—1 hour and 45 minutes
7 Questions

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.

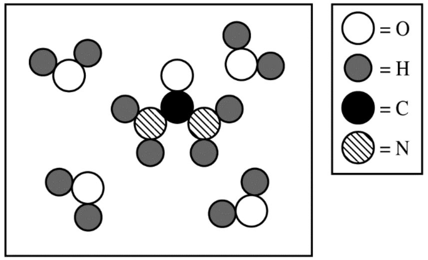
Write your response in the space provided following each question. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer. 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.

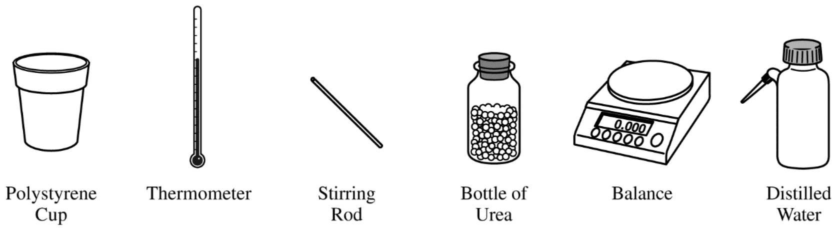


$$H_2NCONH_2(s) \rightleftarrows H_2NCONH_2(aq)$$

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))
$H_2NCONH_2(s)$	104.6
$H_2NCONH_2(aq)$	?

(f) The entropy change for the dissolution of urea, ΔS°_{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 ΔS°_{soln} is positive for the dissolution of urea in water.

(h) The student claims that $\Delta S°$ 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.

$$NaHCO_3(s) + HC_2H_3O_2(aq) \rightarrow NaC_2H_3O_2(aq) + H_2O(l) + CO_2(g)$$

2. A student designs an experiment to study the reaction between $NaHCO_3$ and $HC_2H_3O_2$. 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* $HC_2H_3O_2$. 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.

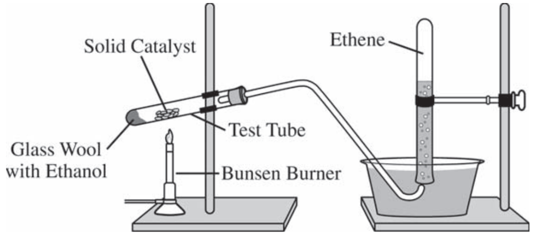
(i) Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between $NaHCO_3(s)$ and $HC_2H_3O_2(aq)$? Answer by drawing a circle around one of the choices below.

Enthalpy only　　　　Entropy only　　　　Both enthalpy and entropy

(ii) Justify your selection in part (d)(i) in terms of $\Delta G°$.

(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 $HC_2H_3O_2$ and $NaC_2H_3O_2$. The pH of the solution is measured to be 4.7. The student adds two drops of 3.0 *M* $HNO_3(aq)$ and stirs the sample, observing that the pH remains at 4.7. Write a balanced, net-ionic equation for the reaction between $HNO_3(aq)$ and the chemical species in the sample that is responsible for the pH remaining at 4.7.



2. Ethene, $C_2H_4(g)$ (molar mass 28.1 g/mol), may be prepared by the dehydration of ethanol, $C_2H_5OH(g)$ (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.

$$\underset{\text{ethanol}}{C_2H_5OH(g)} \xrightarrow{\text{catalyst}} \underset{\text{ethene}}{C_2H_4(g)} + \underset{\text{water}}{H_2O(g)} \quad \Delta H^\circ_{298} = 45.5 \text{ kJ/mol}_{rxn}; \; \Delta S^\circ_{298} = 126 \text{ J/(K}\cdot\text{mol}_{rxn})$$

A student added a 0.200 g sample of $C_2H_5OH(l)$ to a test tube using the setup shown above. The student heated the test tube gently with a Bunsen burner until all of the $C_2H_5OH(l)$ 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 $C_2H_4(g)$

(i) that are actually produced in the experiment and measured in the gas collection tube and

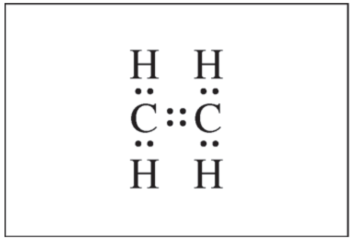
(ii) that would be produced if the dehydration reaction went to completion.

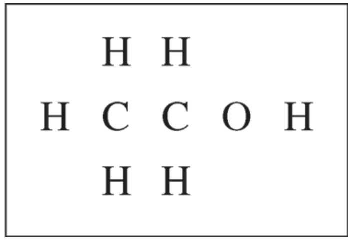
(b) Calculate the percent yield of $C_2H_4(g)$ in the experiment.

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 C_2H_5OH 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, $C_2H_4(g)$ and unreacted $C_2H_5OH(g)$ passed through the tube into the water. The C_2H_4 was quantitatively collected as a gas, but the unreacted C_2H_5OH was not. Explain this observation in terms of the intermolecular forces between water and each of the two gases.