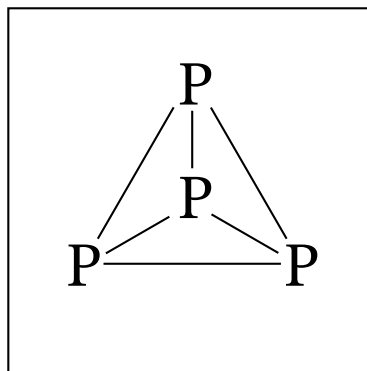
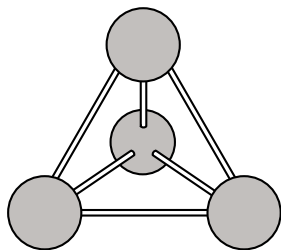
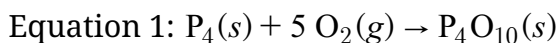


3. White phosphorus is composed of P_4 molecules with a tetrahedral structure, as shown in the diagram on the left. Each P atom is bonded to the other three P atoms by single bonds, as shown in the incomplete Lewis diagram on the right.

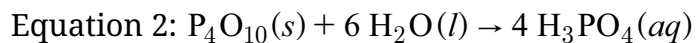


- A. In the box in part A, complete the Lewis diagram for P_4 by drawing the nonbonding electrons.
- B. The reaction of white phosphorus with oxygen to form $P_4O_{10}(s)$ is thermodynamically favorable at 298 K. The reaction is represented by equation 1.

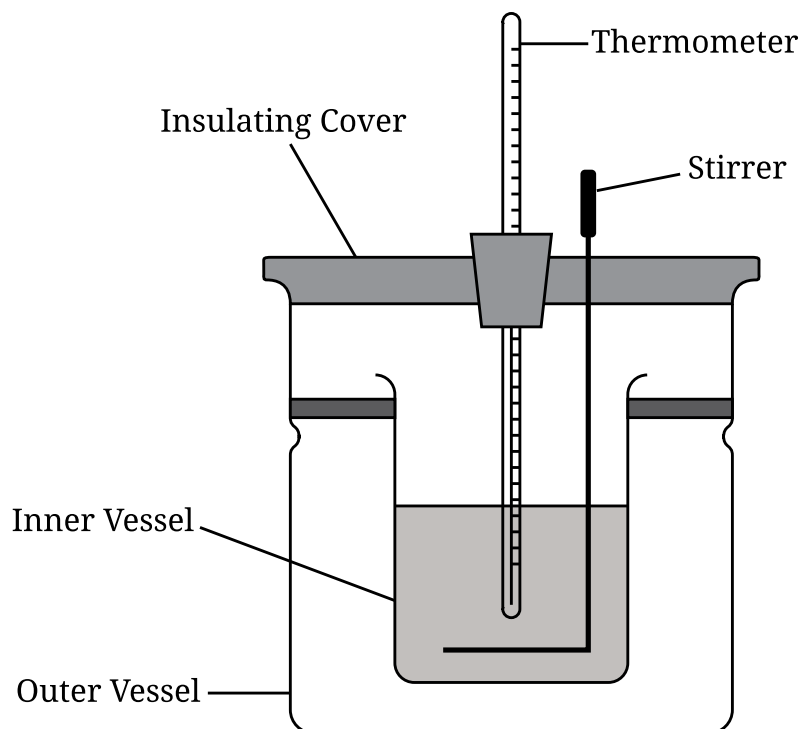


- i. The entropy change of the reaction, ΔS° , is negative. Using particle-level reasoning, explain why the entropy decreases as the reaction progresses.
- ii. The enthalpy change of the reaction, ΔH° , is also negative. A student claims that the favorability of the reaction is driven by enthalpy and **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.



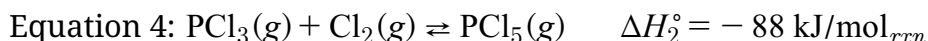
C. The chemist carries out the calorimetry experiment and records the following information.

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)

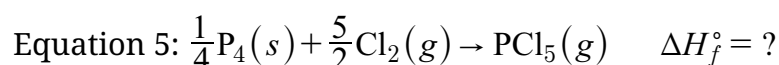
- Calculate the amount of heat, q , released during the experiment, in kJ. Assume that the specific heat of the solution is the same as that of water.
- Calculate the value of $\Delta H^\circ_{\text{rxn}}$ for equation 2 in kJ/mol $_{\text{rxn}}$. Include the sign in your answer.

- 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.

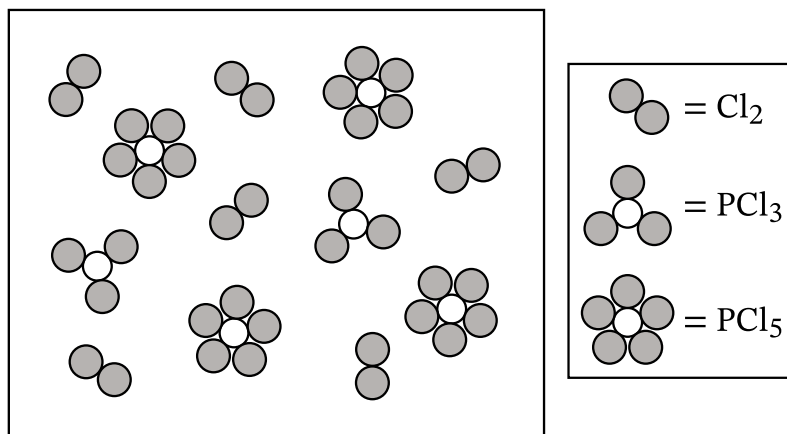
$\text{P}_4(s)$ also reacts readily with $\text{Cl}_2(g)$ to produce phosphorus trichloride, $\text{PCl}_3(g)$, which in turn reacts with $\text{Cl}_2(g)$ in an equilibrium process to produce $\text{PCl}_5(g)$. The reactions are represented by equations 3 and 4.



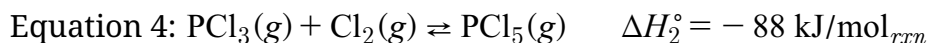
- E. Calculate the standard enthalpy of formation of $\text{PCl}_5(g)$ represented by equation 5.



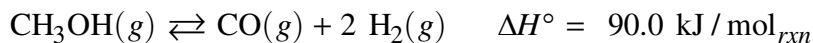
The following particle-level diagram represents the contents of the vessel in an equilibrium mixture at 546 K involving equation 4.



- 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° .



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

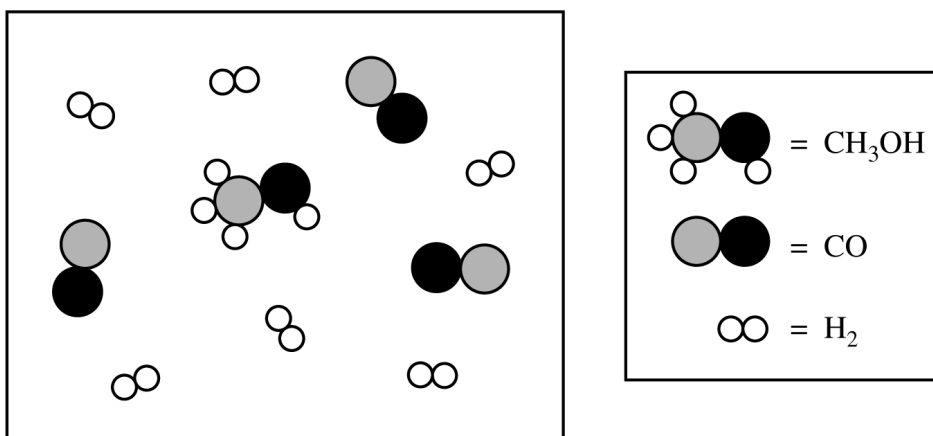
(i) Use the data in the table to calculate the value of the standard entropy change, ΔS° , in J/(K·mol_{rxn}), for the reaction.

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.

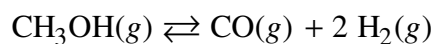
The following particle-level diagram shows a representative sample of the equilibrium mixture represented by the equation given.



- (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.

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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

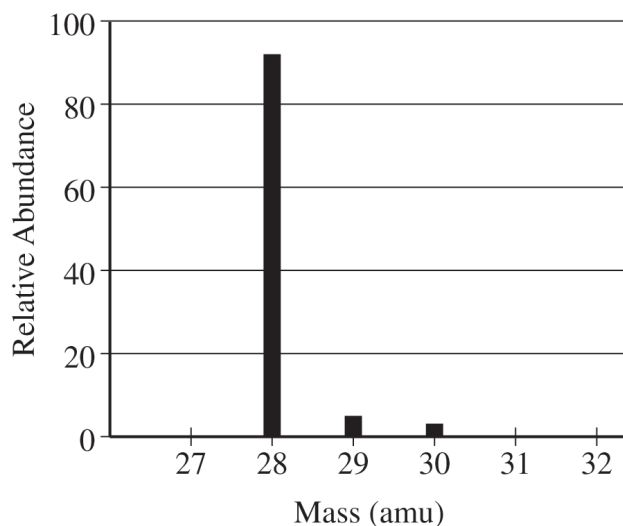
(f) Use the information in the table to calculate the value of the equilibrium constant, K_p , at the new temperature.

(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 .

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.

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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.

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° (J/(mol · 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 $\text{H}_2(g)$.

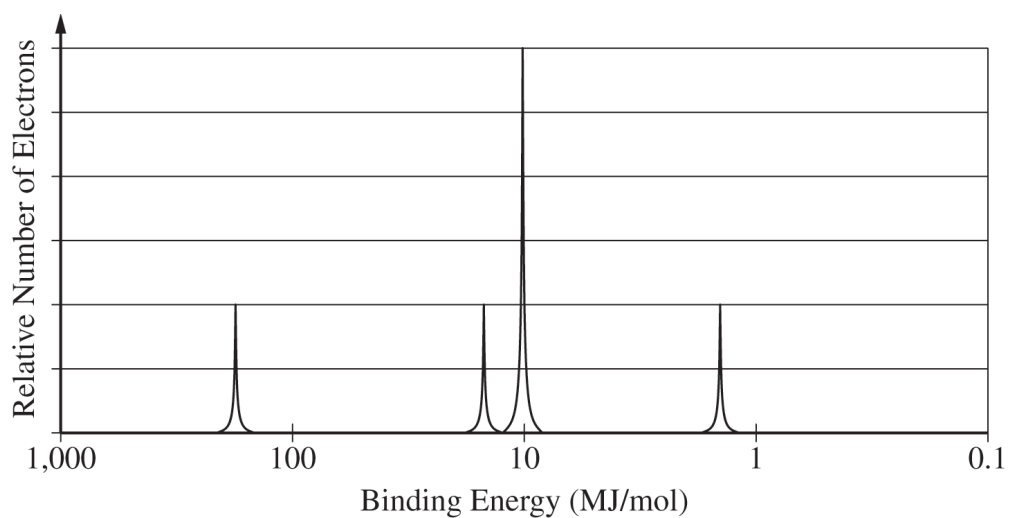
(e) Calculate the value, in J/(mol · K), of ΔS° for the reaction.

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

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(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.

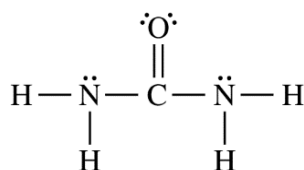
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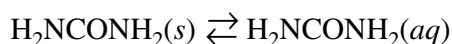
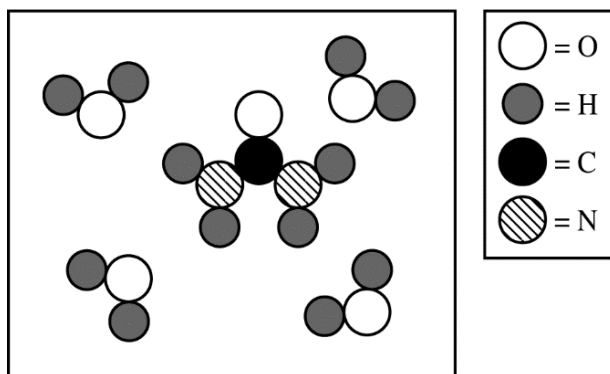
CHEMISTRY**Section II****Time—1 hour and 45 minutes****7 Questions****YOU MAY USE YOUR CALCULATOR FOR THIS SECTION.**

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.

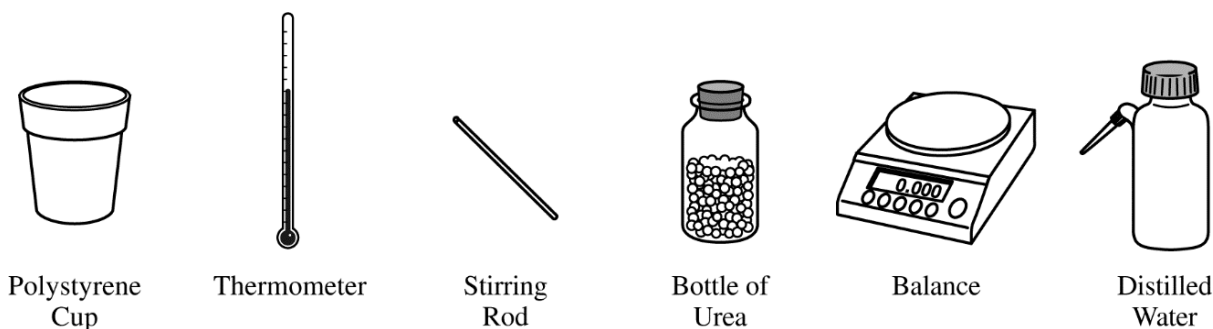


1. The compound urea, H_2NCONH_2 , is widely used in chemical fertilizers. The complete Lewis electron-dot diagram for the urea molecule is shown above.
- (a) Identify the hybridization of the valence orbitals of the carbon atom in the urea molecule.
- (b) Urea has a high solubility in water, due in 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.



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.

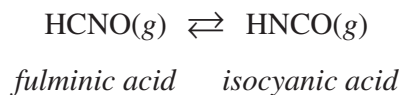
2. Answer the following questions about the isomers fulminic acid and isocyanic acid.

Two possible Lewis electron-dot diagrams for fulminic acid, HCNO, are shown below.



- (a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

Fulminic acid can convert to isocyanic acid according to the equation below.



Fulminic Acid	Isocyanic Acid
$\text{H}-\text{C}\equiv\text{N}-\ddot{\text{O}}:$	$\text{H}-\ddot{\text{N}}=\text{C}=\ddot{\text{O}}:$

- (b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of ΔH° for the reaction of HCNO(g) to form HNCO(g).

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N–O	201	C=N	615	H–C	413
C=O	745	C≡N	891	H–N	391

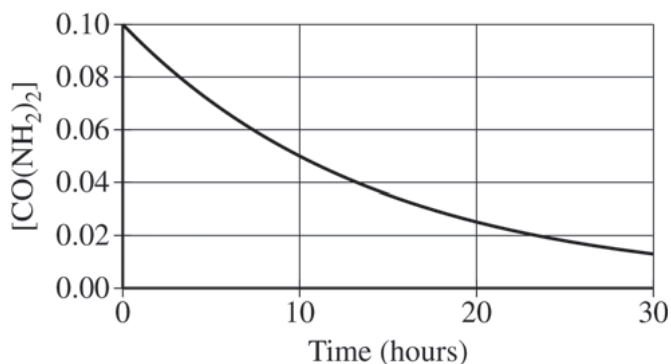
- (c) A student claims that ΔS° for the reaction is close to zero. Explain why the student's claim is accurate.
- (d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

The ammonium salt of isocyanic acid is a product of the decomposition of urea, $\text{CO}(\text{NH}_2)_2$, represented below.



A student studying the decomposition reaction runs the reaction at 90°C . The student collects data on the concentration of urea as a function of time, as shown by the data table and the graph below.

Time (hours)	$[\text{CO}(\text{NH}_2)_2]$
0	0.1000
5	0.0707
10	0.0500
15	0.0354
20	0.0250
25	0.0177
30	0.0125



- (e) The student proposes that the rate law is $\text{rate} = k[\text{CO}(\text{NH}_2)_2]$.
- Explain how the data support the student's proposed rate law.
 - Using the proposed rate law and the student's results, determine the value of the rate constant, k . Include units with your answer.
- (f) The student learns that the decomposition reaction was run in a solution with a pH of 13. Briefly describe an experiment, including the initial conditions that you would change and the data you would gather, to determine whether the rate of the reaction depends on the concentration of $\text{OH}^-(aq)$.