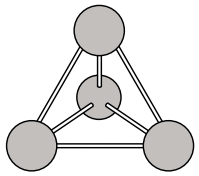
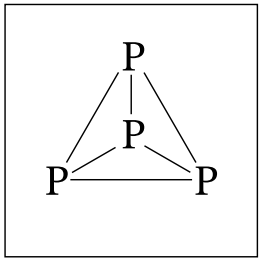
3. White phosphorus is composed of P_4 molecules with a tetrahedral structure, as shown in the diagram on the left. Each P atom is bonded to the other three P atoms by single bonds, as shown in the incomplete Lewis diagram on the right.





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.

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

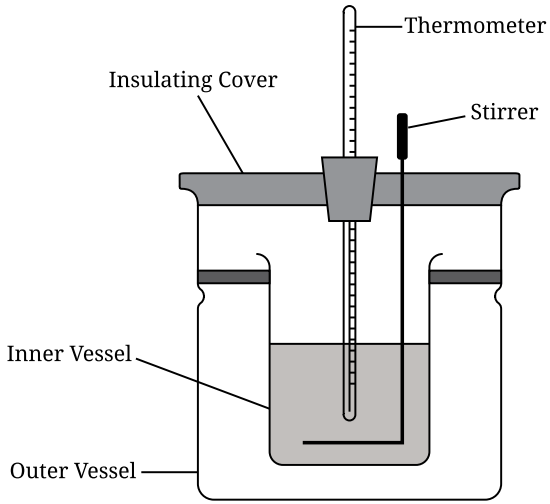
i. The entropy change of the reaction, ΔS°, is negative. Using particle-level reasoning, explain why the entropy decreases as the reaction progresses.

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 $J/(g\cdot°C)$

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.

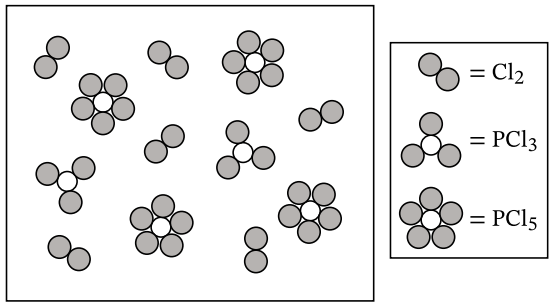
Equation 3: $P_4(s) + 6\ Cl_2(g) \rightarrow 4\ PCl_3(g) \qquad \Delta H_1^\circ = -1148\ \text{kJ/mol}_{rxn}$

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.

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.

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°.

CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

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.

For each question, show your work for each part in the space provided after that part. 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.

. 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.

$$x\ Mn(s) + y\ HCl(aq) \rightarrow Mn_xCl_y(aq) + \frac{y}{2}H_2(g)$$

GO ON TO THE NEXT PAGE.

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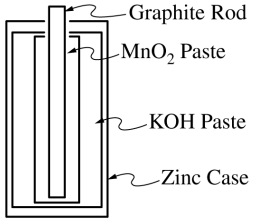
Continue your response to **QUESTION 1** on this page.

(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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$$CH_3OH(g) \rightleftarrows CO(g) + 2\ H_2(g) \qquad \Delta H^\circ = 90.0\ \text{kJ / mol}_{rxn}$$

. 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

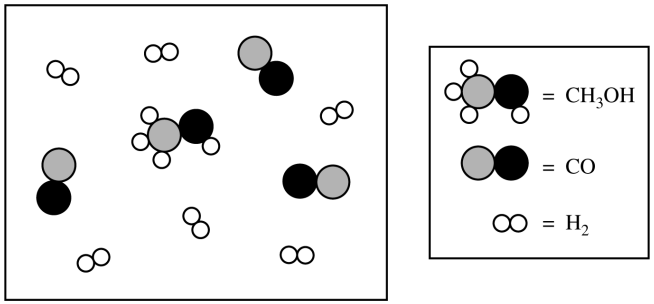
(i) Use the data in the table to calculate the value of the standard entropy change, ΔS°, in J/(K·mol$_{rxn}$), for the reaction.

GO ON TO THE NEXT PAGE.

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

(ii) Calculate the value of ΔG°, in kJ/mol$_{rxn}$, 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.

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

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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