Week 28

AP Chemistry

Homework bundle for this week

本周作业合集

exercises.lol

Contents 目录

AP Chemistry   Name: ____________   Score: ______

1. When ice melts to water, the entropy...
   - ☐ increases
   - ☐ decreases
   - ☐ stays the same
2. A reaction's entropy change is...
   - ☐ sum of products minus sum of reactants
   - ☐ sum of reactants minus sum of products
   - ☐ the sum of everything
3. A reaction is thermodynamically favourable when ΔG is...
   - ☐ negative
   - ☐ positive
   - ☐ exactly 100
4. Which quantity tells you whether a reaction is thermodynamically favourable?
   - ☐ ΔG
   - ☐ the activation energy
   - ☐ the molar mass
5. A reaction with $\Delta G° < 0$ has an equilibrium constant that is...
   - ☐ greater than 1
   - ☐ less than 1
   - ☐ exactly 0
6. Reaction A has $\Delta G = +15$; reaction B has $\Delta G = -40$. The total ΔG coupled?

   ____
7. A current of 5 A flows for 200 s. The total charge (in C)?

   ____________ C
8. An element in its standard state has a standard entropy of zero.

   ☐ True   ☐ False

9. With $\Delta H = -100$ kJ, $T = 300$ K, $\Delta S = 0.2$ kJ/K, find ΔG (in kJ).

_________________ kJ

10. A reaction with $\Delta G < 0$ can still be far too slow to observe.

☐ True ☐ False

AP Chemistry

1. **increases**

   Liquid water is more disordered than solid ice.

2. **sum of products minus sum of reactants**

   $\Delta S = \sum S°(\text{products}) - \sum S°(\text{reactants})$.

3. **negative**

   $\Delta G < 0$ means the reaction is favourable.

4. ΔG

   ΔG decides favourability; activation energy decides speed.

5. **greater than 1**

   Negative $\Delta G°$ favours products, so $K > 1$.

6. **-25**

   $15 + (-40) = -25$, so the pair is favourable.

7. **1000 C**

   $Q = It = 5 \times 200 = 1000$ C.

8. **False**

   Unlike formation enthalpy, every substance has a positive $S°$.

9. **-160 kJ**

   $\Delta G = \Delta H - T\Delta S = -100 - (300)(0.2) = -160$ kJ.

10. **True**

    A large activation energy makes a favourable reaction slow.

9.1 Introduction to Entropy

Name: ____________ Class: ________ Date: __________ **Total: 9 marks**

KEY WORDS entropy 熵

Objective

Build the skills to answer exam questions on **entropy** — the measure of disorder.

You must be able to:

- describe **entropy** 熵 as the number of ways to arrange a system
- predict the **sign of** ΔS for a process
- rank states by entropy (gas > liquid > solid)

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

What entropy is

Entropy (S) measures disorder — the number of ways energy and particles can be arranged. More spread-out, more random ⇒ higher entropy.

Entropy by state

For the same substance, $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$. Gases have far more ways to arrange their particles.

Predicting the sign of ΔS

$\Delta S > 0$ (increase) when:

- a solid or liquid becomes a **gas**;
- the number of **gas molecules increases**;
- a solid **dissolves**.

$\Delta S < 0$ when the reverse happens (gas → liquid, fewer gas moles).

A worked prediction

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$: 3 gas moles → 0 gas moles (a liquid), so $\Delta S < 0$ (a decrease).

2 Practice

Now apply the methods above.

2.1 Rank solid, liquid, and gas by entropy. [1]

2.2 State the sign of ΔS when a liquid boils. [1]

2.3 State the sign of ΔS for $2NO_2(g) \rightarrow N_2O_4(g)$ (2 gas moles $\rightarrow$ 1). [1]

3 Exam-style questions

3.1 Which process has $\Delta S > 0$? [1]

- **A** gas condensing to liquid
- **B** water freezing
- **C** a solid subliming to gas
- **D** 2 gas moles forming 1 gas mole

3.2 Predict the sign of ΔS for each:

(a) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ [1]

(b) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ [1]

(c) dissolving salt in water [1]

3.3 Explain, in terms of arrangements, why a gas has higher entropy than the same substance as a solid. [2]

Solutions

2.1 gas > liquid > solid.

2.2 Positive ($\Delta S > 0$).

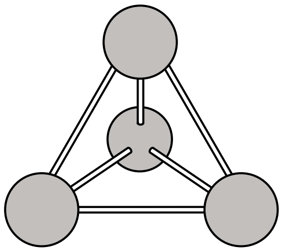
2.3 Negative (fewer gas moles).

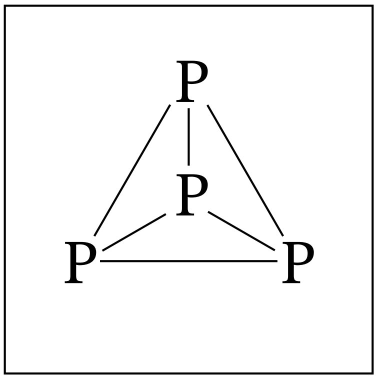
3.1 **C** — subliming a solid to gas greatly increases disorder.

3.2 (a) positive (a gas is produced); (b) negative (4 gas moles $\rightarrow$ 2); (c) positive.

3.3 A gas has vastly more available positions and energy arrangements than a rigid, ordered solid, so far more microstates — hence higher entropy.

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.

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

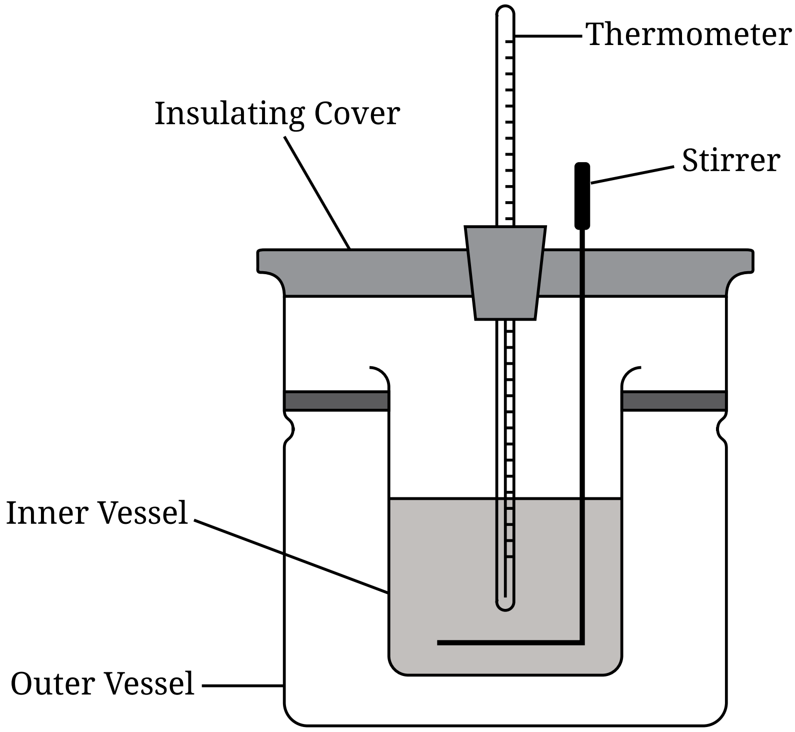
i. The entropy change of the reaction, ΔS°, is negative. Using particle-level reasoning, explain why the entropy decreases as the reaction progresses.

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.

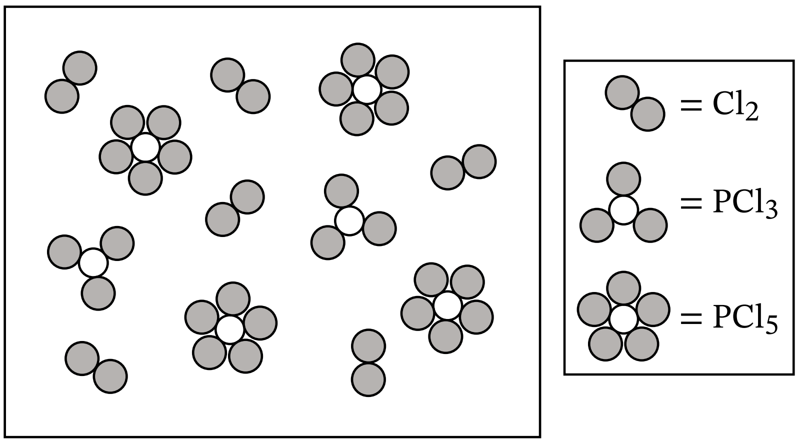
$$\text{Equation 3: } P_4(s) + 6\ Cl_2(g) \rightarrow 4\ PCl_3(g) \qquad \Delta H_1^\circ = -\ 1148\ \text{kJ/mol}_{rxn}$$

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

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.

GO ON TO THE NEXT PAGE.

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

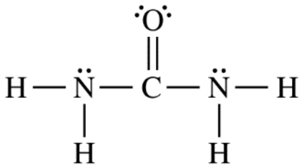
Time—1 hour and 45 minutes

7 Questions

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.

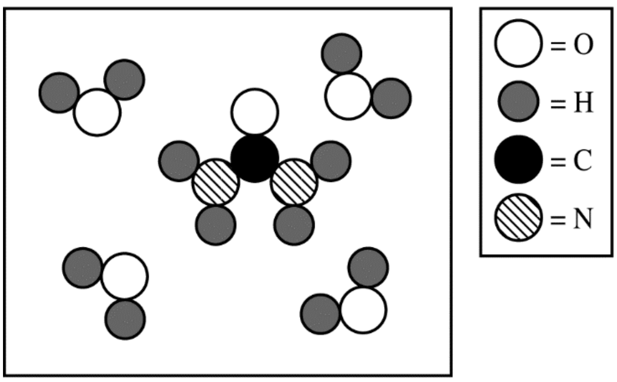
Write your response in the space provided following each question. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer.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

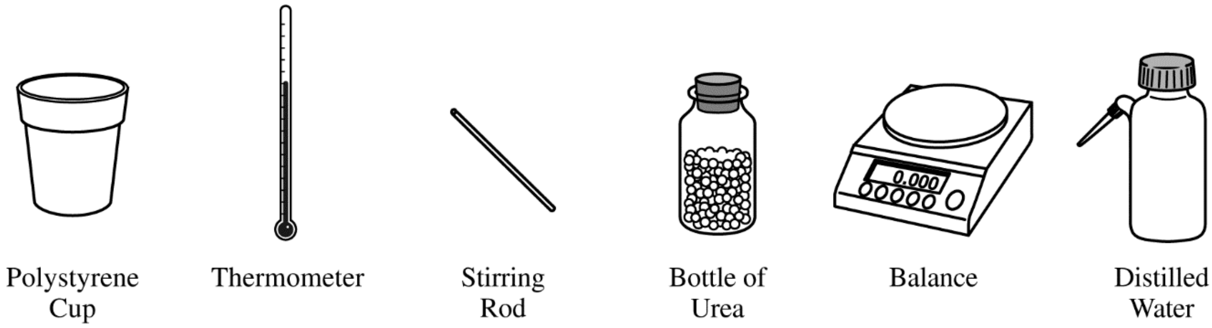


$$H_2NCONH_2(s) \rightleftarrows H_2NCONH_2(aq)$$

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.

AP CHEMISTRY • EXERCISE SHEET

9.2 Absolute Entropy and Entropy Change

Name: ______________ Class: __________ Date: ____________ **Total: 11 marks**

KEY WORDS entropy 熵

Objective

Build the skills to answer exam questions on **absolute entropy and entropy change**.

You must be able to:

- use $\Delta S° = \Sigma S°(\text{products}) - \Sigma S°(\text{reactants})$
- weight each $S°$ by its coefficient
- interpret the sign of the result

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Standard molar entropy

Every substance has a positive **standard molar entropy** $S°$ (unlike ΔH_f, elements are **not** zero). Gases have the largest $S°$.

■ The entropy-change formula

$$\Delta S° = \sum S°(\text{products}) - \sum S°(\text{reactants}),$$

each weighted by its coefficient.

■ A worked calculation

For $N_2 + 3H_2 \rightarrow 2NH_3$, with $S°$: $N_2 = 192$, $H_2 = 131$, $NH_3 = 193$ J mol^{-1}K^{-1}:

$$\Delta S° = 2(193) - [192 + 3(131)] = 386 - 585 = -199 \text{ J K}^{-1}.$$

Negative — consistent with 4 gas moles becoming 2.

■ Sign check

The calculated sign should match the qualitative prediction (fewer gas moles → negative). If not, recheck the coefficients.

2 Practice

Now apply the methods above.

2.1 Write the formula for $\Delta S°$ of a reaction. [1]

2.2 Is $S°$ of an element zero? [1]

2.3 For products summing to 400 and reactants to 550 J/K, find $\Delta S°$. [2]

3 Exam-style questions

3.1 Unlike $\Delta H_f°$, the standard entropy $S°$ of an element is [1]

- **A** zero
- **B** a positive value
- **C** negative
- **D** undefined

3.2 For $2SO_2(g)+O_2(g) \rightarrow 2SO_3(g)$, with $S°$: $SO_2 = 248$, $O_2 = 205$, $SO_3 = 257$ J mol^{-1}K^{-1}.

(a) Calculate $\Delta S°$. [3]

(b) Is the sign consistent with the change in gas moles? [1]

3.3 Explain why $\Delta S°$ is negative for a reaction that goes from 3 moles of gas to 2 moles of gas. [2]

Solutions

2.1 $\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})$.

2.2 No — it is a positive value.

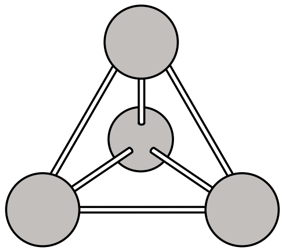
2.3 $400 - 550 = -150$ J/K.

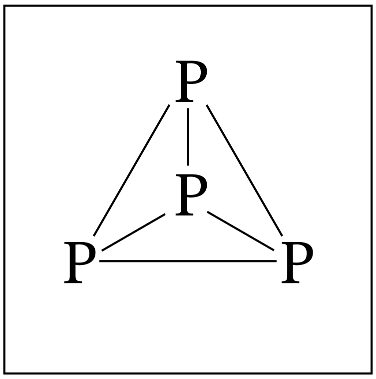
3.1 **B** — a positive value.

3.2 (a) $\Delta S^\circ = 2(257) - [2(248) + 205] = 514 - 701 = -187$ J K^{-1}. (b) Yes — 3 gas moles become 2, so a decrease is expected.

3.3 Fewer gas molecules means fewer ways to arrange the particles, so the disorder (entropy) decreases, giving a negative ΔS°.

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.

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

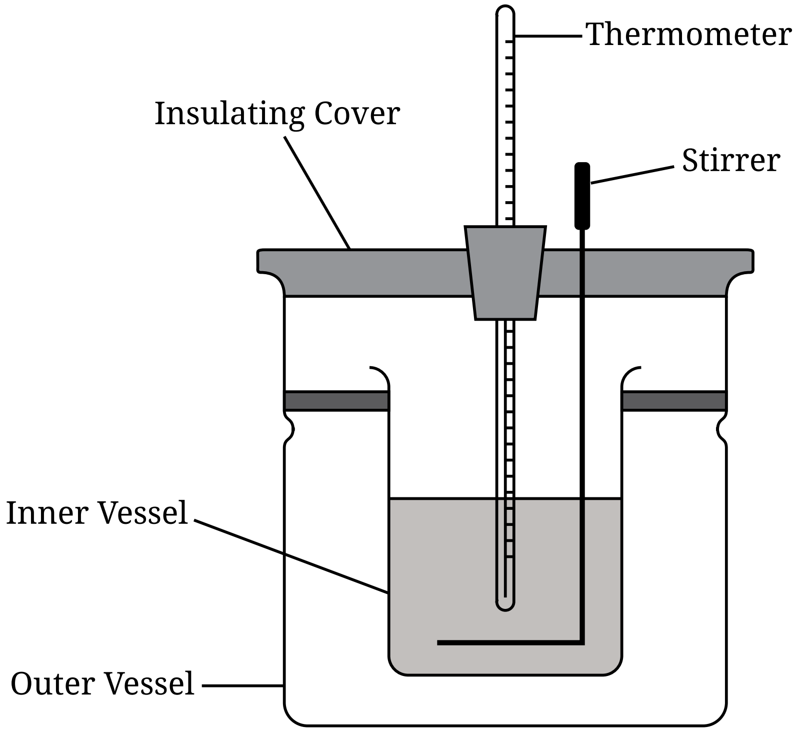
i. The entropy change of the reaction, $\Delta S°$, is negative. Using particle-level reasoning, explain why the entropy decreases as the reaction progresses.

ii. The enthalpy change of the reaction, $\Delta H°$, 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 $\Delta G°$, $\Delta H°$, and $\Delta S°$.

$P_4O_{10}(s)$ 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.

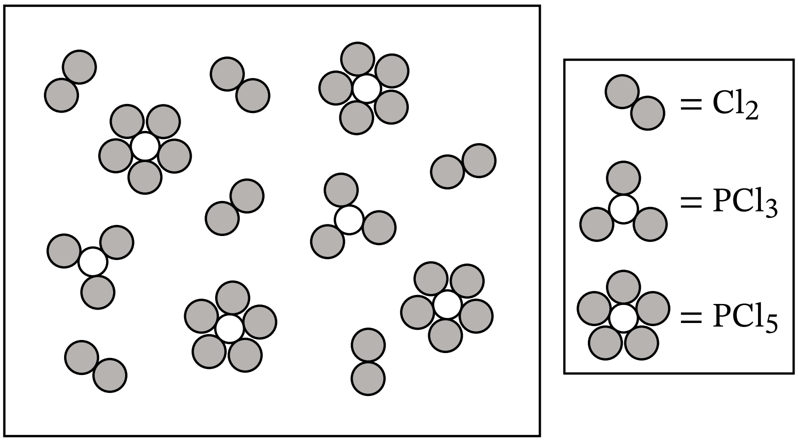
$$\text{Equation 3: } P_4(s) + 6\ Cl_2(g) \rightarrow 4\ PCl_3(g) \qquad \Delta H_1^\circ = -\ 1148\ \text{kJ/mol}_{rxn}$$

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

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°.

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

. 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

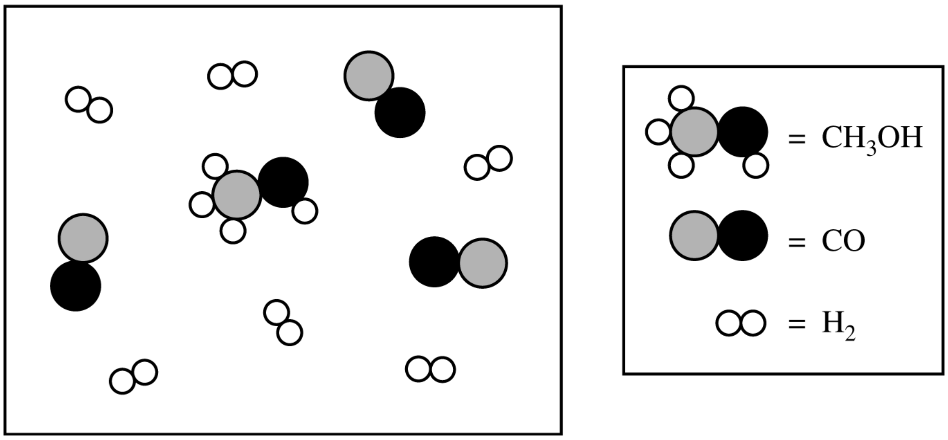
(i) Use the data in the table to calculate the value of the standard entropy change, $\Delta S°$, in J/(K·mol$_{rxn}$), for the reaction.

GO ON TO THE NEXT PAGE.

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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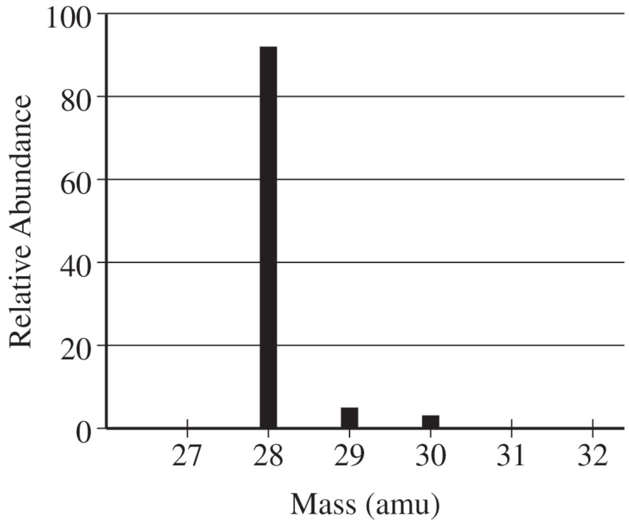
2. Answer the following questions about the element Si and some of its compounds.

(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.

GO ON TO THE NEXT PAGE.

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))
$H_2(g)$	131
$Si(s)$	18
$SiH_4(g)$	205

(d) Explain why the absolute molar entropy of $Si(s)$ is less than that of $H_2(g)$.

(e) Calculate the value, in J/(mol· K), of $\Delta S°$ 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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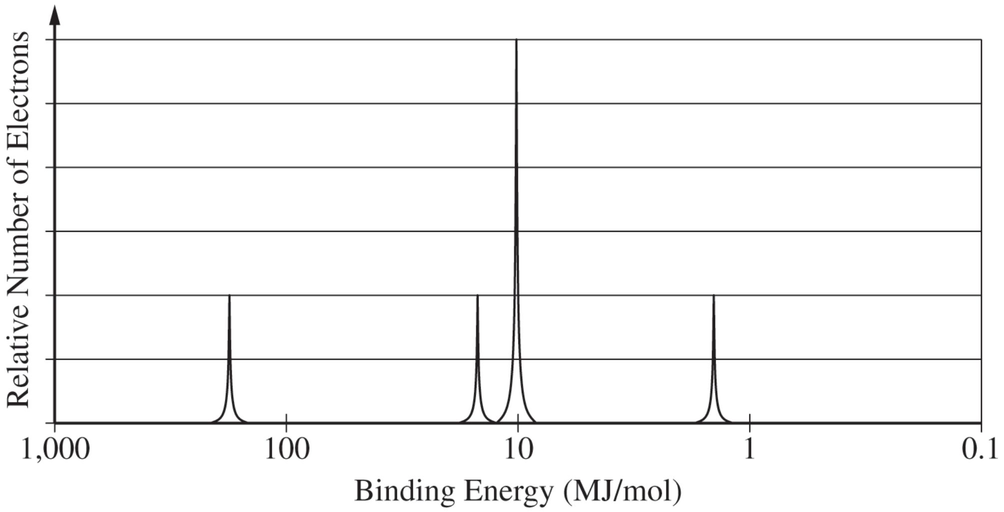
(g) A partial photoelectron spectrum of pure Si is shown below. On the spectrum, draw the missing peak that corresponds to the electrons in the $3p$ sublevel.



(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 4.00×10^{-7} m is absorbed by the Si sample. Calculate the energy of the photon in joules.

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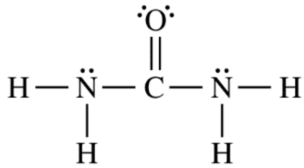
CHEMISTRY
Section II
Time—1 hour and 45 minutes
7 Questions

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.

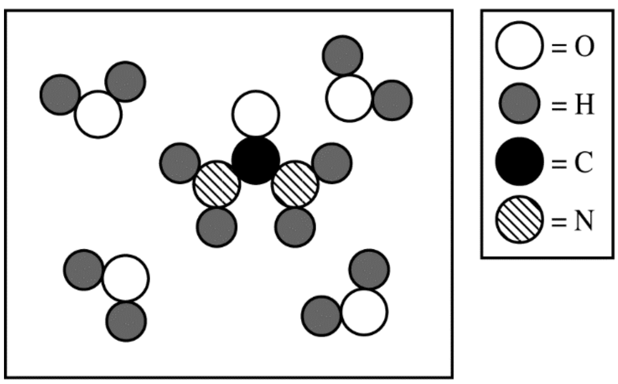
Write your response in the space provided following each question. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer.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

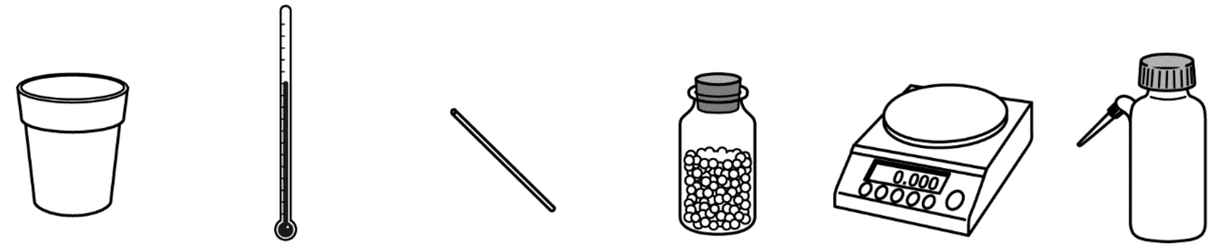


$$H_2NCONH_2(s) \rightleftarrows H_2NCONH_2(aq)$$

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.

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.

$$\mathrm{H{-}C{\equiv}N{-}\underset{..}{\ddot{O}}}\!: \qquad\qquad \mathrm{H{-}\ddot{C}{=}N{=}\ddot{O}}\!:$$

(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.

$$HCNO(g) \rightleftarrows HNCO(g)$$

fulminic acid *isocyanic acid*

Fulminic Acid	Isocyanic Acid
$\mathrm{H{-}C{\equiv}N{-}\underset{..}{\ddot{O}}}\!:$	$\mathrm{H{-}\ddot{N}{=}C{=}\ddot{O}}\!:$

(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 $\Delta H°$ 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 $\Delta S°$ for the reaction is close to zero. Explain why the student's claim is accurate.

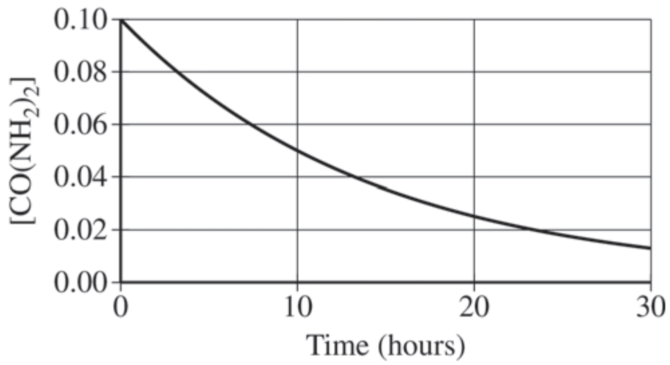
(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

The ammonium salt of isocyanic acid is a product of the decomposition of urea, $CO(NH_2)_2$, represented below.

$$CO(NH_2)_2(aq) \rightleftarrows NH_4^+(aq) + OCN^-(aq)$$

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)	$[CO(NH_2)_2]$
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 $rate = k[CO(NH_2)_2]$.

(i) Explain how the data support the student's proposed rate law.

(ii) 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 $OH^-(aq)$.

9.3 Gibbs Free Energy and Thermodynamic Favorability

Name: ________ Class: ________ Date: ________ **Total: 11 marks**

KEY WORDS thermodynamically favorable 热力学有利 • gibbs free energy 吉布斯自由能

Objective

Build the skills to answer exam questions on **Gibbs free energy** and thermodynamic favorability.

You must be able to:

- use $\Delta G = \Delta H - T\Delta S$
- interpret the sign of ΔG (favorable if < 0)
- find the temperature where a reaction becomes favorable

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The Gibbs equation

$$\Delta G = \Delta H - T\Delta S,$$

with T in **kelvin**. A reaction is **thermodynamically favorable** (spontaneous) when $\Delta G < 0$.

■ The four cases

- $\Delta H < 0$, $\Delta S > 0$: **always** favorable ($\Delta G < 0$ at all T).
- $\Delta H > 0$, $\Delta S < 0$: **never** favorable.
- $\Delta H < 0$, $\Delta S < 0$: favorable at **low** T.
- $\Delta H > 0$, $\Delta S > 0$: favorable at **high** T.

■ A worked ΔG

$\Delta H = -100$ kJ, $\Delta S = +50$ J/K $= 0.050$ kJ/K, $T = 300$ K:

$$\Delta G = -100 - 300(0.050) = -100 - 15 = -115 \text{ kJ (favorable).}$$

■ **Crossover temperature**

The reaction switches at $\Delta G = 0$: $T = \dfrac{\Delta H}{\Delta S}$. Watch **units** — convert ΔS to kJ/K to match ΔH.

2 Practice

Now apply the methods above.

2.1 Write the Gibbs free energy equation. [1]

2.2 A reaction has $\Delta G = -40$ kJ. Is it favorable? [1]

2.3 For $\Delta H = -50$ kJ, $\Delta S = +0.100$ kJ/K, $T = 300$ K, find ΔG. [2]

3 Exam-style questions

3.1 A reaction is thermodynamically favorable when ΔG is [1]

- **A** positive
- **B** negative
- **C** zero
- **D** equal to ΔH

3.2 A reaction has $\Delta H = +30$ kJ and $\Delta S = +0.10$ kJ/K.

(a) Is it favorable at low or high temperature? [1]

(b) Find the temperature at which $\Delta G = 0$. [3]

3.3 A reaction has $\Delta H < 0$ and $\Delta S < 0$. Explain at what temperatures it is favorable and why. [2]

Solutions

2.1 $\Delta G = \Delta H - T\Delta S$.

2.2 Yes ($\Delta G < 0$).

2.3 $\Delta G = -50 - 300(0.100) = -50 - 30 = -80$ kJ.

3.1 **B** — negative.

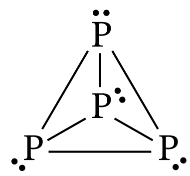
3.2 (a) High temperature (both positive). (b) $T = \dfrac{\Delta H}{\Delta S} = \dfrac{30}{0.10} = 300$ K.

3.3 Favorable at **low** temperature — with $\Delta S < 0$, the $-T\Delta S$ term is positive and grows with T; only at low T is it small enough for the negative ΔH to dominate and keep $\Delta G < 0$.

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

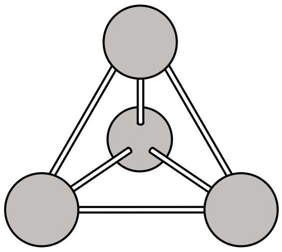
A sample of $P_4(s)$ is placed in a sealed rigid container and heated to 1600. K, at which point the initial partial pressure of $P_4(g)$ is 0.470 atm. Some of the $P_4(g)$ decomposes into $P_2(g)$ as the system reaches equilibrium. At equilibrium, the partial pressure of $P_2(g)$ is determined to be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

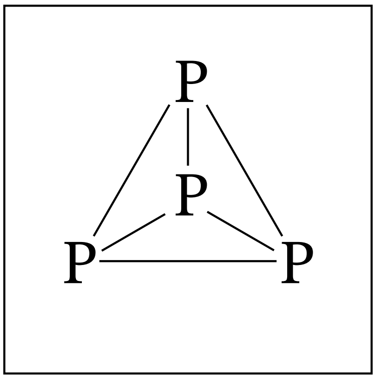
Calculate the value of the equilibrium constant, K_p, for the reaction at 1600. K. Show the work that leads to your answer.

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.

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

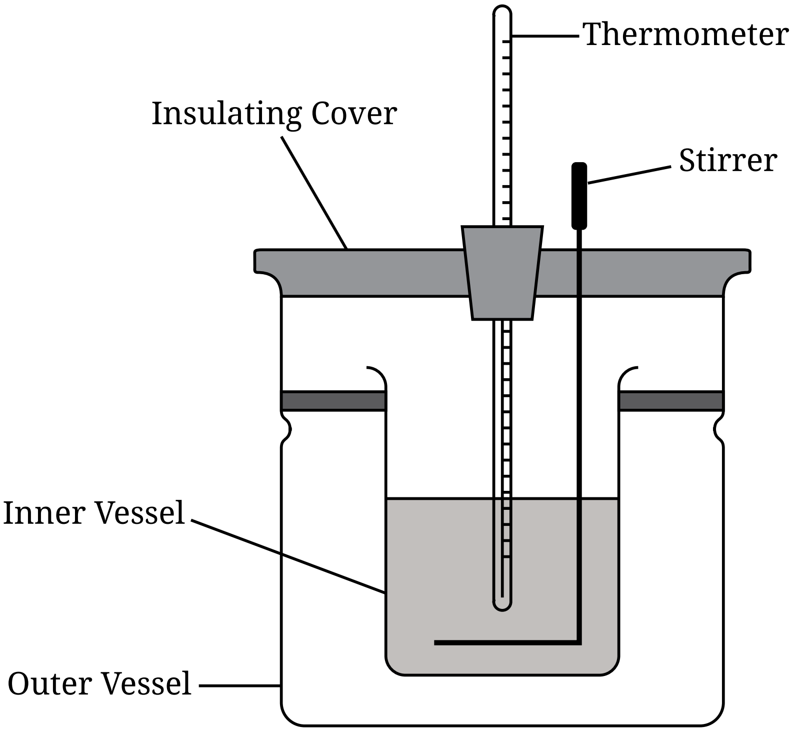
i. The entropy change of the reaction, ΔS°, is negative. Using particle-level reasoning, explain why the entropy decreases as the reaction progresses.

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.

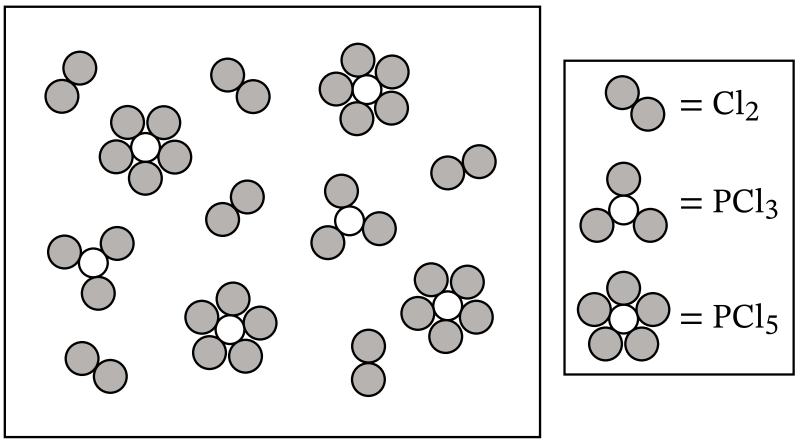
$$\text{Equation 3: } P_4(s) + 6\ Cl_2(g) \rightarrow 4\ PCl_3(g) \qquad \Delta H_1^\circ = -\ 1148\ \text{kJ/mol}_{rxn}$$

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

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.

GO ON TO THE NEXT PAGE.

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.

GO ON TO THE NEXT PAGE.

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 ıvolved 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.

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

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.

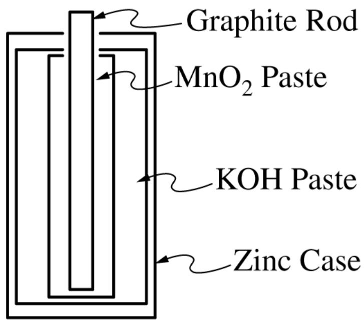
(d) The student determines that 0.0199 mol of Mn was used in the experiment. Use the data to determine the empirical formula of the $Mn_xCl_y(s)$.

(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.

GO ON TO THE NEXT PAGE.

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.

GO ON TO THE NEXT PAGE.

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

. 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

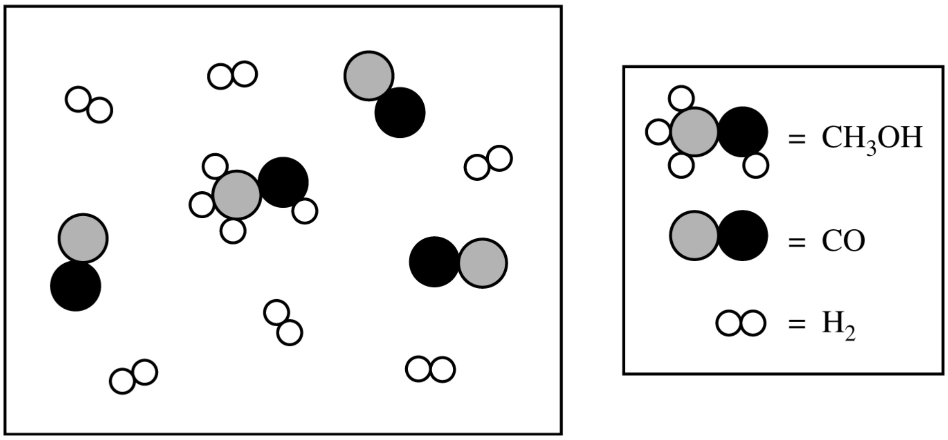
(i) Use the data in the table to calculate the value of the standard entropy change, $\Delta S°$, in J/(K·mol$_{rxn}$), for the reaction.

GO ON TO THE NEXT PAGE.

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.

GO ON TO THE NEXT PAGE.

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

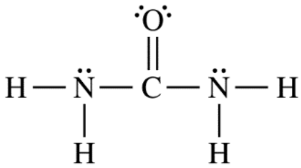
Time—1 hour and 45 minutes

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.

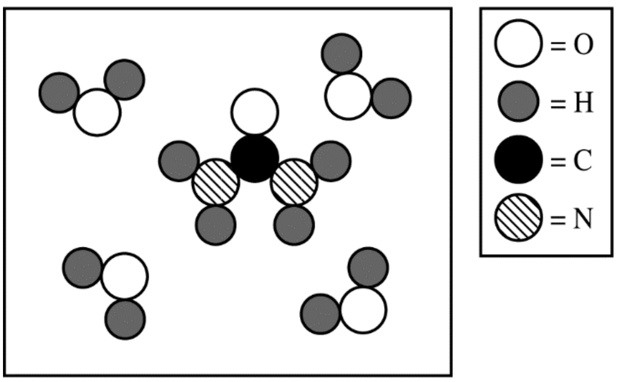
Write your response in the space provided following each question. Examples and equations may be included in your responses where appropriate. For calculations, clearly show the method used and the steps involved in arriving at your answers. You must show your work to receive credit for your answer.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

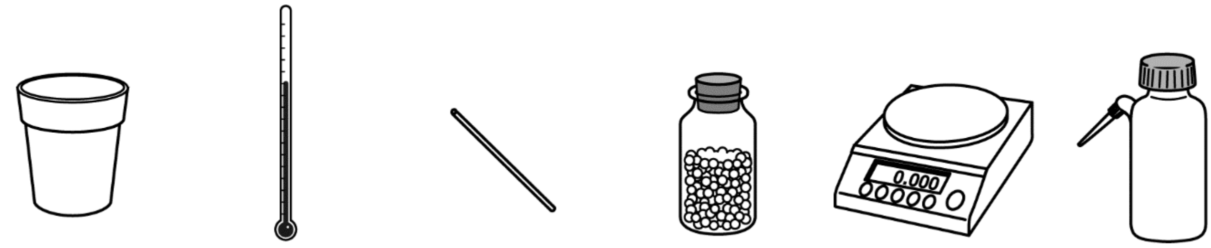


$$H_2NCONH_2(s) \rightleftarrows H_2NCONH_2(aq)$$

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.



Polystyrene Cup | Thermometer | Stirring Rod | Bottle of Urea | Balance | Distilled Water

(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.

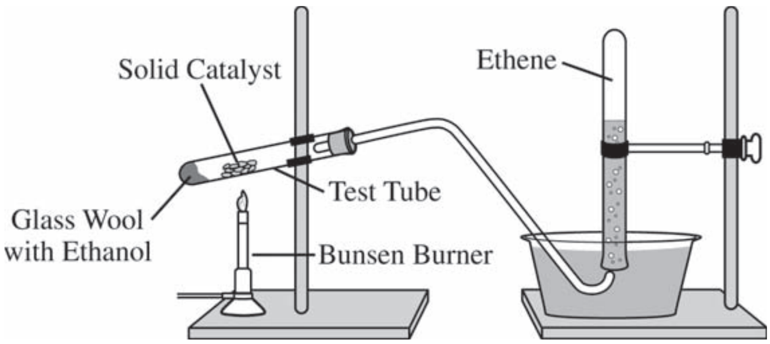
(i) Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between $NaHCO_3(s)$ and $HC_2H_3O_2(aq)$? Answer by drawing a circle around one of the choices below.

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

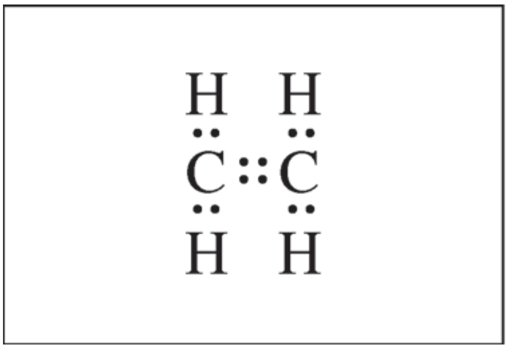
(ii) that would be produced if the dehydration reaction went to completion.

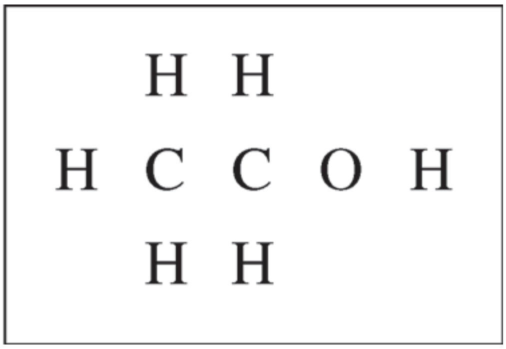
(b) Calculate the percent yield of $C_2H_4(g)$ in the experiment.

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.

9.4 Thermodynamic and Kinetic Control

Name: ______________ Class: __________ Date: ____________ **Total: 9 marks**

KEY WORDS thermodynamically favorable 热力学有利 • entropy 熵

Objective

Build the skills to answer exam questions on **thermodynamic vs kinetic control**.

You must be able to:

- distinguish **thermodynamic favorability** ($\Delta G < 0$) from **kinetic** speed
- explain why a favorable reaction can still be slow
- link a slow favorable reaction to a high **activation energy**

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

Two separate questions

- **Thermodynamics** (ΔG) asks: *will* it happen (is it favorable)?
- **Kinetics** (E_a) asks: *how fast* will it happen?

A reaction can be favorable ($\Delta G < 0$) but extremely **slow**.

A worked example

Diamond → graphite has $\Delta G < 0$ (favorable), yet diamonds do not visibly change — the activation energy is enormous, so the rate is effectively zero.

Why favorable can be slow

A large **activation-energy barrier** blocks the reaction even when the products are lower in free energy. A catalyst can speed it up without changing ΔG.

The takeaway

"Favorable" (spontaneous) does **not** mean "fast". Both a negative ΔG and a surmountable E_a are needed for a reaction to proceed noticeably.

2 Practice

Now apply the methods above.

2.1 What does a negative ΔG tell you? [1]

2.2 What controls how fast a reaction goes? [1]

2.3 Can a favorable reaction be slow? [1]

3 Exam-style questions

3.1 A reaction with $\Delta G < 0$ that proceeds very slowly is limited by [1]

- **A** thermodynamics
- **B** a high activation energy (kinetics)
- **C** a negative ΔH
- **D** a positive entropy

3.2 The conversion of diamond to graphite has $\Delta G < 0$ but is not observed.

(a) State whether it is thermodynamically favorable. [1]

(b) Explain why it does not happen at a noticeable rate. [2]

3.3 Explain how a catalyst can make a favorable-but-slow reaction proceed, and what it does **not** change. [2]

Solutions

2.1 The reaction is thermodynamically favorable (spontaneous).

2.2 The activation energy (kinetics).

2.3 Yes.

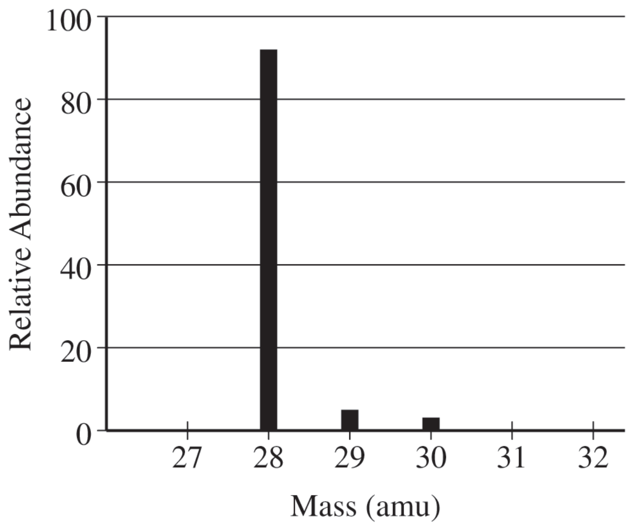
3.1 **B** — a high activation energy (kinetics).

3.2 (a) Yes ($\Delta G < 0$). (b) The activation energy is extremely high, so almost no molecules can cross the barrier and the rate is effectively zero.

3.3 A catalyst lowers the activation energy, providing a faster pathway; it does **not** change ΔG (the favorability).

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.

GO ON TO THE NEXT PAGE.

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))
$H_2(g)$	131
$Si(s)$	18
$SiH_4(g)$	205

(d) Explain why the absolute molar entropy of $Si(s)$ is less than that of $H_2(g)$.

(e) Calculate the value, in J/(mol· K), of $\Delta S°$ 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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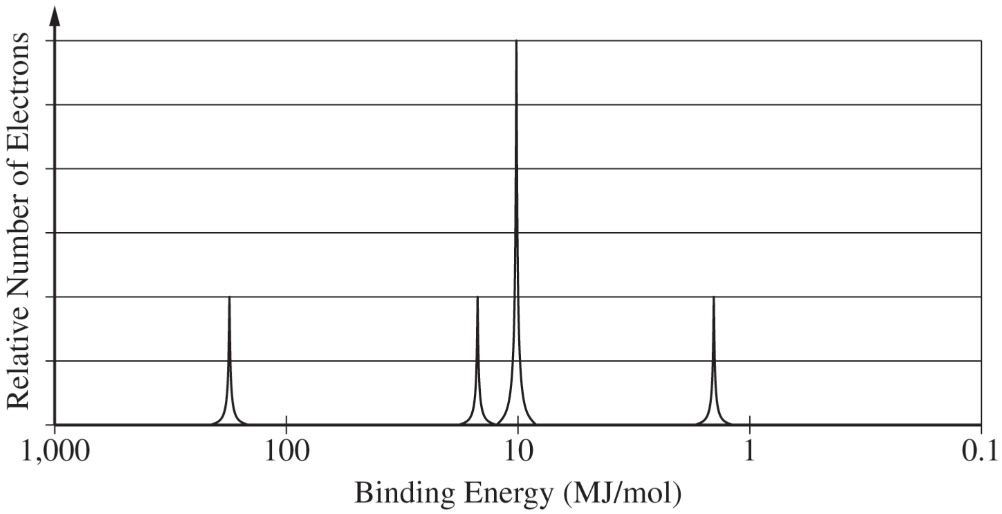
(g) A partial photoelectron spectrum of pure Si is shown below. On the spectrum, draw the missing peak that corresponds to the electrons in the $3p$ sublevel.



(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 4.00×10^{-7} m is absorbed by the Si sample. Calculate the energy of the photon in joules.

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9.5 Free Energy and Equilibrium

Name: ____________ Class: ________ Date: __________ **Total: 10 marks**

Objective

Build the skills to answer exam questions on **free energy and equilibrium**.

You must be able to:

- use $\Delta G^\circ = -RT \ln K$
- relate the sign of ΔG° to whether $K > 1$ or $K < 1$
- reason about the connection

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The link

$$\Delta G^\circ = -RT \ln K,$$

with $R = 8.314$ J mol^{-1}K^{-1} and T in kelvin. Free energy and the equilibrium constant carry the same information.

■ Sign and K

- $\Delta G^\circ < 0 \Rightarrow K > 1$ (products favored);
- $\Delta G^\circ > 0 \Rightarrow K < 1$ (reactants favored);
- $\Delta G^\circ = 0 \Rightarrow K = 1$.

■ A worked value

If $K = 100$ at 298 K: $\Delta G^\circ = -(8.314)(298)\ln(100) = -(8.314)(298)(4.605) = -11\,400$ J $= -11.4$ kJ.

■ Reading the connection

A large positive ΔG° means a very small K (little product). The more negative ΔG°, the larger K and the further the equilibrium lies toward products.

2 Practice

Now apply the methods above.

2.1 Write the equation linking ΔG° and K. [1]

2.2 If $\Delta G^\circ < 0$, is K greater or less than 1? [1]

2.3 If $\Delta G^\circ = 0$, what is K? [1]

3 Exam-style questions

3.1 A reaction with $K < 1$ has ΔG° that is [1]

- **A** negative
- **B** positive
- **C** zero
- **D** equal to K

3.2 A reaction has $K = 1 \times 10^{-3}$ at 298 K.

(a) State the sign of ΔG°. [1]

(b) Calculate ΔG° (use $R = 8.314$, $\ln(10^{-3}) = -6.9$). [3]

3.3 Explain why a more negative ΔG° corresponds to a larger equilibrium constant. [2]

Solutions

2.1 $\Delta G^\circ = -RT \ln K$.

2.2 Greater than 1.

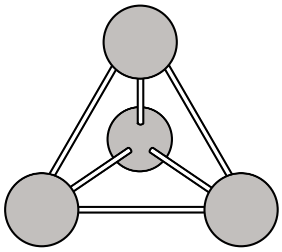
2.3 $K = 1$.

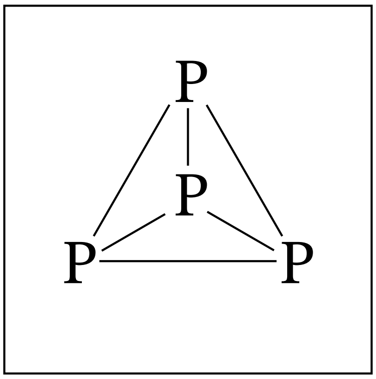
3.1 **B** — positive.

3.2 (a) Positive. (b) $\Delta G^\circ = -(8.314)(298)(-6.9) = +17\,100$ J $\approx +17$ kJ.

3.3 $\Delta G^\circ = -RT \ln K$: a more negative ΔG° requires a larger $\ln K$, hence a larger K — the equilibrium lies further toward products.

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.

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

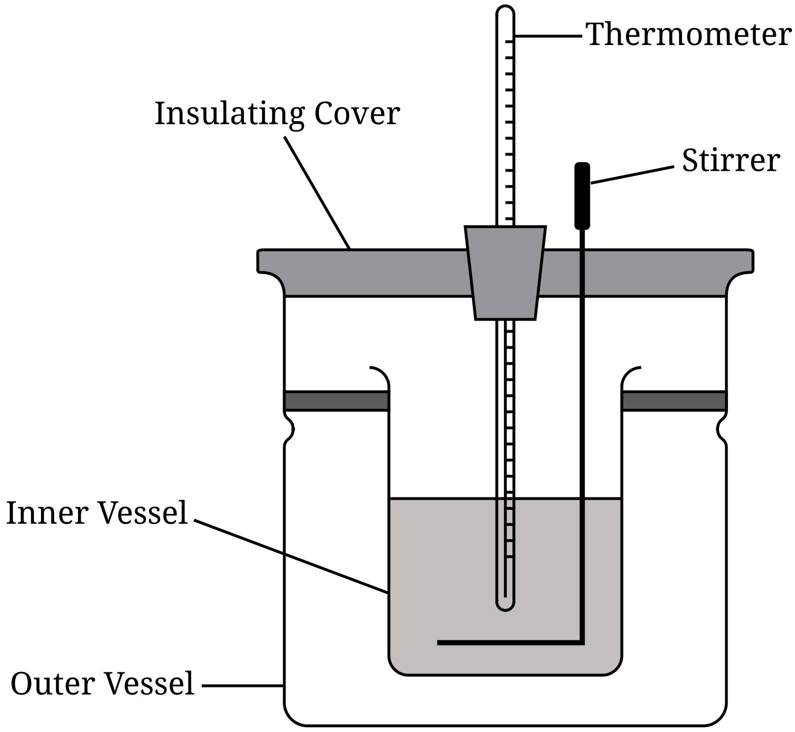
i. The entropy change of the reaction, $\Delta S°$, is negative. Using particle-level reasoning, explain why the entropy decreases as the reaction progresses.

ii. The enthalpy change of the reaction, $\Delta H°$, 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 $\Delta G°$, $\Delta H°$, and $\Delta S°$.

$P_4O_{10}(s)$ 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.

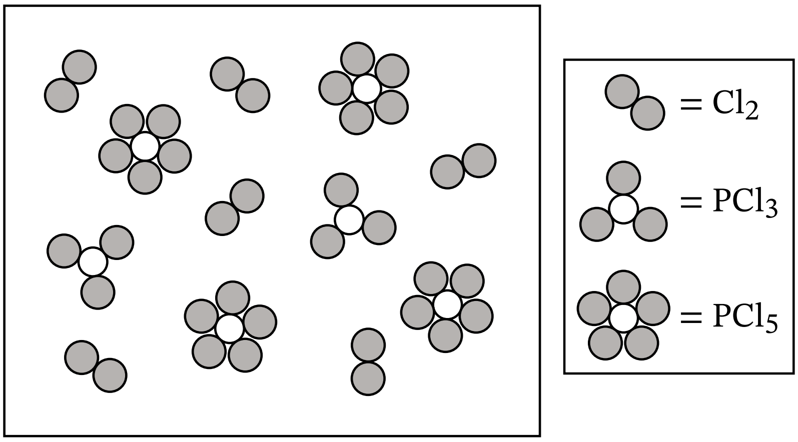
$$\text{Equation 3: } P_4(s) + 6\ Cl_2(g) \rightarrow 4\ PCl_3(g) \qquad \Delta H_1^\circ = -\ 1148\ \text{kJ/mol}_{rxn}$$

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

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°.

3. Answer the following questions relating to the element aluminum, Al.

(a) Write the complete ground-state electron configuration of an Al atom.

(b) Based on principles of atomic structure, explain why the radius of the Al atom is larger than the radius of the Al^{3+} ion.

A student plans to combine solid aluminum with an aqueous solution of silver ions. The student determines the mass of solid $AgNO_3$ needed to prepare the solution with a specific concentration.

(c) In the following table, briefly list the steps necessary to prepare 200.0 mL of an aqueous solution of $AgNO_3$ using only equipment selected from the choices given. Assume that all appropriate safety measures are already in place. Not all equipment or lines in the table may be needed.

- Solid $AgNO_3$
- Distilled water
- Balance
- Weighing paper and scoop
- 200.00 mL volumetric flask
- 50.0 mL graduated cylinder
- 250 mL beakers
- Pipet

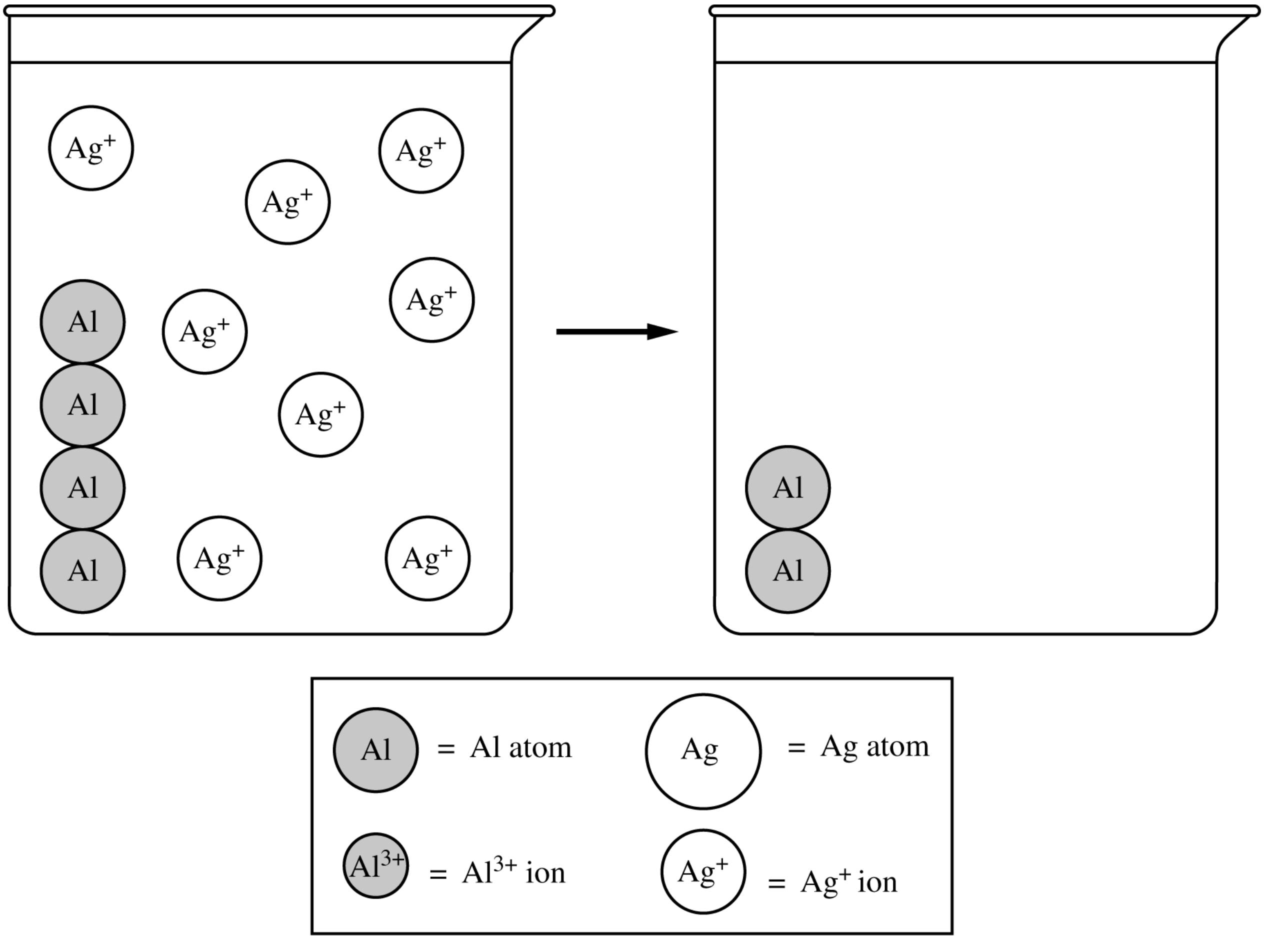
Step	Step Description
1.	Use weighing paper to measure the determined mass of solid $AgNO_3$ on a balance.
2.	

GO ON TO THE NEXT PAGE.

After preparing the solution, the student places some of the solution into a beaker and adds a sample of aluminum. The reaction represented by the following equation occurs.

$$Al(s) + 3\ Ag^{+}(aq) \rightarrow Al^{3+}(aq) + 3\ Ag(s)$$

(d) The following diagram gives an incomplete particulate representation of the reaction. The beaker on the left represents the system before the mixture reacts. Complete the drawing on the right to represent the system after the reaction has occurred. Be sure to include 1) the correct type and number of particles based on the number shown on the left and 2) the relative spacing to depict the appropriate phases.



The student finds the standard reduction potentials given in the table, which are related to the reaction that occurs.

Half-Reaction	$E°$
$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$	0.80 V
$Al^{3+}(aq) + 3\,e^{-} \rightarrow Al(s)$	−1.66 V

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

(e) Using the standard reduction potentials, calculate the value of $E°$ for the reaction.

(f) Based on the value of $E°$, would the standard free energy change of the reaction under standard conditions, $\Delta G°$, be positive, negative, or zero? Justify your answer.

(g) Once the reaction appears to stop progressing, would the change in free energy, ΔG, be positive, negative, or zero? Justify your answer.

GO ON TO THE NEXT PAGE.

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.

$$\mathrm{H-C\equiv N-\ddot{\underset{..}{O}}:} \qquad\qquad \mathrm{H-\ddot{C}=N=\ddot{O}:}$$

(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.

$$\mathrm{HCNO}(g) \rightleftarrows \mathrm{HNCO}(g)$$

fulminic acid *isocyanic acid*

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

(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 $\Delta H°$ for the reaction of $\mathrm{HCNO}(g)$ to form $\mathrm{HNCO}(g)$.

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 $\Delta S°$ for the reaction is close to zero. Explain why the student's claim is accurate.

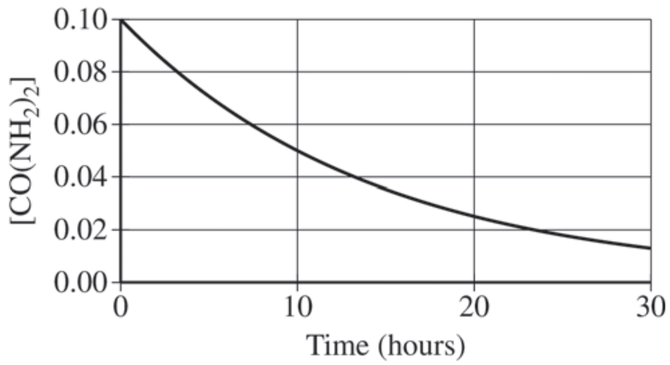
(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K? Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

The ammonium salt of isocyanic acid is a product of the decomposition of urea, $\mathrm{CO(NH_2)_2}$, represented below.

$$\mathrm{CO(NH_2)_2}(aq) \rightleftarrows \mathrm{NH_4^+}(aq) + \mathrm{OCN^-}(aq)$$

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)	$[CO(NH_2)_2]$
0	0.1000
5	0.0707
10	0.0500
15	0.0354
20	0.0250
25	0.0177
30	0.0125

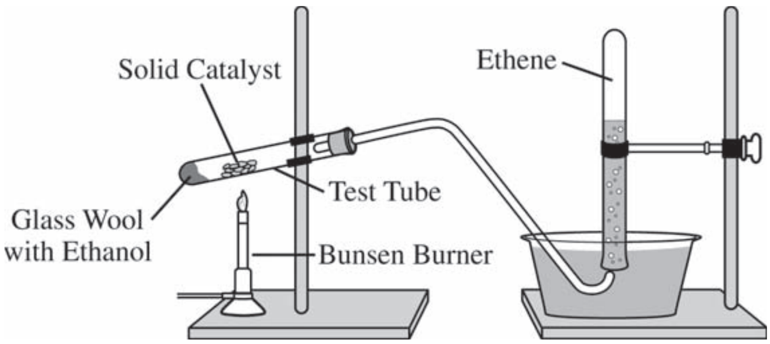


(e) The student proposes that the rate law is $rate = k[CO(NH_2)_2]$.

(i) Explain how the data support the student's proposed rate law.

(ii) 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 $OH^-(aq)$.



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

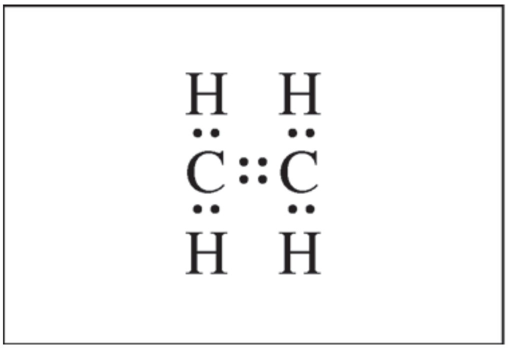
(ii) that would be produced if the dehydration reaction went to completion.

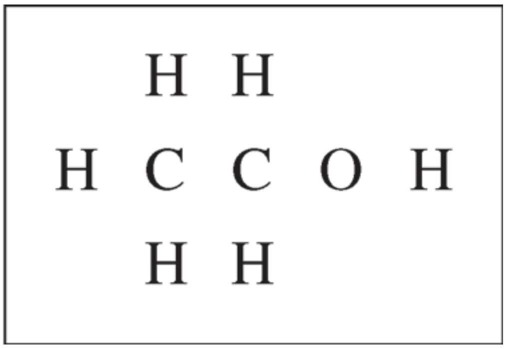
(b) Calculate the percent yield of $C_2H_4(g)$ in the experiment.

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.

AP CHEMISTRY • EXERCISE SHEET

9.6 Free Energy of Dissolution

Name: ______________ Class: __________ Date: ____________ **Total: 12 marks**

KEY WORDS entropy 熵

Objective

Build the skills to answer exam questions on the **free energy of dissolution**.

You must be able to:

- split dissolution into ΔH_{soln} and ΔS_{soln}
- use $\Delta G = \Delta H - T\Delta S$ to judge whether a salt dissolves
- reason about temperature dependence

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Dissolution has an enthalpy and entropy part

Dissolving a salt has ΔH_{soln} (may be + or −) and usually $\Delta S_{\text{soln}} > 0$ (ions spread out into solution — more disorder).

■ Judging with ΔG

The salt dissolves spontaneously when $\Delta G_{\text{soln}} = \Delta H_{\text{soln}} - T\Delta S_{\text{soln}} < 0$. Because ΔS is usually positive, higher T makes $-T\Delta S$ more negative — favoring dissolution.

■ A worked case

$\Delta H_{\text{soln}} = +25$ kJ (endothermic), $\Delta S_{\text{soln}} = +0.10$ kJ/K: at 300 K, $\Delta G = 25 - 300(0.10) = 25 - 30 = -5$ kJ — dissolves.

■ Why some salts dissolve more when heated

Many salts have endothermic dissolution but positive ΔS; heating makes ΔG more negative, so they dissolve **more** at higher temperature.

2 Practice

Now apply the methods above.

2.1 What is usually the sign of ΔS_{soln} for a dissolving salt? [1]

2.2 A salt dissolves when ΔG_{soln} is what sign? [1]

2.3 For $\Delta H = +20$ kJ, $\Delta S = +0.10$ kJ/K, $T = 300$ K, find ΔG_{soln}. [2]

3 Exam-style questions

3.1 An endothermic dissolution with positive ΔS becomes favorable at [1]

- **A** low temperature
- **B** high temperature
- **C** all temperatures
- **D** no temperature

3.2 A salt has $\Delta H_{\text{soln}} = +15$ kJ and $\Delta S_{\text{soln}} = +0.060$ kJ/K.

(a) Find ΔG_{soln} at 250 K and state if it dissolves. [3]

(b) Find the temperature at which $\Delta G_{\text{soln}} = 0$. [2]

3.3 Explain why many salts dissolve more readily in hot water than cold water. [2]

Solutions

2.1 Positive.

2.2 Negative.

2.3 $\Delta G = 20 - 300(0.10) = 20 - 30 = -10$ kJ.

3.1 **B** — high temperature.

3.2 (a) $\Delta G = 15 - 250(0.060) = 15 - 15 = 0$ kJ — at the borderline (just favorable above this T). (b) $T = \dfrac{15}{0.060} = 250$ K.

3.3 Their dissolution is endothermic but has positive ΔS; raising T makes $-T\Delta S$ more negative, so ΔG becomes negative and more salt dissolves.

9.7 Coupled Reactions

Name: ______________ Class: __________ Date: ____________ **Total: 9 marks**

Objective

Build the skills to answer exam questions on **coupled reactions**.

You must be able to:

- add a favorable reaction to an unfavorable one to drive it
- add the ΔG values
- decide whether the coupled reaction is favorable overall

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Coupling reactions

An **unfavorable** reaction ($\Delta G > 0$) can be driven by **coupling** it to a **favorable** one ($\Delta G < 0$) that shares a species, if the total ΔG is negative.

■ Adding the ΔG values

Like Hess's law, when reactions are added their ΔG values add:

$$\Delta G_{\text{total}} = \Delta G_1 + \Delta G_2.$$

■ A worked coupling

Reaction 1: $\Delta G = +30$ kJ (unfavorable). Reaction 2: $\Delta G = -50$ kJ (favorable). Coupled: $\Delta G = +30 + (-50) = -20$ kJ — now favorable.

■ Biological example

Cells couple the very favorable hydrolysis of ATP ($\Delta G \ll 0$) to otherwise-unfavorable reactions to make them go — the basis of metabolism.

2 Practice

Now apply the methods above.

2.1 When two reactions are added, how do their ΔG values combine? [1]

2.2 Reaction A (+20 kJ) is coupled to B (−35 kJ). Find the total ΔG. [1]

2.3 Is the coupled reaction in 2.2 favorable? [1]

3 Exam-style questions

3.1 An unfavorable reaction can be driven by coupling it to a reaction with [1]

- **A** a larger positive ΔG
- **B** a sufficiently negative ΔG
- **C** zero ΔG
- **D** a higher activation energy

3.2 Reaction 1 ($\Delta G = +25$ kJ) is coupled with reaction 2 ($\Delta G = -40$ kJ).

(a) Find the total ΔG. [2]

(b) State whether the coupled process is favorable. [1]

3.3 Explain how cells use ATP hydrolysis to drive unfavorable reactions. [2]

Solutions

2.1 They add.

2.2 $20 + (-35) = -15$ kJ.

2.3 Yes ($\Delta G < 0$).

3.1 **B** — a sufficiently negative ΔG to make the sum negative.

3.2 (a) $25 + (-40) = -15$ kJ. (b) Favorable ($\Delta G < 0$).

3.3 ATP hydrolysis is strongly favorable ($\Delta G \ll 0$); coupling it to an unfavorable reaction makes the combined ΔG negative, so the overall process proceeds.

9.8 Galvanic and Electrolytic Cells

Name: ______________ Class: _________ Date: ____________ **Total: 9 marks**

KEY WORDS anode 阳极 • cathode 阴极 • electrolytic 电解池 • galvanic (voltaic) 原电池

Objective

Build the skills to answer exam questions on **galvanic and electrolytic cells**.

You must be able to:

- distinguish a **galvanic (voltaic) 原电池** cell from an **electrolytic 电解池** cell
- identify the **anode** (oxidation) and **cathode** (reduction)
- state the direction of electron flow

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Two kinds of cell

- **Galvanic (voltaic)** cell — a **favorable** redox reaction produces electricity ($\Delta G < 0$, $E_{\text{cell}} > 0$).
- **Electrolytic** cell — electricity **drives** an unfavorable reaction ($\Delta G > 0$, needs an external power source).

■ Anode and cathode

In **both** cells: **oxidation** happens at the **anode**; **reduction** at the **cathode** (remember "an ox, red cat"). Electrons flow from anode to cathode through the wire.

■ A worked galvanic cell

$Zn|Zn^{2+}\,||\,Cu^{2+}|Cu$: Zn is oxidized (anode), Cu^{2+} is reduced (cathode); electrons flow $Zn \rightarrow Cu$.

■ The salt bridge

A **salt bridge** keeps each half-cell electrically neutral by letting ions move, completing the circuit.

2 Practice

Now apply the methods above.

2.1 At which electrode does oxidation occur? [1]

2.2 Which cell produces electricity from a favorable reaction? [1]

2.3 In which direction do electrons flow in a galvanic cell? [1]

3 Exam-style questions

3.1 In any electrochemical cell, reduction occurs at the [1]

- **A** anode
- **B** cathode
- **C** salt bridge
- **D** wire

3.2 A galvanic cell uses $Zn|Zn^{2+}\,||\,Cu^{2+}|Cu$.

(a) Identify the anode and cathode. [2]

(b) State the direction of electron flow. [1]

3.3 Explain the difference between a galvanic and an electrolytic cell in terms of ΔG and energy. [2]

Solutions

2.1 The anode.

2.2 A galvanic (voltaic) cell.

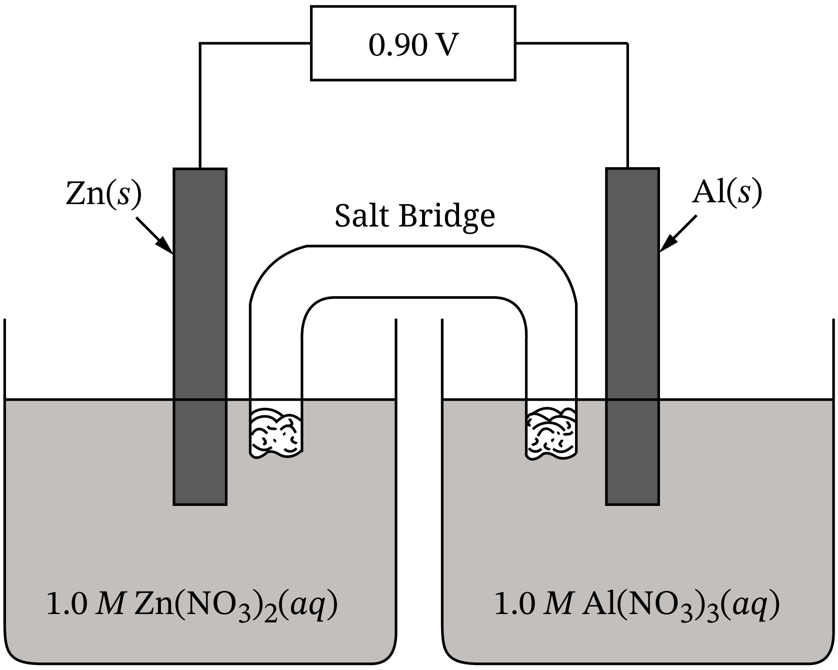
2.3 From the anode to the cathode.

3.1 **B** — the cathode.

3.2 (a) Anode: Zn (oxidized); cathode: Cu (where Cu^{2+} is reduced). (b) From the Zn electrode to the Cu electrode.

3.3 A galvanic cell runs a favorable reaction ($\Delta G < 0$) and **releases** electrical energy; an electrolytic cell uses an external power source to drive an unfavorable reaction ($\Delta G > 0$).

6. A scientist constructs a galvanic cell as shown in the diagram. As the cell operates, the $Zn(s)$ electrode increases in mass and the $Al(s)$ electrode decreases in mass. A data table with the standard reduction potentials for the substances follows the diagram.



Half-Reaction	E° (V)
$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$	-0.76
$Al^{3+}(aq) + 3\,e^- \rightarrow Al(s)$	-1.66

A. Write the half-reaction for the oxidation that occurs at the anode.

B. Write the balanced net ionic equation for the overall reaction that occurs in the galvanic cell.

C. Initially, each electrode has a mass of 50.0 g. The cell is allowed to run for a period of time and is then stopped. Which electrode's mass changed the most? Justify your answer with a calculation.

Reduction Half-Reaction	E° (V)
$Au^{3+}(aq) + 3\,e^- \rightarrow Au(s)$	$+1.50$
$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$	-0.76
$Mn^{2+}(aq) + 2\,e^- \rightarrow Mn(s)$	-1.19
$Al^{3+}(aq) + 3\,e^- \rightarrow Al(s)$	-1.66
$Be^{2+}(aq) + 2\,e^- \rightarrow Be(s)$	-1.85

D. The standard Zn/Al cell has a value of E°_{cell} equal to 0.90 V. The scientist needs a galvanic cell that produces a greater voltage. The scientist has access to the chemical systems in the table. If the scientist uses the Zn half-cell and one of the other options from the table, what is the MAXIMUM voltage that could be generated at standard conditions?

Begin your response to **QUESTION 3** on this page.

3. Sterling silver is an alloy that is commonly used to make jewelry and consists of 92.5% silver and 7.5% other metals, such as copper, by mass. Over time, the alloy can form a tarnish of $Ag_2S(s)$ when it reacts with hydrogen sulfide, as represented by the following equation.

$$2\ Ag(s) + H_2S(g) \rightarrow Ag_2S(s) + H_2(g)$$

(a) What are the oxidation numbers of silver in $Ag(s)$ and $Ag_2S(s)$?

$Ag(s)$__________ $Ag_2S(s)$__________

(b) The following table contains the atomic radii for silver and copper.

Element	Silver (Ag)	Copper (Cu)
Atomic radius (pm)	165	145

(i) Explain why sterling silver is better classified as a substitutional alloy than as an interstitial alloy.

(ii) Using principles of atomic structure and Coulomb's law, explain why silver has a larger atomic radius than copper does.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

The Ag_2S tarnish on sterling silver can be removed until only sterling silver remains. A student weighs a tarnished sterling silver sample both before and after removing the $Ag_2S(s)$ (molar mass 247.80 g / mol) and records the data in the following table.

	Before Tarnish Removal	After Tarnish Removal
Mass	409.21 g	398.94 g

(c) Assuming that only $Ag_2S(s)$ is removed, calculate the number of moles of silver atoms removed.

Rhodium plating is a process used to protect sterling silver from tarnishing. This involves electroplating (depositing) solid rhodium, $Rh(s)$, onto the surface of the metal from an acidified solution of $Rh_2(SO_4)_3(aq)$. Oxygen gas is produced during this process.

(d) A table of half-reactions related to the overall reaction is provided.

Half-Reaction	$E°$ (V)
$Rh^{3+}(aq) + 3\ e^- \rightarrow Rh(s)$	+0.80
$O_2(g) + 4\ H^+(aq) + 4\ e^- \rightarrow 2\ H_2O(l)$	+1.23

(i) Write the balanced net ionic equation for plating $Rh(s)$ from the acidified $Rh_2(SO_4)_3(aq)$ solution.

(ii) Calculate the value of E°_{cell} for the reaction in part (d)(i).

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

(iii) Based on your answer to part (d)(ii), explain why this process requires the use of an external power source.

(e) Calculate the length of time, in seconds, required to plate 2.8 g of $Rh(s)$ onto a piece of sterling silver if 2.0 C / s of current is applied.

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CHEMISTRY

SECTION II

Time—1 hour and 45 minutes

7 Questions

ɔirections: 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 ıvolved 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.

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

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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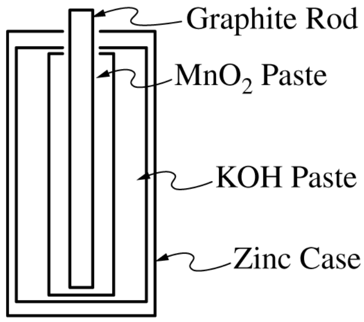
(f) Another compound of manganese, MnO_2, is used in alkaline batteries, represented by the following diagram. Some half-reactions are given in the table.



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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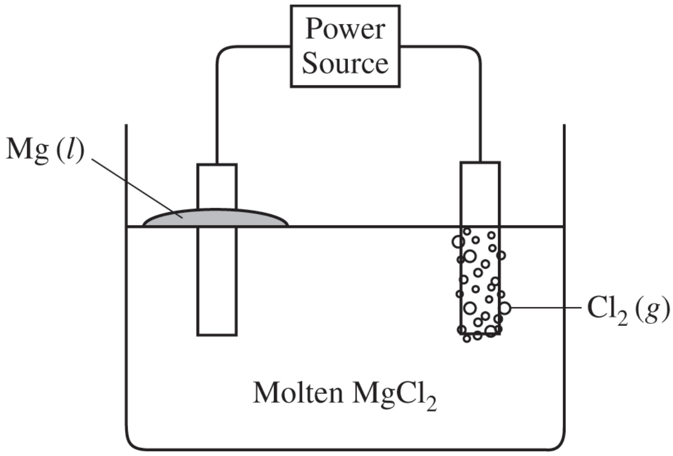
Begin your response to **QUESTION 5** on this page.



Half-Reaction	$E°$ (V)
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+ 1.36

5. Molten $MgCl_2$ can be decomposed into its elements if a sufficient voltage is applied using inert electrodes. The products of the reaction are liquid Mg (at the cathode) and Cl_2 gas (at the anode). A simplified representation of the cell is shown above. The reduction half-reactions related to the overall reaction in the cell are given in the table.

(a) Draw an arrow on the diagram to show the direction of electron flow through the external circuit as the cell operates.

(b) Would an applied voltage of 2.0 V be sufficient for the reaction to occur? Support your claim with a calculation as part of your answer.

(c) If the current in the cell is kept at a constant 5.00 amps, how many seconds does it take to produce 2.00 g of Mg(l) at the cathode?

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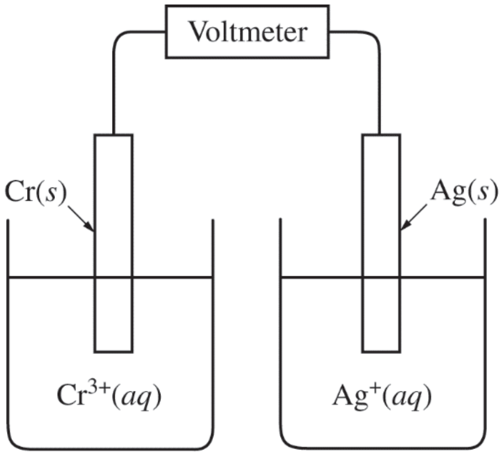


6. A student sets up a galvanic cell at 298 K that has an electrode of Ag(*s*) immersed in a 1.0 *M* solution of $Ag^{+}(aq)$ and an electrode of Cr(*s*) immersed in a 1.0 *M* solution of $Cr^{3+}(aq)$, as shown in the diagram above.

   (a) The student measures the voltage of the cell shown above and discovers that it is zero. Identify the missing component of the cell, and explain its importance for obtaining a nonzero voltage.

Half-Reaction	$E°$ (V)
$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$	+ 0.80
$Cr^{3+}(aq) + 3\,e^{-} \rightarrow Cr(s)$	?

   (b) The student adds the missing component to the cell and measures $E°_{cell}$ to be +1.54 V. As the cell operates, Ag^{+} ions are reduced. Use this information and the information in the table above to do the following.

      (i) Calculate the value of $E°$ for the half-reaction $Cr^{3+}(aq) + 3\,e^{-} \rightarrow Cr(s)$.

      (ii) Write the balanced net-ionic equation for the overall reaction that occurs as the cell operates.

      (iii) Calculate the value of $\Delta G°$ for the overall cell reaction in J/mol_{rxn}.

CHEMISTRY

Section II

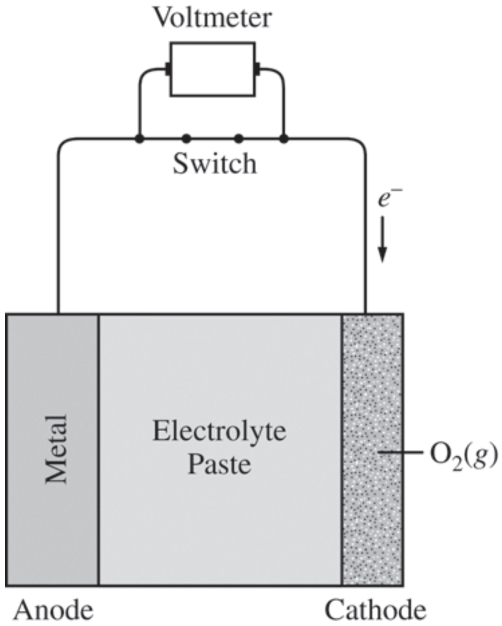
7 Questions

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.



1. Metal-air cells are a relatively new type of portable energy source consisting of a metal anode, an alkaline electrolyte paste that contains water, and a porous cathode membrane that lets in oxygen from the air. A schematic of the cell is shown above. Reduction potentials for the cathode and three possible metal anodes are given in the table below.

Half Reaction	E at pH 11 and 298 K (V)
$O_2(g) + 2\,H_2O(l) + 4\,e^- \rightarrow 4\,OH^-(aq)$	+0.34
$ZnO(s) + H_2O(l) + 2\,e^- \rightarrow Zn(s) + 2\,OH^-(aq)$	−1.31
$Na_2O(s) + H_2O(l) + 2\,e^- \rightarrow 2\,Na(s) + 2\,OH^-(aq)$	−1.60
$CaO(s) + H_2O(l) + 2\,e^- \rightarrow Ca(s) + 2\,OH^-(aq)$	−2.78

(a) Early forms of metal-air cells used zinc as the anode. Zinc oxide is produced as the cell operates according to the overall equation below.

$$2\,Zn(s) + O_2(g) \rightarrow 2\,ZnO(s)$$

(i) Using the data in the table above, calculate the cell potential for the zinc-air cell.

(ii) The electrolyte paste contains OH^- ions. On the diagram of the cell above, draw an arrow to indicate the direction of migration of OH^- ions through the electrolyte as the cell operates.

(b) A fresh zinc-air cell is weighed on an analytical balance before being placed in a hearing aid for use.

(i) As the cell operates, does the mass of the cell increase, decrease, or remain the same?

(ii) Justify your answer to part (b)(i) in terms of the equation for the overall cell reaction.

(c) The zinc-air cell is taken to the top of a mountain where the air pressure is lower.

(i) Will the cell potential be higher, lower, or the same as the cell potential at the lower elevation?

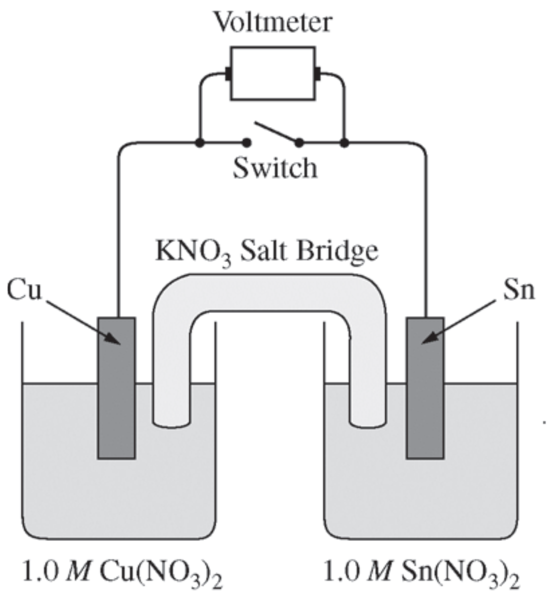
(ii) Justify your answer to part (c)(i) based on the equation for the overall cell reaction and the information above.

(d) Metal-air cells need to be lightweight for many applications. In order to transfer more electrons with a smaller mass, Na and Ca are investigated as potential anodes. A 1.0 g anode of which of these metals would transfer more electrons, assuming that the anode is totally consumed during the lifetime of a cell? Justify your answer with calculations.

(e) The only common oxide of zinc has the formula ZnO.

(i) Write the electron configuration for a Zn atom in the ground state.

(ii) From which sublevel are electrons removed when a Zn atom in the ground state is oxidized?

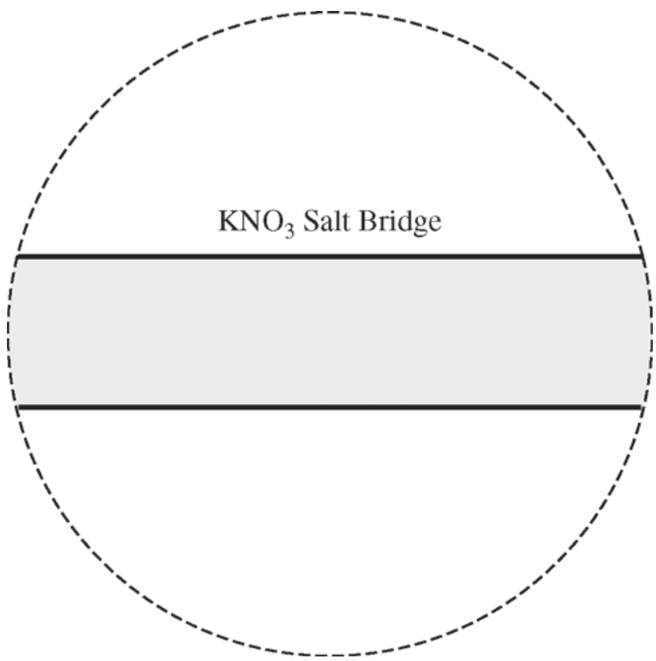


3. A student is given a standard galvanic cell, represented above, that has a Cu electrode and a Sn electrode. As current flows through the cell, the student determines that the Cu electrode increases in mass and the Sn electrode decreases in mass.

   (a) Identify the electrode at which oxidation is occurring. Explain your reasoning based on the student's observations.

   (b) As the mass of the Sn electrode decreases, where does the mass go?

   (c) In the expanded view of the center portion of the salt bridge shown in the diagram below, draw and label a particle view of what occurs in the salt bridge as the cell begins to operate. Omit solvent molecules and use arrows to show the movement of particles.



(d) A nonstandard cell is made by replacing the 1.0 *M* solutions of $Cu(NO_3)_2$ and $Sn(NO_3)_2$ in the standard cell with 0.50 *M* solutions of $Cu(NO_3)_2$ and $Sn(NO_3)_2$. The volumes of solutions in the nonstandard cell are identical to those in the standard cell.

(i) Is the cell potential of the nonstandard cell greater than, less than, or equal to the cell potential of the standard cell? Justify your answer.

(ii) Both the standard and nonstandard cells can be used to power an electronic device. Would the nonstandard cell power the device for the same time, a longer time, or a shorter time as compared with the standard cell? Justify your answer.

(e) In another experiment, the student places a new Sn electrode into a fresh solution of 1.0 *M* $Cu(NO_3)_2$.

Half-Reaction	$E°$ (V)
$Cu^+ + e^- \rightarrow Cu(s)$	0.52
$Cu^{2+} + 2e^- \rightarrow Cu(s)$	0.34
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.15
$Sn^{2+} + 2e^- \rightarrow Sn(s)$	–0.14

(i) Using information from the table above, write a net-ionic equation for the reaction between the Sn electrode and the $Cu(NO_3)_2$ solution that would be thermodynamically favorable. Justify that the reaction is thermodynamically favorable.

(ii) Calculate the value of $\Delta G°$ for the reaction. Include units with your answer.

AP CHEMISTRY • EXERCISE SHEET

9.9 Cell Potential and Free Energy

Name: ______________ Class: __________ Date: ____________ **Total: 12 marks**

KEY WORDS cell potential 电池电势 • anode 阳极 • cathode 阴极

Objective

Build the skills to answer exam questions on **cell potential and free energy**.

You must be able to:

- calculate $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$
- use $\Delta G^\circ = -nFE^\circ_{\text{cell}}$
- link a positive E°_{cell} to a favorable cell

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Standard cell potential

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}},$$

using standard reduction potentials. A **positive** E°_{cell} means a favorable (galvanic) cell.

■ A worked cell potential

Cu^{2+} ($E^\circ = +0.34$) as cathode, Zn^{2+} ($E^\circ = -0.76$) as anode:

$$E^\circ_{\text{cell}} = 0.34 - (-0.76) = +1.10 \text{ V}.$$

■ Linking to free energy

$$\Delta G^\circ = -nFE^\circ_{\text{cell}},$$

where n is moles of electrons transferred and $F = 96\,500$ C/mol. A **positive** E° gives a **negative** ΔG° — favorable.

■ A worked ΔG

For $n = 2$, $E^\circ = 1.10$ V: $\Delta G^\circ = -(2)(96\,500)(1.10) = -2.12 \times 10^5$ J $= -212$ kJ.

2 Practice

Now apply the methods above.

2.1 Write E°_{cell} in terms of the electrode potentials. [1]

2.2 For cathode +0.80 V and anode −0.44 V, find E°_{cell}. [2]

2.3 A cell has a positive E°_{cell}. Is it galvanic or electrolytic? [1]

3 Exam-style questions

3.1 A galvanic (favorable) cell has an E°_{cell} that is [1]

- **A** positive
- **B** negative
- **C** zero
- **D** undefined

3.2 A cell has $E^\circ_{\text{cathode}} = +0.34$ V and $E^\circ_{\text{anode}} = -0.76$ V, with $n = 2$.

(a) Find E°_{cell}. [2]

(b) Find ΔG° (use $F = 96\,500$ C/mol). [3]

3.3 Explain why a positive E°_{cell} corresponds to a negative ΔG°. [2]

Solutions

2.1 $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$.

2.2 $0.80 - (-0.44) = +1.24$ V.

2.3 Galvanic.

3.1 **A** — positive.

3.2 (a) $E^\circ_{\text{cell}} = 0.34 - (-0.76) = +1.10$ V. (b) $\Delta G^\circ = -(2)(96\,500)(1.10) = -2.12 \times 10^5$ J $= -212$ kJ.

3.3 $\Delta G^\circ = -nFE^\circ$; with n and F positive, a positive E° makes ΔG° negative — a favorable reaction.

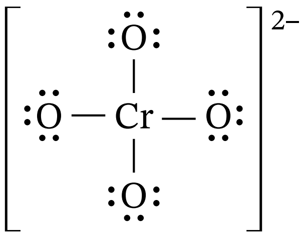
Question 2: Version J

2. Answer the following questions about the chromate ion, CrO_4^{2-}, and the dichromate ion, $Cr_2O_7^{2-}$.

Part A

The bonds between chromium and oxygen in CrO_4^{2-} can be represented as covalent bonds. One possible Lewis diagram for the CrO_4^{2-} ion is shown in Figure 1.

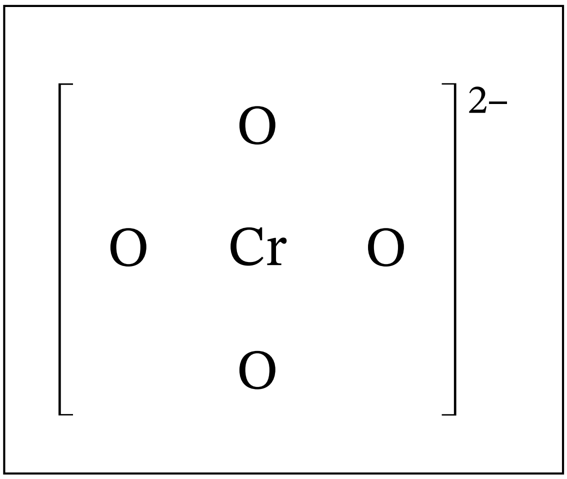
Figure 1



i. Based on VSEPR theory, **predict** the molecular geometry of the CrO_4^{2-} ion.

ii. On Figure 2, **draw** a complete Lewis diagram for a resonance structure of CrO_4^{2-} that results in a formal charge of zero on two of the O atoms and a formal charge of −1 on the other two O atoms. Your diagram should contain the same number of valence electrons as in Figure 1.

Figure 2



Part B

When reacted with a strong acid like $HNO_3(aq)$, $CrO_4^{2-}(aq)$ can be converted to $Cr_2O_7^{2-}(aq)$ and $H_2O(l)$ in a reversible reaction.

i. **Write** a balanced net ionic equation for the reaction between $CrO_4^{2-}(aq)$ and a strong acid.

ii. Is the reaction a redox reaction? **Justify** your answer based on the oxidation number of Cr.

The following information applies to parts C and D.

In acidic solutions, $Cr_2O_7^{2-}(aq)$ reacts to form $CrO_3(aq)$ according to Equation 1.

$$\text{Equation 1: } Cr_2O_7^{2-}(aq) + 2\ H_3O^+(aq) \rightarrow 2\ CrO_3(aq) + 3\ H_2O(l)$$

$CrO_3(aq)$ can be electrolyzed to plate objects with a thin layer of chromium metal according to Equation 2.

$$\text{Equation 2: } CrO_3(aq) + 6\ H^+(aq) + 6\ e^- \rightarrow Cr(s) + 3\ H_2O(l) \qquad E^\circ = -1.32\ \text{V}$$

Part C

Is the reaction represented by Equation 2 thermodynamically favorable or unfavorable under standard conditions? **Justify** your answer with a calculation of ΔG°. Show the work that leads to your answer.

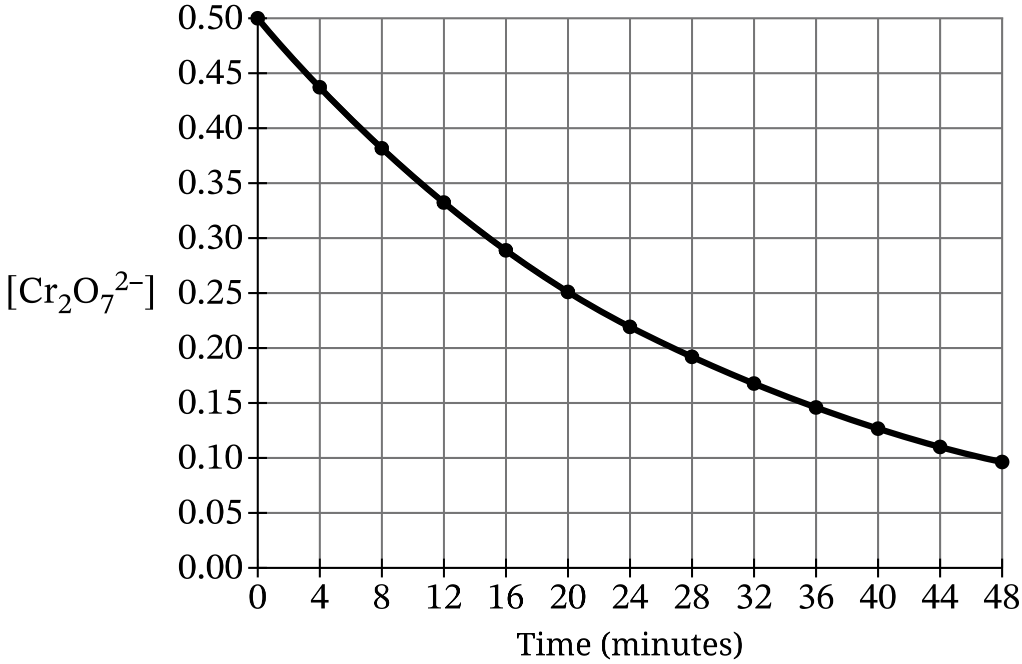
Part D

Calculate the number of grams of $Cr(s)$ that could be plated onto the surface of a steel rod when 15.0 A of current is applied for 3250 seconds. Show the work that leads to your answer.

Part E

In a separate experiment, an iron wire is placed directly in a solution of 0.50 M $Cr_2O_7^{2-}(aq)$ with pH = 1.99. The concentration of $Cr_2O_7^{2-}(aq)$ remaining is recorded over time, and the results are presented in Figure 3.

Figure 3

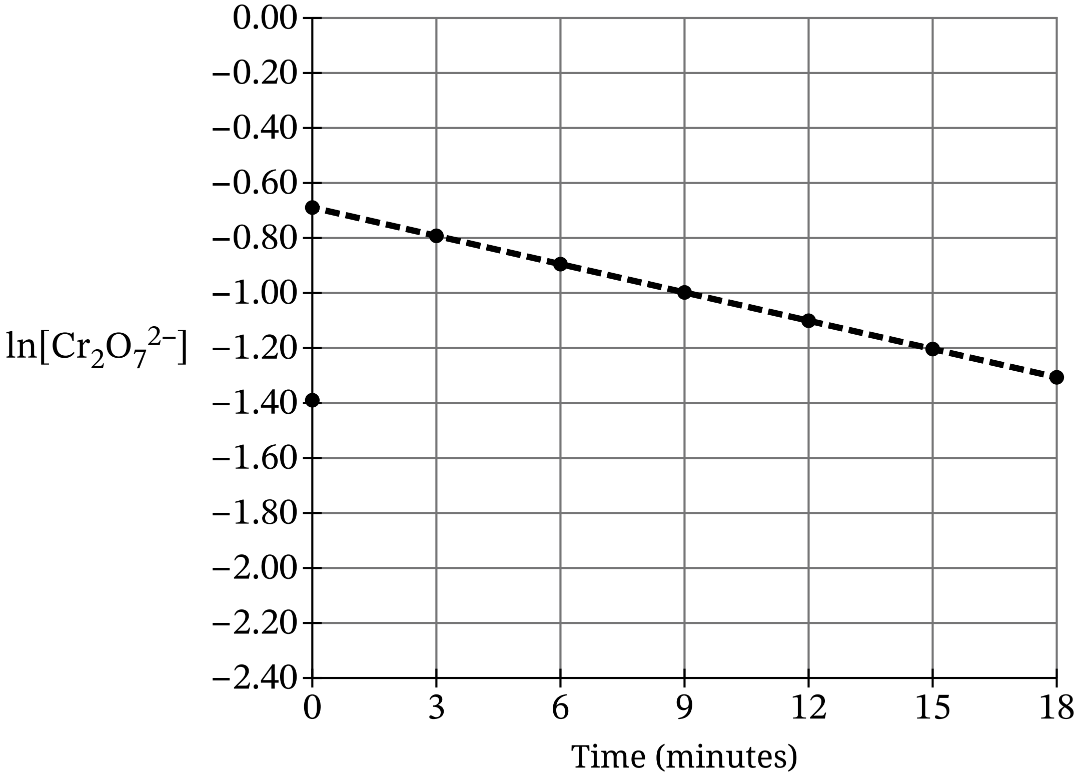


Explain how the data in Figure 3 support the conclusion that the reaction is first order with respect to $Cr_2O_7^{2-}$.

The following information applies to parts F and G.

The student creates a plot of $\ln\left[Cr_2O_7^{2-}\right]$ versus time for a trial with an initial concentration of $0.50\ M\ Cr_2O_7^{2-}(aq)$, as shown in Figure 4.

Figure 4



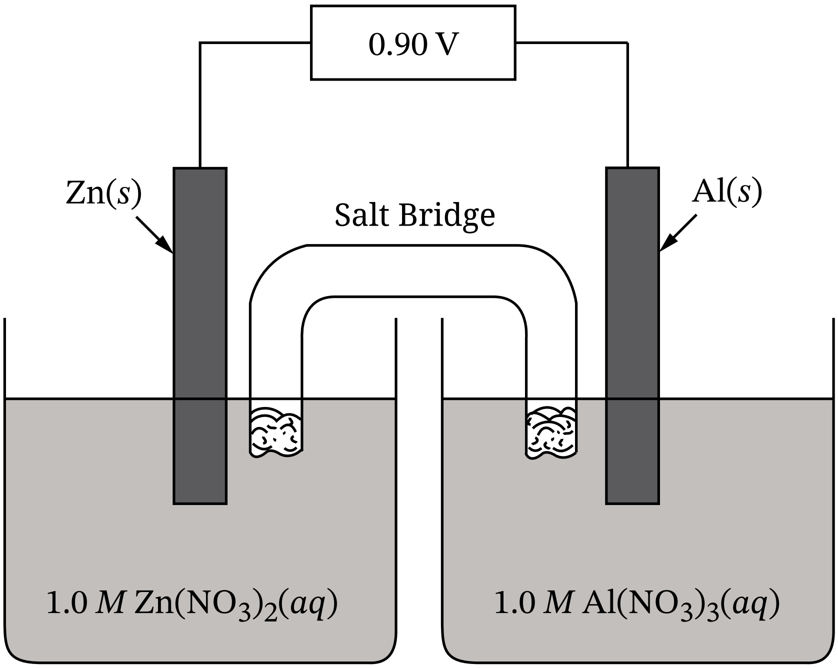
Part F

Calculate the value of the rate constant, k, for the reaction. Report your answer in units of min^{-1}. Show the work that leads to your answer.

Part G

The student then runs a second trial of the experiment under identical conditions but uses an initial concentration of $0.25\ M\ Cr_2O_7^{2-}(aq)$ instead of $0.50\ M\ Cr_2O_7^{2-}(aq)$. On Figure 4, carefully **draw** the plot of $\ln\left[Cr_2O_7^{2-}\right]$ versus time that would be expected for the second experiment. The point at time zero has already been plotted.

6. A scientist constructs a galvanic cell as shown in the diagram. As the cell operates, the $Zn(s)$ electrode increases in mass and the $Al(s)$ electrode decreases in mass. A data table with the standard reduction potentials for the substances follows the diagram.



Half-Reaction	E° (V)
$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$	-0.76
$Al^{3+}(aq) + 3\,e^- \rightarrow Al(s)$	-1.66

A. Write the half-reaction for the oxidation that occurs at the anode.

B. Write the balanced net ionic equation for the overall reaction that occurs in the galvanic cell.

C. Initially, each electrode has a mass of 50.0 g. The cell is allowed to run for a period of time and is then stopped. Which electrode's mass changed the most? Justify your answer with a calculation.

Reduction Half-Reaction	E° (V)
$Au^{3+}(aq) + 3\,e^- \rightarrow Au(s)$	$+1.50$
$Zn^{2+}(aq) + 2\,e^- \rightarrow Zn(s)$	-0.76
$Mn^{2+}(aq) + 2\,e^- \rightarrow Mn(s)$	-1.19
$Al^{3+}(aq) + 3\,e^- \rightarrow Al(s)$	-1.66
$Be^{2+}(aq) + 2\,e^- \rightarrow Be(s)$	-1.85

D. The standard Zn/Al cell has a value of E°_{cell} equal to 0.90 V. The scientist needs a galvanic cell that produces a greater voltage. The scientist has access to the chemical systems in the table. If the scientist uses the Zn half-cell and one of the other options from the table, what is the MAXIMUM voltage that could be generated at standard conditions?

Begin your response to **QUESTION 3** on this page.

3. Sterling silver is an alloy that is commonly used to make jewelry and consists of 92.5% silver and 7.5% other metals, such as copper, by mass. Over time, the alloy can form a tarnish of $Ag_2S(s)$ when it reacts with hydrogen sulfide, as represented by the following equation.

$$2\,Ag(s) + H_2S(g) \rightarrow Ag_2S(s) + H_2(g)$$

(a) What are the oxidation numbers of silver in $Ag(s)$ and $Ag_2S(s)$?

$Ag(s)$__________ $Ag_2S(s)$__________

(b) The following table contains the atomic radii for silver and copper.

Element	Silver (Ag)	Copper (Cu)
Atomic radius (pm)	165	145

(i) Explain why sterling silver is better classified as a substitutional alloy than as an interstitial alloy.

(ii) Using principles of atomic structure and Coulomb's law, explain why silver has a larger atomic radius than copper does.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

The Ag_2S tarnish on sterling silver can be removed until only sterling silver remains. A student weighs a tarnished sterling silver sample both before and after removing the $Ag_2S(s)$ (molar mass 247.80 g / mol) and records the data in the following table.

	Before Tarnish Removal	After Tarnish Removal
Mass	409.21 g	398.94 g

(c) Assuming that only $Ag_2S(s)$ is removed, calculate the number of moles of silver atoms removed.

Rhodium plating is a process used to protect sterling silver from tarnishing. This involves electroplating (depositing) solid rhodium, $Rh(s)$, onto the surface of the metal from an acidified solution of $Rh_2(SO_4)_3(aq)$. Oxygen gas is produced during this process.

(d) A table of half-reactions related to the overall reaction is provided.

Half-Reaction	$E°$ (V)
$Rh^{3+}(aq) + 3\,e^- \rightarrow Rh(s)$	+0.80
$O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)$	+1.23

(i) Write the balanced net ionic equation for plating $Rh(s)$ from the acidified $Rh_2(SO_4)_3(aq)$ solution.

(ii) Calculate the value of E°_{cell} for the reaction in part (d)(i).

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

(iii) Based on your answer to part (d)(ii), explain why this process requires the use of an external power source.

(e) Calculate the length of time, in seconds, required to plate 2.8 g of $Rh(s)$ onto a piece of sterling silver if 2.0 C / s of current is applied.

GO ON TO THE NEXT PAGE.

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 nvolved 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.

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

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.

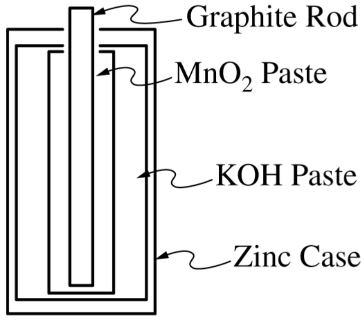
(d) The student determines that 0.0199 mol of Mn was used in the experiment. Use the data to determine the empirical formula of the $Mn_xCl_y(s)$.

(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.

GO ON TO THE NEXT PAGE.

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.

GO ON TO THE NEXT PAGE.

3. Answer the following questions relating to the element aluminum, Al.

(a) Write the complete ground-state electron configuration of an Al atom.

(b) Based on principles of atomic structure, explain why the radius of the Al atom is larger than the radius of the Al^{3+} ion.

A student plans to combine solid aluminum with an aqueous solution of silver ions. The student determines the mass of solid $AgNO_3$ needed to prepare the solution with a specific concentration.

(c) In the following table, briefly list the steps necessary to prepare 200.0 mL of an aqueous solution of $AgNO_3$ using only equipment selected from the choices given. Assume that all appropriate safety measures are already in place. Not all equipment or lines in the table may be needed.

- Solid $AgNO_3$
- Distilled water
- Balance
- Weighing paper and scoop
- 200.00 mL volumetric flask
- 50.0 mL graduated cylinder
- 250 mL beakers
- Pipet

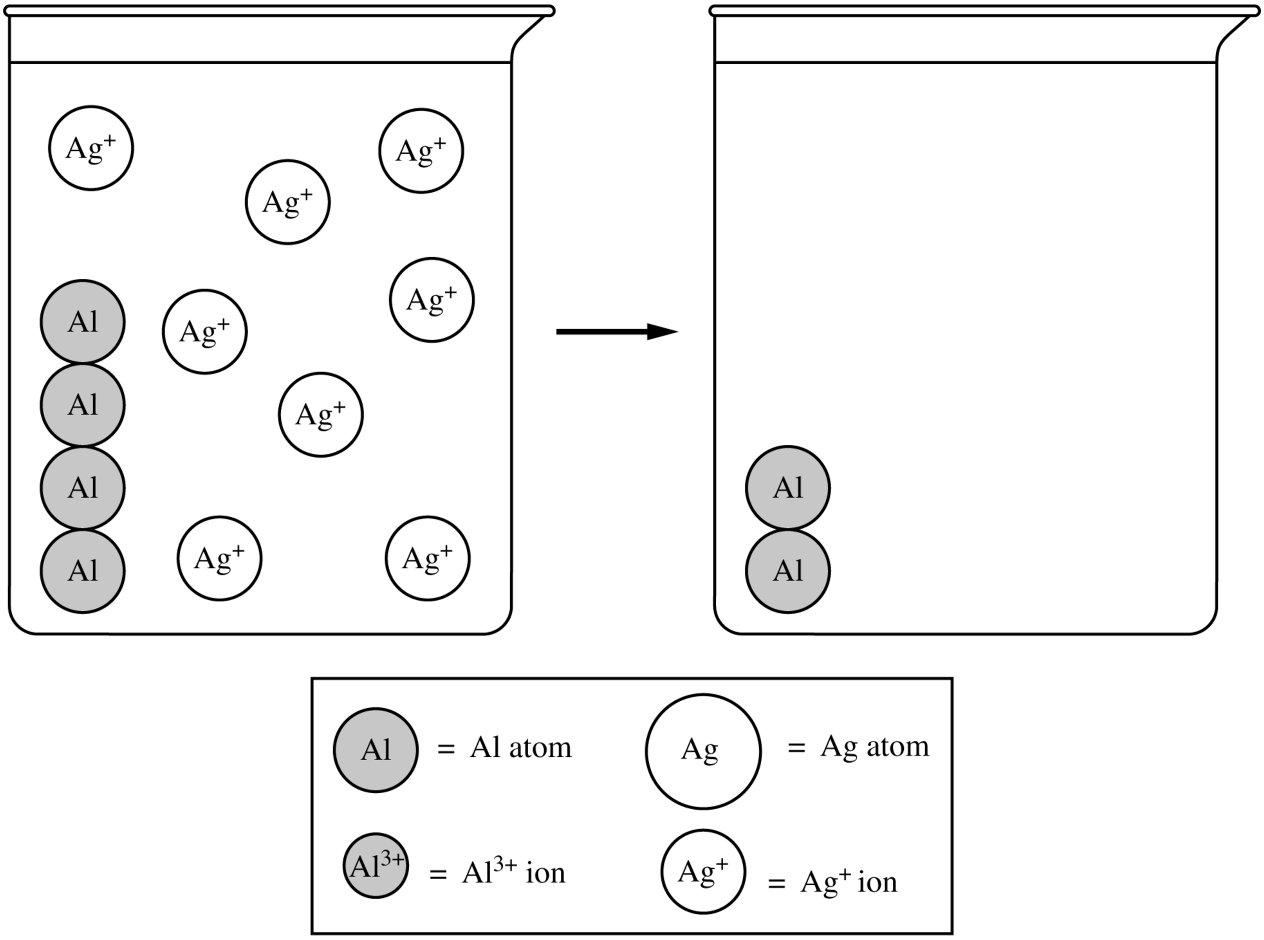
Step	Step Description
1.	Use weighing paper to measure the determined mass of solid $AgNO_3$ on a balance.
2.	

GO ON TO THE NEXT PAGE.

After preparing the solution, the student places some of the solution into a beaker and adds a sample of aluminum. The reaction represented by the following equation occurs.

$$Al(s) + 3\ Ag^{+}(aq) \rightarrow Al^{3+}(aq) + 3\ Ag(s)$$

(d) The following diagram gives an incomplete particulate representation of the reaction. The beaker on the left represents the system before the mixture reacts. Complete the drawing on the right to represent the system after the reaction has occurred. Be sure to include 1) the correct type and number of particles based on the number shown on the left and 2) the relative spacing to depict the appropriate phases.



The student finds the standard reduction potentials given in the table, which are related to the reaction that occurs.

Half-Reaction	$E°$
$Ag^{+}(aq) + e^{-} \rightarrow Ag(s)$	0.80 V
$Al^{3+}(aq) + 3\,e^{-} \rightarrow Al(s)$	−1.66 V

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

(e) Using the standard reduction potentials, calculate the value of $E°$ for the reaction.

(f) Based on the value of $E°$, would the standard free energy change of the reaction under standard conditions, $\Delta G°$, be positive, negative, or zero? Justify your answer.

(g) Once the reaction appears to stop progressing, would the change in free energy, ΔG, be positive, negative, or zero? Justify your answer.

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.

Br_2 Cl_2 F_2 I_2

A chemistry teacher wants to prepare Br_2. The teacher has access to the following three reagents: $NaBr(aq)$, $Cl_2(g)$, and $I_2(s)$.

Half-Reaction	$E°$ at 25°C (V)
$Br_2 + 2\,e^- \rightarrow 2\,Br^-$	1.07
$Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$	1.36
$I_2 + 2\,e^- \rightarrow 2\,I^-$	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 <u>each</u> substance.

The compound $BrCl$ can decompose into Br_2 and Cl_2, as represented by the balanced chemical equation below.

$$2\,BrCl(g) \rightleftarrows Br_2(g) + Cl_2(g) \qquad \Delta H° = 1.6\text{ kJ/mol}_{rxn}$$

A 0.100 mole sample of pure $BrCl(g)$ 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.

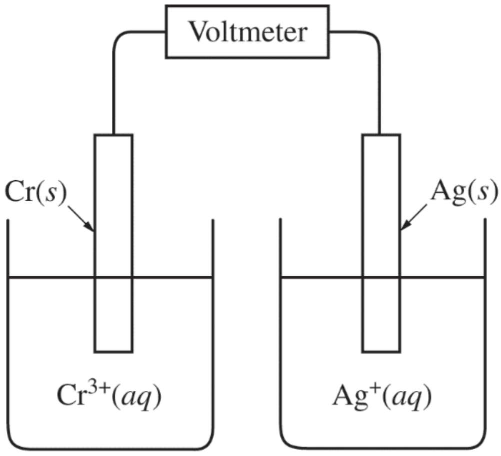
(e) Write the expression for the equilibrium constant, K_{eq}, for the decomposition of $BrCl$.

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 $\Delta H°$ 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	?



6. A student sets up a galvanic cell at 298 K that has an electrode of Ag(*s*) immersed in a 1.0 *M* solution of $Ag^+(aq)$ and an electrode of Cr(*s*) immersed in a 1.0 *M* solution of $Cr^{3+}(aq)$, as shown in the diagram above.

(a) The student measures the voltage of the cell shown above and discovers that it is zero. Identify the missing component of the cell, and explain its importance for obtaining a nonzero voltage.

Half-Reaction	$E°$ (V)
$Ag^+(aq) + e^- \rightarrow Ag(s)$	+ 0.80
$Cr^{3+}(aq) + 3\,e^- \rightarrow Cr(s)$	?

(b) The student adds the missing component to the cell and measures $E°_{cell}$ to be +1.54 V. As the cell operates, Ag^+ ions are reduced. Use this information and the information in the table above to do the following.

(i) Calculate the value of $E°$ for the half-reaction $Cr^{3+}(aq) + 3\,e^- \rightarrow Cr(s)$.

(ii) Write the balanced net-ionic equation for the overall reaction that occurs as the cell operates.

(iii) Calculate the value of $\Delta G°$ for the overall cell reaction in J/mol_{rxn}.

7. A student wants to determine the concentration of H_2O_2 in a solution of $H_2O_2(aq)$. The student can use one of two titrants, either dichromate ion, $Cr_2O_7^{2-}(aq)$, or cobalt(II) ion, $Co^{2+}(aq)$. The balanced chemical equations for the two titration reactions are shown below.

Dichromate as titrant: $Cr_2O_7^{2-}(aq) + 3\ H_2O_2(aq) + 8\ H^+(aq) \rightarrow 2\ Cr^{3+}(aq) + 3\ O_2(g) + 7\ H_2O(l)$

Cobalt(II) as titrant: $2\ Co^{2+}(aq) + H_2O_2(aq) + 2\ H^+(aq) \rightarrow 2\ Co^{3+}(aq) + 2\ H_2O(l)$

The half-reactions and the $E°$ values for the systems related to the titrations above are given in the following table.

Half-Reaction	$E°$ (V) at 298 K
$Co^{3+}(aq) + e^- \rightarrow Co^{2+}(aq)$	1.84
$H_2O_2(aq) + 2\ H^+(aq) + 2\ e^- \rightarrow 2\ H_2O(l)$	1.77
$Cr_2O_7^{2-}(aq) + 14\ H^+(aq) + 6\ e^- \rightarrow 2\ Cr^{3+}(aq) + 7\ H_2O(l)$	1.33
$O_2(g) + 2\ H^+(aq) + 2\ e^- \rightarrow H_2O_2(aq)$	0.70

(a) Use the information in the table to calculate the following.

(i) $E°$ for the reaction between $Cr_2O_7^{2-}(aq)$ and $H_2O_2(aq)$ at 298 K

(ii) $E°$ for the reaction between $Co^{2+}(aq)$ and $H_2O_2(aq)$ at 298 K

(b) Based on the calculated values of $E°$, the student must choose the titrant for which the titration reaction is thermodynamically favorable at 298 K.

(i) Which titrant should the student choose? Explain your reasoning.

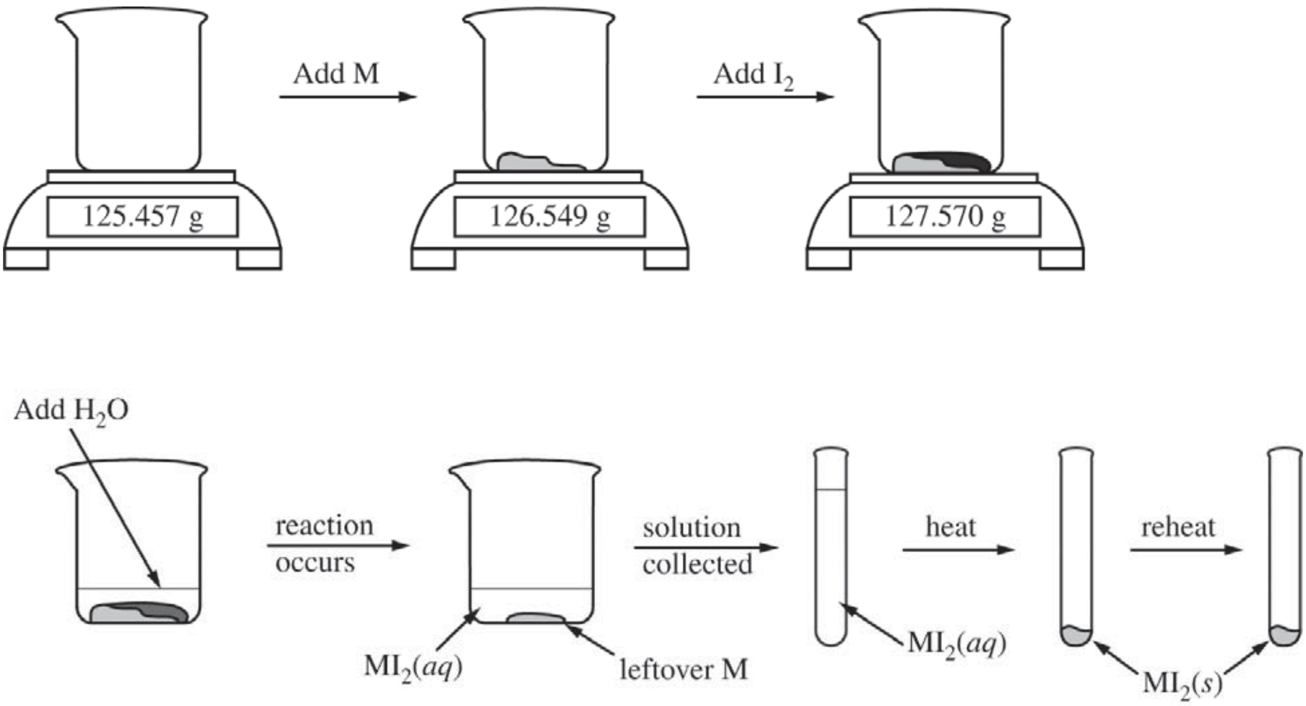
(ii) Calculate the value of $\Delta G°$, in kJ/mol$_{rxn}$, for the reaction between the chosen titrant and $H_2O_2(aq)$.

STOP

END OF EXAM

$$M + I_2 \rightarrow MI_2$$

3. To determine the molar mass of an unknown metal, M, a student reacts iodine with an excess of the metal to form the water-soluble compound MI_2, as represented by the equation above. The reaction proceeds until all of the I_2 is consumed. The $MI_2(aq)$ solution is quantitatively collected and heated to remove the water, and the product is dried and weighed to constant mass. The experimental steps are represented below, followed by a data table.



Data for Unknown Metal Lab	
Mass of beaker	125.457 g
Mass of beaker + metal M	126.549 g
Mass of beaker + metal M + I_2	127.570 g
Mass of MI_2, first weighing	1.284 g
Mass of MI_2, second weighing	1.284 g

(a) Given that the metal M is in excess, calculate the number of moles of I_2 that reacted.

(b) Calculate the molar mass of the unknown metal M.

The student hypothesizes that the compound formed in the synthesis reaction is ionic.

(c) Propose an experimental test the student could perform that could be used to support the hypothesis. Explain how the results of the test would support the hypothesis if the substance was ionic.

The student hypothesizes that Br_2 will react with metal M more vigorously than I_2 did because Br_2 is a liquid at room temperature.

(d) Explain why I_2 is a solid at room temperature whereas Br_2 is a liquid. Your explanation should clearly reference the types and relative strengths of the intermolecular forces present in each substance.

While cleaning up after the experiment, the student wishes to dispose of the unused solid I_2 in a responsible manner. The student decides to convert the solid I_2 to $I^-(aq)$ anion. The student has access to three solutions, $H_2O_2(aq)$, $Na_2S_2O_3(aq)$, and $Na_2S_4O_6(aq)$, and the standard reduction table shown below.

Half reaction	$E°$ (V)
$S_4O_6^{2-}(aq) + 2\,e^- \rightarrow 2\,S_2O_3^{2-}(aq)$	0.08
$I_2(s) + 2\,e^- \rightarrow 2\,I^-(aq)$	0.54
$O_2(g) + 2\,H^+(aq) + 2\,e^- \rightarrow H_2O_2(aq)$	0.68

(e) Which solution should the student add to $I_2(s)$ to reduce it to $I^-(aq)$? Circle your answer below. Justify your answer, including a calculation of $E°$ for the overall reaction.

$H_2O_2(aq)$ $\qquad$ $Na_2S_2O_3(aq)$ $\qquad$ $Na_2S_4O_6(aq)$

(f) Write the balanced net-ionic equation for the reaction between I_2 and the solution you selected in part (e).

CHEMISTRY

Section II

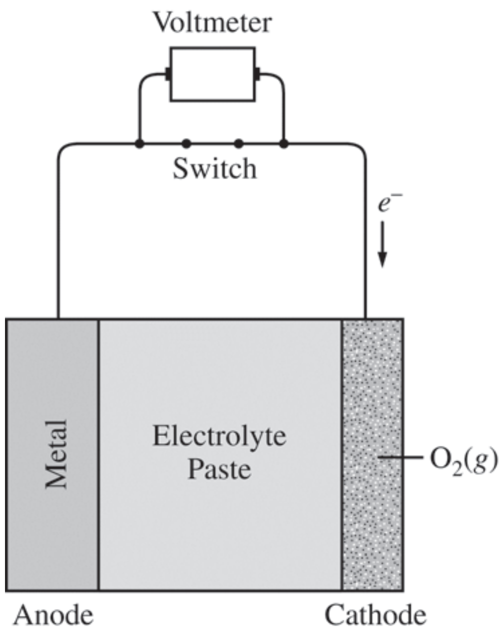
7 Questions

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.



1. Metal-air cells are a relatively new type of portable energy source consisting of a metal anode, an alkaline electrolyte paste that contains water, and a porous cathode membrane that lets in oxygen from the air. A schematic of the cell is shown above. Reduction potentials for the cathode and three possible metal anodes are given in the table below.

Half Reaction	*E* at pH 11 and 298 K (V)
$O_2(g) + 2\,H_2O(l) + 4\,e^- \rightarrow 4\,OH^-(aq)$	+0.34
$ZnO(s) + H_2O(l) + 2\,e^- \rightarrow Zn(s) + 2\,OH^-(aq)$	−1.31
$Na_2O(s) + H_2O(l) + 2\,e^- \rightarrow 2\,Na(s) + 2\,OH^-(aq)$	−1.60
$CaO(s) + H_2O(l) + 2\,e^- \rightarrow Ca(s) + 2\,OH^-(aq)$	−2.78

(a) Early forms of metal-air cells used zinc as the anode. Zinc oxide is produced as the cell operates according to the overall equation below.

$$2\ Zn(s) + O_2(g) \rightarrow 2\ ZnO(s)$$

(i) Using the data in the table above, calculate the cell potential for the zinc-air cell.

(ii) The electrolyte paste contains OH^- ions. On the diagram of the cell above, draw an arrow to indicate the direction of migration of OH^- ions through the electrolyte as the cell operates.

(b) A fresh zinc-air cell is weighed on an analytical balance before being placed in a hearing aid for use.

(i) As the cell operates, does the mass of the cell increase, decrease, or remain the same?

(ii) Justify your answer to part (b)(i) in terms of the equation for the overall cell reaction.

(c) The zinc-air cell is taken to the top of a mountain where the air pressure is lower.

(i) Will the cell potential be higher, lower, or the same as the cell potential at the lower elevation?

(ii) Justify your answer to part (c)(i) based on the equation for the overall cell reaction and the information above.

(d) Metal-air cells need to be lightweight for many applications. In order to transfer more electrons with a smaller mass, Na and Ca are investigated as potential anodes. A 1.0 g anode of which of these metals would transfer more electrons, assuming that the anode is totally consumed during the lifetime of a cell? Justify your answer with calculations.

(e) The only common oxide of zinc has the formula ZnO.

(i) Write the electron configuration for a Zn atom in the ground state.

(ii) From which sublevel are electrons removed when a Zn atom in the ground state is oxidized?

AP CHEMISTRY • EXERCISE SHEET

9.10 Cell Potential Under Nonstandard Conditions

Name: ____________ Class: ________ Date: __________ **Total: 9 marks**

KEY WORDS cell potential 电池电势

Objective

Build the skills to answer exam questions on **cell potential under nonstandard conditions**.

You must be able to:

- use the **Nernst** idea: E falls as products build up
- predict how changing concentrations changes E_{cell}
- relate $E = 0$ to equilibrium

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ Nonstandard conditions

The measured cell potential E differs from $E°$ when concentrations are not 1 M. As the cell runs, reactants deplete and products build, so Q rises and E **falls**.

■ Qualitative Nernst reasoning

- Increasing **reactant** concentration (or decreasing product) makes Q smaller $\rightarrow$ E **larger** (more favorable).
- Increasing **product** (or decreasing reactant) makes Q larger $\rightarrow$ E **smaller**.

■ At equilibrium

When the cell reaches equilibrium, $Q = K$ and $E = 0$ — the battery is "dead" (no more driving force).

■ A worked prediction

For $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$: raising $[Cu^{2+}]$ (a reactant) lowers Q, so E **increases** above $E°$.

2 Practice

Now apply the methods above.

2.1 As a battery runs, does E rise or fall? [1]

2.2 What is E when the cell reaches equilibrium? [1]

2.3 Increasing a reactant's concentration does what to E? [1]

3 Exam-style questions

3.1 When a galvanic cell reaches equilibrium, its cell potential is [1]

- **A** at a maximum
- **B** zero
- **C** negative
- **D** equal to $E°$

3.2 For $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$:

(a) State the effect on E of increasing $[Cu^{2+}]$. [2]

(b) State the effect on E of increasing $[Zn^{2+}]$. [1]

3.3 Explain why the voltage of a battery gradually drops to zero as it is used. [2]

Solutions

2.1 Falls.

2.2 Zero.

2.3 Increases it.

3.1 **B** — zero.

3.2 (a) Increasing [Cu^{2+}] (a reactant) lowers Q, so E increases. (b) Increasing [Zn^{2+}] (a product) raises Q, so E decreases.

3.3 As the cell runs, reactants are used up and products accumulate, so Q rises toward K and E falls; at equilibrium $Q = K$ and $E = 0$.

CHEMISTRY

Section II

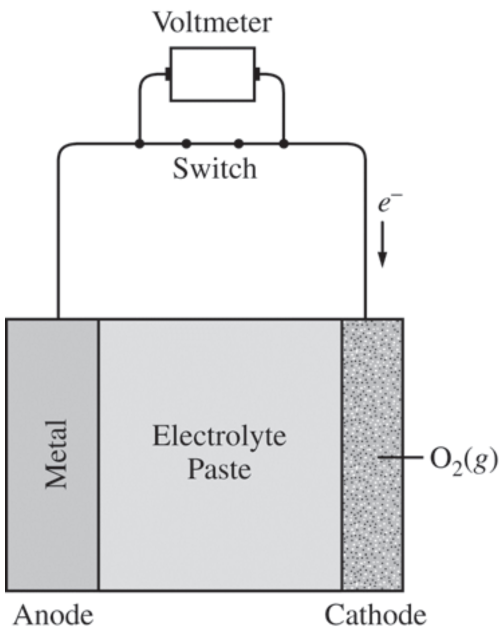
7 Questions

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.



1. Metal-air cells are a relatively new type of portable energy source consisting of a metal anode, an alkaline electrolyte paste that contains water, and a porous cathode membrane that lets in oxygen from the air. A schematic of the cell is shown above. Reduction potentials for the cathode and three possible metal anodes are given in the table below.

Half Reaction	E at pH 11 and 298 K (V)
$O_2(g) + 2\,H_2O(l) + 4\,e^- \rightarrow 4\,OH^-(aq)$	+0.34
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$Na_2O(s) + H_2O(l) + 2\,e^- \rightarrow 2\,Na(s) + 2\,OH^-(aq)$	−1.60
$CaO(s) + H_2O(l) + 2\,e^- \rightarrow Ca(s) + 2\,OH^-(aq)$	−2.78

(a) Early forms of metal-air cells used zinc as the anode. Zinc oxide is produced as the cell operates according to the overall equation below.

$$2\ Zn(s) + O_2(g) \rightarrow 2\ ZnO(s)$$

(i) Using the data in the table above, calculate the cell potential for the zinc-air cell.

(ii) The electrolyte paste contains OH^- ions. On the diagram of the cell above, draw an arrow to indicate the direction of migration of OH^- ions through the electrolyte as the cell operates.

(b) A fresh zinc-air cell is weighed on an analytical balance before being placed in a hearing aid for use.

(i) As the cell operates, does the mass of the cell increase, decrease, or remain the same?

(ii) Justify your answer to part (b)(i) in terms of the equation for the overall cell reaction.

(c) The zinc-air cell is taken to the top of a mountain where the air pressure is lower.

(i) Will the cell potential be higher, lower, or the same as the cell potential at the lower elevation?

(ii) Justify your answer to part (c)(i) based on the equation for the overall cell reaction and the information above.

(d) Metal-air cells need to be lightweight for many applications. In order to transfer more electrons with a smaller mass, Na and Ca are investigated as potential anodes. A 1.0 g anode of which of these metals would transfer more electrons, assuming that the anode is totally consumed during the lifetime of a cell? Justify your answer with calculations.

(e) The only common oxide of zinc has the formula ZnO.

(i) Write the electron configuration for a Zn atom in the ground state.

(ii) From which sublevel are electrons removed when a Zn atom in the ground state is oxidized?

AP CHEMISTRY • EXERCISE SHEET

9.11 Electrolysis and Faraday's Law

Name: ____________ Class: ________ Date: __________ **Total: 13 marks**

KEY WORDS charge 电荷 • electrolysis 电解 • faraday's law 法拉第定律

Objective

Build the skills to answer exam questions on **electrolysis and Faraday's law**.

You must be able to:

- convert **charge 电荷** to **moles of electrons** with $F = 96\,500$ C/mol
- use $Q = It$ (current × time)
- find the mass or moles of product deposited

1 Worked examples

Study these first. Each one shows the method for a question type used later — follow the steps and you can do the Practice and Exam-style questions yourself.

■ The electrolysis chain

Current deposits or releases substances at the electrodes. The route:

$$\text{charge } Q = It \;\rightarrow\; \text{mol } e^- = \frac{Q}{F} \;\rightarrow\; \text{mol product} \;\rightarrow\; \text{mass.}$$

$F = 96\,500$ C/mol is the charge on one mole of electrons.

■ A worked deposit

A current of 2.0 A for 965 s: $Q = It = (2.0)(965) = 1930$ C; mol $e^- = 1930/96\,500 = 0.020$ mol.

■ Electrons per ion

Use the half-reaction's electron count. $Cu^{2+} + 2e^- \rightarrow Cu$ needs **2** electrons per Cu, so mol Cu = (mol e^-)/2.

■ Finish with mass

Mass = mol × molar mass. For 0.020 mol e^- depositing Cu: mol Cu = 0.010; mass = 0.010 × 63.5 = 0.635 g.

2 Practice

Now apply the methods above.

2.1 Write the equation for charge in terms of current and time. [1]

2.2 Find the charge from 3.0 A for 200 s. [2]

2.3 How many moles of electrons are in 9650 C? [2]

3 Exam-style questions

3.1 One mole of electrons carries a charge of about [1]

- **A** 6.02×10^{23} C
- **B** 96 500 C
- **C** 1 C
- **D** 8.314 C

3.2 A current of 5.0 A flows for 1930 s through molten NaCl, depositing sodium ($Na^+ + e^- \rightarrow Na$).

(a) Find the total charge and the moles of electrons. [3]

(b) Find the mass of sodium deposited ($M = 23$ g/mol). [2]

3.3 A current deposits copper from Cu^{2+}. If 0.40 mol of electrons pass, find the moles of

Cu deposited. [2]

Solutions

2.1 $Q = It$.

2.2 $Q = (3.0)(200) = 600$ C.

2.3 $\dfrac{9650}{96\,500} = 0.10$ mol.

3.1 **B** — 96 500 C (Faraday's constant).

3.2 (a) $Q = (5.0)(1930) = 9650$ C; mol $e^- = 9650/96\,500 = 0.10$ mol. (b) $Na^+ + e^- \rightarrow Na$ (1:1), so 0.10 mol Na; mass $= 0.10 \times 23 = 2.3$ g.

3.3 $Cu^{2+} + 2e^- \rightarrow Cu$, so mol Cu $= 0.40/2 = 0.20$ mol.

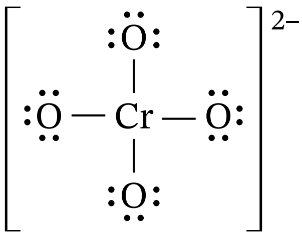
Question 2: Version J

2. Answer the following questions about the chromate ion, CrO_4^{2-}, and the dichromate ion, $Cr_2O_7^{2-}$.

Part A

The bonds between chromium and oxygen in CrO_4^{2-} can be represented as covalent bonds. One possible Lewis diagram for the CrO_4^{2-} ion is shown in Figure 1.

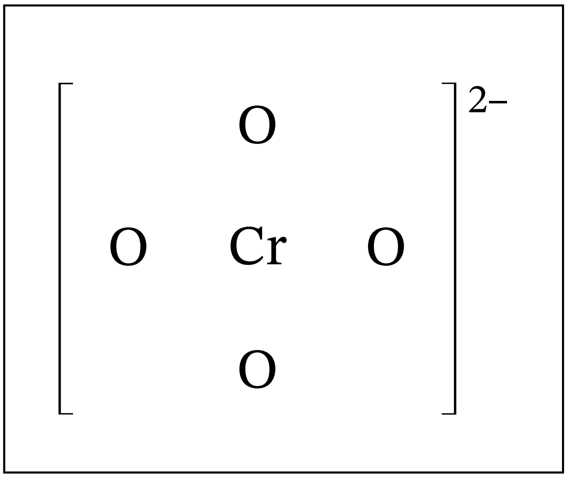
Figure 1



i. Based on VSEPR theory, **predict** the molecular geometry of the CrO_4^{2-} ion.

ii. On Figure 2, **draw** a complete Lewis diagram for a resonance structure of CrO_4^{2-} that results in a formal charge of zero on two of the O atoms and a formal charge of −1 on the other two O atoms. Your diagram should contain the same number of valence electrons as in Figure 1.

Figure 2



Part B

When reacted with a strong acid like $HNO_3(aq)$, $CrO_4^{2-}(aq)$ can be converted to $Cr_2O_7^{2-}(aq)$ and $H_2O(l)$ in a reversible reaction.

i. **Write** a balanced net ionic equation for the reaction between $CrO_4^{2-}(aq)$ and a strong acid.

ii. Is the reaction a redox reaction? **Justify** your answer based on the oxidation number of Cr.

The following information applies to parts C and D.

In acidic solutions, $Cr_2O_7^{2-}(aq)$ reacts to form $CrO_3(aq)$ according to Equation 1.

$$\text{Equation 1: } Cr_2O_7^{2-}(aq) + 2\ H_3O^+(aq) \rightarrow 2\ CrO_3(aq) + 3\ H_2O(l)$$

$CrO_3(aq)$ can be electrolyzed to plate objects with a thin layer of chromium metal according to Equation 2.

$$\text{Equation 2: } CrO_3(aq) + 6\ H^+(aq) + 6\ e^- \rightarrow Cr(s) + 3\ H_2O(l) \qquad E^\circ = -1.32\ \text{V}$$

Part C

Is the reaction represented by Equation 2 thermodynamically favorable or unfavorable under standard conditions? **Justify** your answer with a calculation of ΔG°. Show the work that leads to your answer.

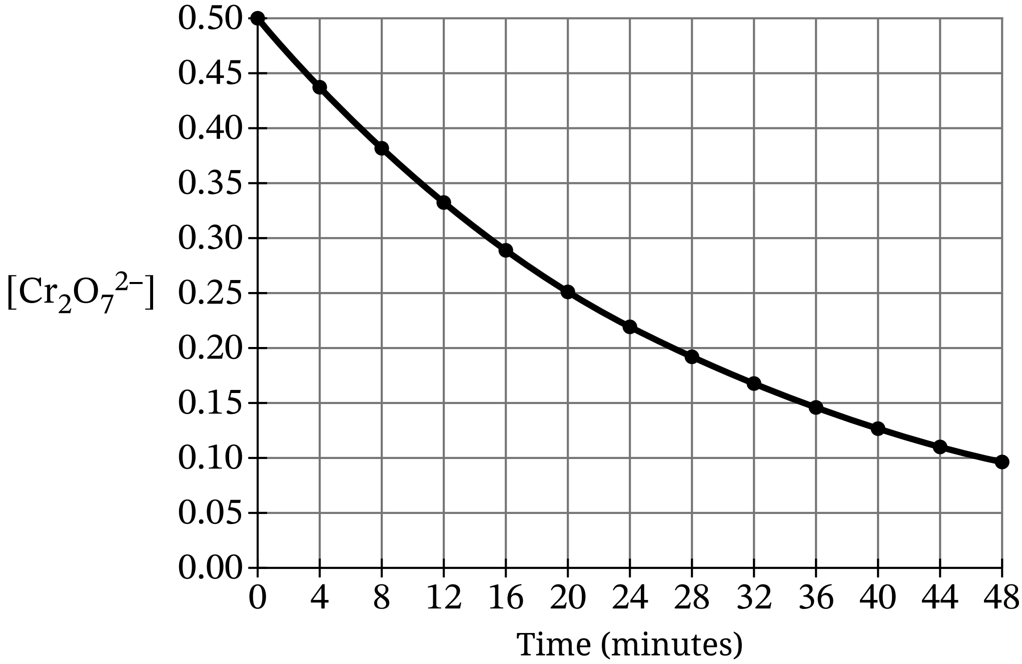
Part D

Calculate the number of grams of $Cr(s)$ that could be plated onto the surface of a steel rod when 15.0 A of current is applied for 3250 seconds. Show the work that leads to your answer.

Part E

In a separate experiment, an iron wire is placed directly in a solution of $0.50\ M\ Cr_2O_7^{2-}(aq)$ with pH $= 1.99$. The concentration of $Cr_2O_7^{2-}(aq)$ remaining is recorded over time, and the results are presented in Figure 3.

Figure 3

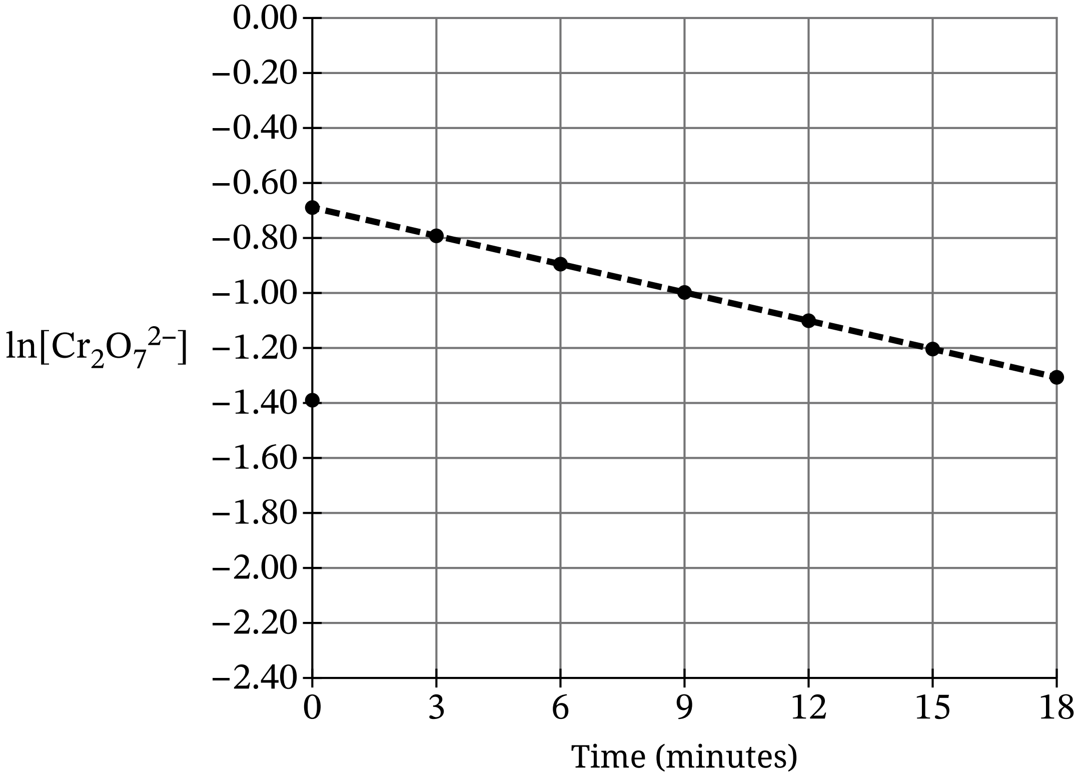


Explain how the data in Figure 3 support the conclusion that the reaction is first order with respect to $Cr_2O_7^{2-}$.

The following information applies to parts F and G.

The student creates a plot of $\ln\left[Cr_2O_7^{2-}\right]$ versus time for a trial with an initial concentration of 0.50 M $Cr_2O_7^{2-}(aq)$, as shown in Figure 4.

Figure 4



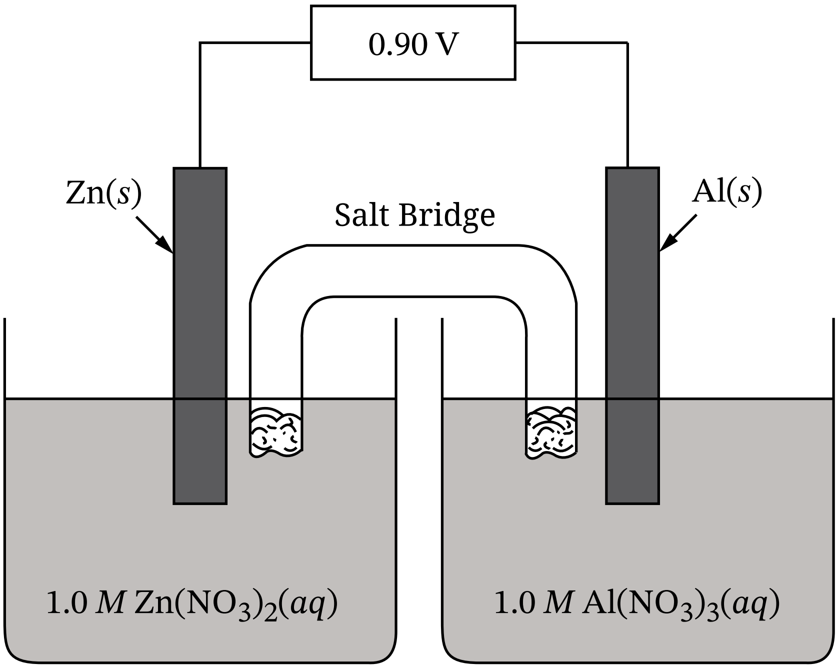
Part F

Calculate the value of the rate constant, k, for the reaction. Report your answer in units of min^{-1}. Show the work that leads to your answer.

Part G

The student then runs a second trial of the experiment under identical conditions but uses an initial concentration of 0.25 M $Cr_2O_7^{2-}(aq)$ instead of 0.50 M $Cr_2O_7^{2-}(aq)$. On Figure 4, carefully **draw** the plot of $\ln\left[Cr_2O_7^{2-}\right]$ versus time that would be expected for the second experiment. The point at time zero has already been plotted.

6. A scientist constructs a galvanic cell as shown in the diagram. As the cell operates, the $Zn(s)$ electrode increases in mass and the $Al(s)$ electrode decreases in mass. A data table with the standard reduction potentials for the substances follows the diagram.



Half-Reaction	E° (V)
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	−1.66

A. Write the half-reaction for the oxidation that occurs at the anode.

B. Write the balanced net ionic equation for the overall reaction that occurs in the galvanic cell.

C. Initially, each electrode has a mass of 50.0 g. The cell is allowed to run for a period of time and is then stopped. Which electrode's mass changed the most? Justify your answer with a calculation.

Reduction Half-Reaction	E° (V)
$Au^{3+}(aq) + 3e^- \rightarrow Au(s)$	+1.50
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	−0.76
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	−1.19
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	−1.66
$Be^{2+}(aq) + 2e^- \rightarrow Be(s)$	−1.85

D. The standard Zn/Al cell has a value of E°_{cell} equal to 0.90 V. The scientist needs a galvanic cell that produces a greater voltage. The scientist has access to the chemical systems in the table. If the scientist uses the Zn half-cell and one of the other options from the table, what is the MAXIMUM voltage that could be generated at standard conditions?

Begin your response to **QUESTION 3** on this page.

3. Sterling silver is an alloy that is commonly used to make jewelry and consists of 92.5% silver and 7.5% other metals, such as copper, by mass. Over time, the alloy can form a tarnish of $Ag_2S(s)$ when it reacts with hydrogen sulfide, as represented by the following equation.

$$2\ Ag(s) + H_2S(g) \rightarrow Ag_2S(s) + H_2(g)$$

(a) What are the oxidation numbers of silver in $Ag(s)$ and $Ag_2S(s)$?

$Ag(s)$__________ $Ag_2S(s)$__________

(b) The following table contains the atomic radii for silver and copper.

Element	Silver (Ag)	Copper (Cu)
Atomic radius (pm)	165	145

(i) Explain why sterling silver is better classified as a substitutional alloy than as an interstitial alloy.

(ii) Using principles of atomic structure and Coulomb's law, explain why silver has a larger atomic radius than copper does.

GO ON TO THE NEXT PAGE.

Continue your response to **QUESTION 3** on this page.

The Ag_2S tarnish on sterling silver can be removed until only sterling silver remains. A student weighs a tarnished sterling silver sample both before and after removing the $Ag_2S(s)$ (molar mass 247.80 g / mol) and records the data in the following table.

	Before Tarnish Removal	After Tarnish Removal
Mass	409.21 g	398.94 g

(c) Assuming that only $Ag_2S(s)$ is removed, calculate the number of moles of silver atoms removed.

Rhodium plating is a process used to protect sterling silver from tarnishing. This involves electroplating (depositing) solid rhodium, $Rh(s)$, onto the surface of the metal from an acidified solution of $Rh_2(SO_4)_3(aq)$. Oxygen gas is produced during this process.

(d) A table of half-reactions related to the overall reaction is provided.

Half-Reaction	$E°$ (V)
$Rh^{3+}(aq) + 3\,e^- \rightarrow Rh(s)$	+0.80
$O_2(g) + 4\,H^+(aq) + 4\,e^- \rightarrow 2\,H_2O(l)$	+1.23

(i) Write the balanced net ionic equation for plating $Rh(s)$ from the acidified $Rh_2(SO_4)_3(aq)$ solution.

(ii) Calculate the value of E°_{cell} for the reaction in part (d)(i).

GO ON TO THE NEXT PAGE.

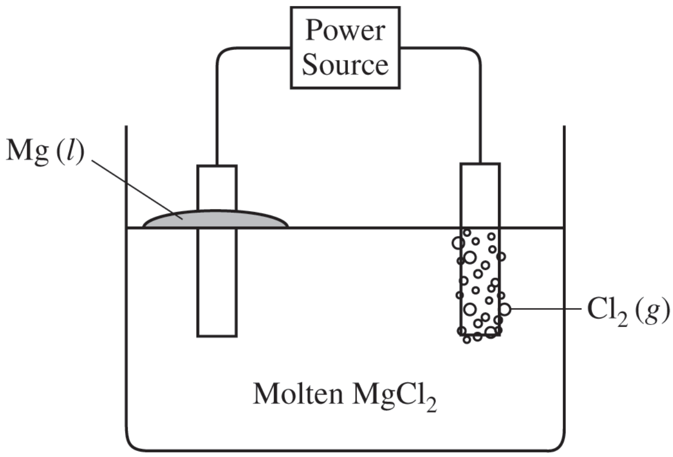
Continue your response to **QUESTION 3** on this page.

(iii) Based on your answer to part (d)(ii), explain why this process requires the use of an external power source.

(e) Calculate the length of time, in seconds, required to plate 2.8 g of $Rh(s)$ onto a piece of sterling silver if 2.0 C / s of current is applied.

GO ON TO THE NEXT PAGE.

Begin your response to **QUESTION 5** on this page.



Half-Reaction	$E°$ (V)
$Mg^{2+} + 2e^- \rightarrow Mg$	-2.37
$Cl_2 + 2e^- \rightarrow 2\,Cl^-$	$+1.36$

5. Molten $MgCl_2$ can be decomposed into its elements if a sufficient voltage is applied using inert electrodes. The products of the reaction are liquid Mg (at the cathode) and Cl_2 gas (at the anode). A simplified representation of the cell is shown above. The reduction half-reactions related to the overall reaction in the cell are given in the table.

(a) Draw an arrow on the diagram to show the direction of electron flow through the external circuit as the cell operates.

(b) Would an applied voltage of 2.0 V be sufficient for the reaction to occur? Support your claim with a calculation as part of your answer.

(c) If the current in the cell is kept at a constant 5.00 amps, how many seconds does it take to produce 2.00 g of $Mg(l)$ at the cathode?

GO ON TO THE NEXT PAGE.

CHEMISTRY
Section II
7 Questions
Time—1 hour and 45 minutes

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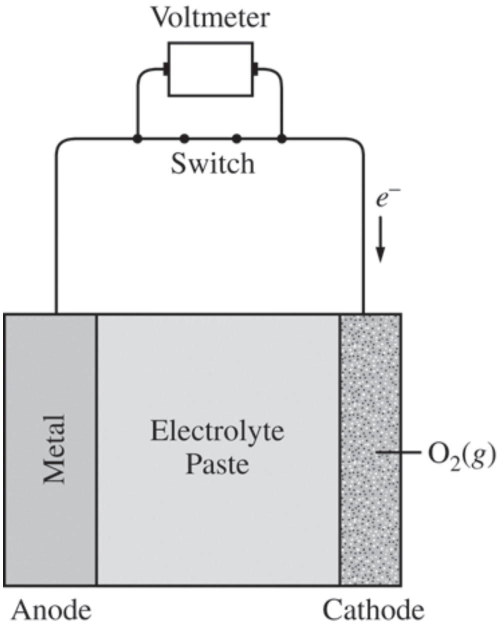

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(a) Early forms of metal-air cells used zinc as the anode. Zinc oxide is produced as the cell operates according to the overall equation below.

$$2\ Zn(s) + O_2(g) \rightarrow 2\ ZnO(s)$$

(i) Using the data in the table above, calculate the cell potential for the zinc-air cell.

(ii) The electrolyte paste contains OH^- ions. On the diagram of the cell above, draw an arrow to indicate the direction of migration of OH^- ions through the electrolyte as the cell operates.

(b) A fresh zinc-air cell is weighed on an analytical balance before being placed in a hearing aid for use.

(i) As the cell operates, does the mass of the cell increase, decrease, or remain the same?

(ii) Justify your answer to part (b)(i) in terms of the equation for the overall cell reaction.

(c) The zinc-air cell is taken to the top of a mountain where the air pressure is lower.

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(e) The only common oxide of zinc has the formula ZnO.

(i) Write the electron configuration for a Zn atom in the ground state.

(ii) From which sublevel are electrons removed when a Zn atom in the ground state is oxidized?