

AP[®] Chemistry Exam

SECTION II: Free Response

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IMPORTANT Identification Information

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 First letter of your first name
- Date of birth

 Month Day Year
- Six-digit school code
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Instructions

The questions for Section II are printed in this booklet. Pages containing a periodic table and lists containing equations and constants are also printed in this booklet.

You may use the pages that the questions are printed on to organize your answers or for scratch work, but you must write your answers in the areas designated for each response. Only material written in the space provided will be scored.

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.

Write clearly and legibly. Cross out any errors you make; erased or crossed-out work will not be scored.

Manage your time carefully. You may proceed freely from one question to the next. You may review your responses if you finish before the end of the exam is announced.

At a Glance

Total Time

1 hour and 45 minutes

Number of Questions

7

Percent of Total Score

50%

Writing Instrument

Either pencil or pen with black or dark blue ink

Electronic Device

Calculator allowed

Suggested Time

Approximately 23 minutes each for questions 1–3 and 9 minutes each for questions 4–7

Weight

Approximate weights:
 Questions 1–3:
 22% each
 Questions 4–7:
 9% each

Form I
 Form Code 4BPB4-S
 25

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AP® CHEMISTRY EQUATIONS AND CONSTANTS

| UNIT SYMBOLS | |
|------------------------|-------|
| gram, | g |
| mole, | mol |
| liter, | L |
| meter, | m |
| second, | s |
| hertz, | Hz |
| atmosphere, | atm |
| millimeter of mercury, | mm Hg |
| degree Celsius, | °C |
| kelvin, | K |
| joule, | J |
| volt, | V |
| coulomb, | C |
| ampere, | A |

| UNIT CONVERSIONS |
|---|
| 1 hertz = 1 s ⁻¹ |
| 1 atm = 760 mm Hg = 760 torr |
| K = °C + 273.15 |
| 1 volt = $\frac{1 \text{ joule}}{1 \text{ coulomb}}$ |
| 1 ampere = $\frac{1 \text{ coulomb}}{1 \text{ second}}$ |

| METRIC PREFIXES | | |
|-------------------|--------|--------|
| Factor | Prefix | Symbol |
| 10 ⁹ | giga | G |
| 10 ⁶ | mega | M |
| 10 ³ | kilo | k |
| 10 ⁻² | centi | c |
| 10 ⁻³ | milli | m |
| 10 ⁻⁶ | micro | μ |
| 10 ⁻⁹ | nano | n |
| 10 ⁻¹² | pico | p |

ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

$$F_{\text{coulombic}} \propto \frac{q_1q_2}{r^2}$$

E = energy

ν = frequency

λ = wavelength

F = force

q = charge

r = separation

Planck's constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light, $c = 2.998 \times 10^8$ m s⁻¹

Avogadro's number = 6.022×10^{23} mol⁻¹

GASES, LIQUIDS, AND SOLUTIONS

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

$$n = \frac{m}{M}$$

$$D = \frac{m}{V}$$

$$KE = \frac{1}{2}mv^2$$

$$M = \frac{n_{\text{solute}}}{L_{\text{solution}}}$$

$$A = \epsilon bc$$

P = pressure

V = volume

T = temperature

n = number of moles

X = mole fraction

m = mass

M = molar mass

D = density

KE = kinetic energy

v = velocity

M = molarity

A = absorbance

ϵ = molar absorptivity

b = path length

c = concentration

Gas constant, $R = 8.314$ J mol⁻¹ K⁻¹

= 0.08206 L atm K⁻¹ mol⁻¹

STP = 273.15 K and 1.0 atm

Ideal gas at STP = 22.4 L mol⁻¹

KINETICS

$$[A]_t - [A]_0 = -kt$$

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

k = rate constant

t = time

$t_{1/2}$ = half-life

EQUILIBRIUM

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{ where } a A + b B \rightleftharpoons c C + d D$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$pK_w = 14 = \text{pH} + \text{pOH} \text{ at } 25^\circ\text{C}$$

$$\text{pH} = -\log[H_3O^+], \quad \text{pOH} = -\log[OH^-]$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}, \quad K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$pK_a = -\log K_a, \quad pK_b = -\log K_b$$

$$K_w = K_a \times K_b, \quad pK_w = pK_a + pK_b$$

$$\text{pH} = pK_a + \log \frac{[A^-]}{[HA]}$$

Equilibrium Constants

K_c (molar concentrations)

K_p (gas pressures)

K_w (water)

K_a (acid)

K_b (base)

THERMODYNAMICS/ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta H^\circ_{\text{reaction}} = \sum \Delta H^\circ_{f \text{ products}} - \sum \Delta H^\circ_{f \text{ reactants}}$$

$$\Delta S^\circ_{\text{reaction}} = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

$$\Delta G^\circ_{\text{reaction}} = \sum \Delta G^\circ_{f \text{ products}} - \sum \Delta G^\circ_{f \text{ reactants}}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -RT \ln K$$

$$= -nFE^\circ$$

$$I = \frac{q}{t}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q$$

q = heat

m = mass

c = specific heat capacity

T = temperature

S° = standard entropy

H° = standard enthalpy

G° = standard Gibbs free energy

R = gas constant

K = equilibrium constant

n = number of moles of electrons

E° = standard potential

I = current (amperes)

q = charge (coulombs)

t = time (seconds)

Q = reaction quotient

Faraday's constant, $F = 96,485 \text{ coulombs} / 1 \text{ mol } e^-$

CHEMISTRY

SECTION II

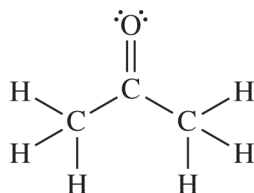
Time—1 hour and 45 minutes

7 Questions

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

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

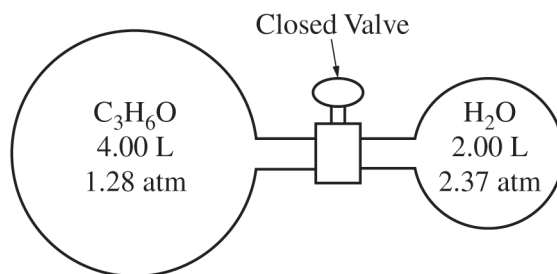
1. Answer the following questions about acetone, C_3H_6O , which is represented in the following Lewis diagram.



(a) The bonding in an acetone molecule can be modeled using sigma and pi bonds. Based on the Lewis diagram, identify the number of sigma bonds and the number of pi bonds.

Sigma bonds: _____

Pi bonds: _____



(b) While held at a constant temperature of 800. K, a sample of $C_3H_6O(g)$ and a sample of $H_2O(g)$ are in containers separated by a closed valve, as shown in the diagram.

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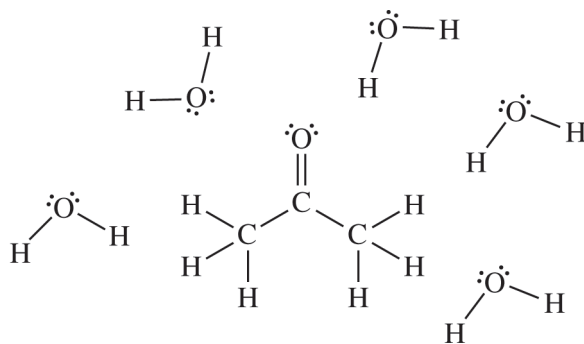
(i) Assuming ideal behavior, constant temperature, and initial volumes of 4.00 L and 2.00 L for the gases shown, what is the partial pressure, in atm, of the $\text{C}_3\text{H}_6\text{O}(g)$ after the valve is opened and the gases have mixed?

(ii) After the gases mix, the system is cooled to 400. K. What is the ratio of the acetone partial

pressures, $\frac{P_{400\text{K}}}{P_{800\text{K}}}$, at the two temperatures? $\frac{P_{400\text{K}}}{P_{800\text{K}}} = \underline{\hspace{2cm}}$

(c) After the gases are cooled to 400. K, the measured pressure of the system is significantly lower than the predicted value, partially because of strong interactions between molecules of $\text{C}_3\text{H}_6\text{O}$ and molecules of H_2O .

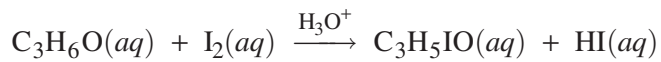
(i) Draw a single dashed line (---) on the following diagram to indicate the location of the strongest interaction between a molecule of $\text{C}_3\text{H}_6\text{O}$ and a molecule of H_2O .



(ii) Using principles of kinetic molecular theory, explain why the attraction between molecules of $\text{C}_3\text{H}_6\text{O}$ and H_2O results in a pressure that is lower than the predicted value.

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Acetone, $\text{C}_3\text{H}_6\text{O}$, reacts with I_2 in acidic solution, as represented by the preceding equation. A student conducts several trials at constant temperature using different concentrations of the reactants. The results of the student's experiment are provided in the following table.

| Trial | $[\text{C}_3\text{H}_6\text{O}] (M)$ | $[\text{I}_2] (M)$ | $[\text{H}_3\text{O}^+] (M)$ | Initial Rate (M/s) |
|-------|--------------------------------------|--------------------|------------------------------|------------------------|
| 1 | 1.33 | 0.00100 | 0.162 | 8.11×10^{-6} |
| 2 | 1.33 | 0.00100 | 0.323 | 16.6×10^{-6} |
| 3 | 0.667 | 0.00100 | 0.323 | 8.25×10^{-6} |

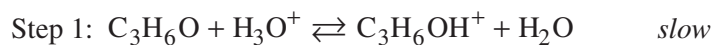
- (d) Explain how the data in the table support that the reaction is first order with respect to $\text{C}_3\text{H}_6\text{O}$.
- (e) The reaction is found to be zero order with respect to I_2 . Use the data to determine the overall rate law for the reaction.
- (f) Using the data from trial 3, calculate the value of the rate constant, k , in $M^{-1} s^{-1}$.

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(g) When the reaction occurs at a higher temperature, the value of the rate constant, k , increases. Based on collision theory, explain why the value of k increases with temperature.

(h) The following mechanism was proposed for the reaction. Explain how this mechanism is consistent with the reaction being zero order with respect to I_2 .

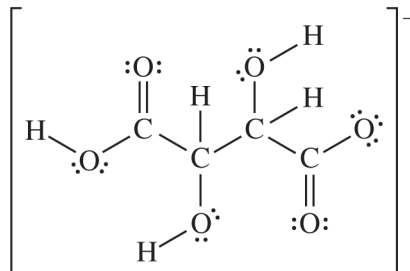


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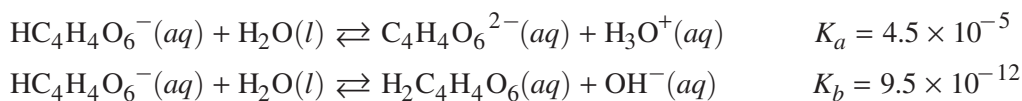
2. Answer the following questions about potassium hydrogen tartrate, $\text{KHC}_4\text{H}_4\text{O}_6$.

When $\text{KHC}_4\text{H}_4\text{O}_6$ dissolves in water, it dissociates into K^+ and $\text{HC}_4\text{H}_4\text{O}_6^-$ ions. The Lewis diagram of $\text{HC}_4\text{H}_4\text{O}_6^-$ is shown.



(a) In the diagram, circle the atom that detaches when $\text{HC}_4\text{H}_4\text{O}_6^-$ acts as a proton donor.

The $\text{HC}_4\text{H}_4\text{O}_6^-$ ion can act as a proton donor and a proton acceptor. The ionization reactions of $\text{HC}_4\text{H}_4\text{O}_6^-(aq)$ in water and their corresponding K values are provided.



(b) Calculate the $\text{p}K_a$ of $\text{HC}_4\text{H}_4\text{O}_6^-(aq)$.

(c) When $\text{HC}_4\text{H}_4\text{O}_6^-$ is dissolved in water, $[\text{C}_4\text{H}_4\text{O}_6^{2-}]$ is greater than $[\text{H}_2\text{C}_4\text{H}_4\text{O}_6]$. Explain this observation based on the information provided.

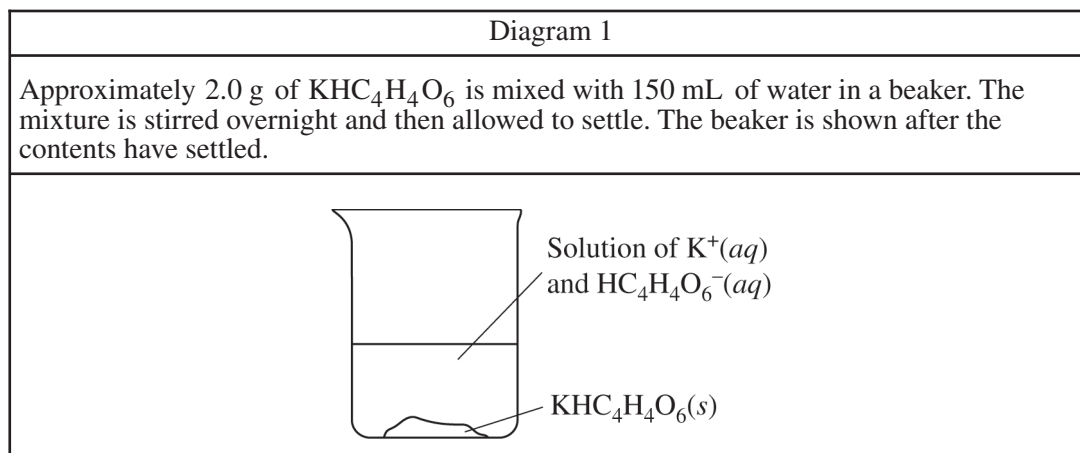
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Unlike many potassium salts, $\text{KHC}_4\text{H}_4\text{O}_6$ is only slightly soluble in water. It dissociates according to the following equation. The K_{sp} expression is given.



In order to determine the K_{sp} of this salt, a student prepares a saturated solution as shown in diagram 1.


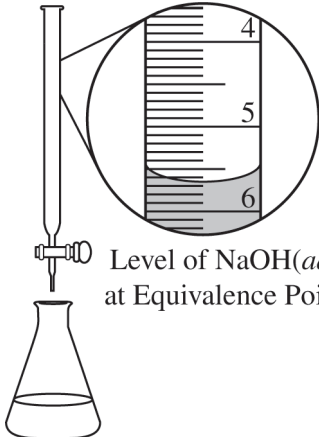


(d) What observation can the student make to confirm that the solution in the beaker is saturated?

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- (e) The student continues the experiment by filtering the saturated solution and then titrating it with $\text{NaOH}(aq)$. These steps are shown in diagrams 2 and 3.

| Diagram 2 | Diagram 3 |
|---|--|
| The mixture is filtered to separate the solid from the solution. | A 25.00 mL sample of the solution is transferred to an Erlenmeyer flask and titrated with 0.1376 M $\text{NaOH}(aq)$. |
|  |  Level of $\text{NaOH}(aq)$ at Equivalence Point |

The magnified view in diagram 3 shows part of the buret at the equivalence point of the titration. The remaining data are shown in the following table.

| | |
|--|----------|
| Volume of $\text{KHC}_4\text{H}_4\text{O}_6$ solution in the flask | 25.00 mL |
| Initial buret reading of $\text{NaOH}(aq)$ | 0.00 mL |
| Final buret reading of $\text{NaOH}(aq)$ | ? |
| Concentration of $\text{NaOH}(aq)$ in the buret | 0.1376 M |

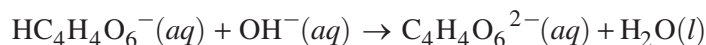
- (i) Based on the magnified view in diagram 3, what should the student record as the final volume reading of $\text{NaOH}(aq)$ in the buret?

_____ mL

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- (ii) Using the data from the titration, calculate the value of $[\text{HC}_4\text{H}_4\text{O}_6^-]$ in the $\text{KHC}_4\text{H}_4\text{O}_6$ solution. The equation shown represents the reaction that occurs during the titration.



- (iii) Using the data from the experiment, calculate the value of K_{sp} for $\text{KHC}_4\text{H}_4\text{O}_6$, given that

$$K_{sp} = [\text{K}^+][\text{HC}_4\text{H}_4\text{O}_6^-].$$

- (f) A second student performs the same experiment, but some $\text{KHC}_4\text{H}_4\text{O}_6(s)$ passes around the filter paper and remains in the 25.00 mL sample that is titrated. As a result, the second student requires a greater volume of $\text{NaOH}(aq)$ to reach the equivalence point of the titration.

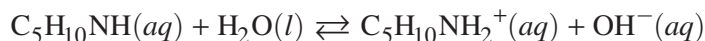
- (i) Assuming no other errors occurred, explain why the presence of the $\text{KHC}_4\text{H}_4\text{O}_6(s)$ increases the volume of $\text{NaOH}(aq)$ needed to reach the equivalence point.

- (ii) Would the second student's calculated value of K_{sp} be larger, smaller, or the same as the first student's calculated value of K_{sp} obtained in part (e)(iii)? Justify your answer.

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3. Piperidine, $C_5H_{10}NH$, is a weak organic base. The reaction of $C_5H_{10}NH(aq)$ with $H_2O(l)$ is represented by the following equation.



- (a) Identify one Brønsted-Lowry conjugate acid-base pair in the reaction of piperidine with water. Be sure to label which species is the acid and which is the base.

- (b) Write the expression for the equilibrium constant, K_b , for piperidine, $C_5H_{10}NH$.

- (c) A 20.0 mL sample of 0.750 M $C_5H_{10}NH(aq)$ is prepared at 25°C.

- (i) The equilibrium concentration of $OH^-(aq)$ in the solution is $3.09 \times 10^{-2} M$. Calculate the pH of the 0.750 M $C_5H_{10}NH(aq)$ solution at 25°C.

- (ii) What is the percent ionization of piperidine in the 0.750 M solution?

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(d) When a small volume of strong acid is added to the 0.750 M $\text{C}_5\text{H}_{10}\text{NH}(aq)$ solution, the number of moles of $\text{C}_5\text{H}_{10}\text{NH}_2^+$ increases.

(i) Write the balanced net ionic equation for the reaction that occurs between major species in solution when the strong acid is added.

(ii) Using Q and K , explain why the moles of $\text{C}_5\text{H}_{10}\text{NH}_2^+$ increase when a small amount of strong acid is added to the solution.

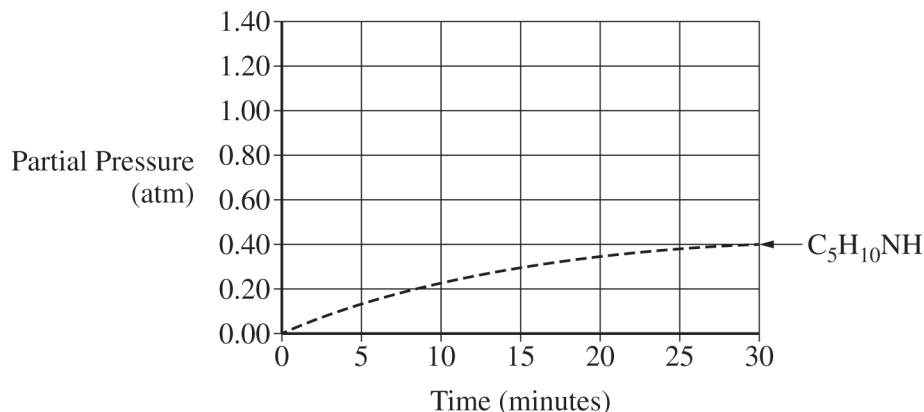
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A scientist prepares piperidine, $C_5H_{10}NH$, by reacting C_5H_5N and H_2 in a nickel-coated container at 400. K according to the following reaction equation.



The scientist fills a previously evacuated, sealed, rigid container with 1.40 atm of C_5H_5N and 1.40 atm of H_2 and records the partial pressure of $C_5H_{10}NH(g)$ as the reaction progresses. The data are shown in the following graph.



(e) On the graph, sketch a single curve that represents the partial pressure of $H_2(g)$ as the reaction proceeds from 0 minutes to 30 minutes. Your curve should reflect

- the rate of change of $H_2(g)$ compared to that of $C_5H_{10}NH(g)$ and
- the initial partial pressure of $H_2(g)$ and the partial pressure of $H_2(g)$ at 30 minutes.

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(f) In this reaction, 4 mol of gaseous reactants produce 1 mol of gaseous product. Based on this fact, a student claims that the entropy change of the forward reaction, ΔS_{rxn}° , is negative.

(i) Use particulate-level reasoning to explain why the student's claim is correct.

(ii) Given the signs of ΔG_{rxn}° and ΔS_{rxn}° at 400. K, is the sign of ΔH_{rxn}° positive or negative? Justify your answer.

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4. A student conducts a calorimetry experiment using $\text{CaBr}_2(s)$ (molar mass 199.88 g / mol) to determine the enthalpy of solution. The student prepares the solution by dissolving $\text{CaBr}_2(s)$ in water. The following data table includes the information from the experiment.



| | |
|-------------------------|---------|
| Mass of water | 46.00 g |
| Mass of CaBr_2 | 7.11 g |
| Initial temperature | 23.5°C |
| Final temperature | 44.0°C |

- (a) Other than preventing the solution from splashing out, explain why it is important to keep the lid on the calorimeter during the experiment.

- (b) Based on the data in the table, what is the sign of the enthalpy of solution, $\Delta H_{\text{solution}}^\circ$? Justify your answer.

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(c) Using the data from the experiment, calculate the magnitude of thermal energy, q , in joules, transferred in the dissolution of CaBr_2 . Assume that the mixture in the calorimeter has a specific heat capacity of $3.61 \text{ J}/(\text{g}\cdot^\circ\text{C})$.

(d) Using the data from the experiment, calculate the magnitude of $\Delta H_{\text{solution}}^\circ$ of CaBr_2 in kJ/mol .

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5. Answer the following questions about magnesium nitrate and sodium carbonate.

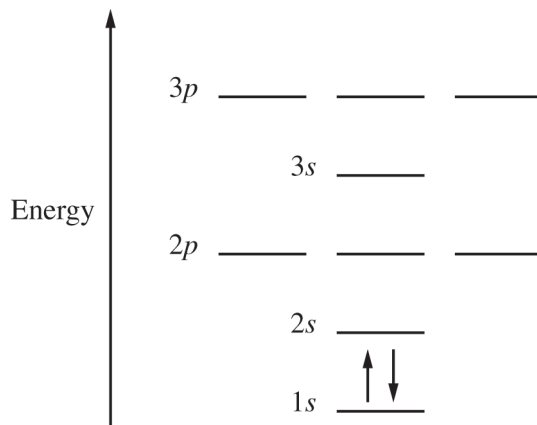
When a student combines equal volumes of 0.1 *M* aqueous solutions of magnesium nitrate, $\text{Mg}(\text{NO}_3)_2$, and sodium carbonate, Na_2CO_3 , a white solid forms.

(a) Write the balanced net ionic equation for the reaction.

(b) A student filters the mixture from part (a) to remove the solid from the solution. Describe an experimental technique that the student can use to demonstrate that ions remain in the filtered solution.

(c) The $\text{Na}_2\text{CO}_3(aq)$ used in the reaction has a 2:1 ratio of cations to anions. Identify a metallic element, *M*, other than sodium that results in a compound that has a formula of M_2CO_3 .

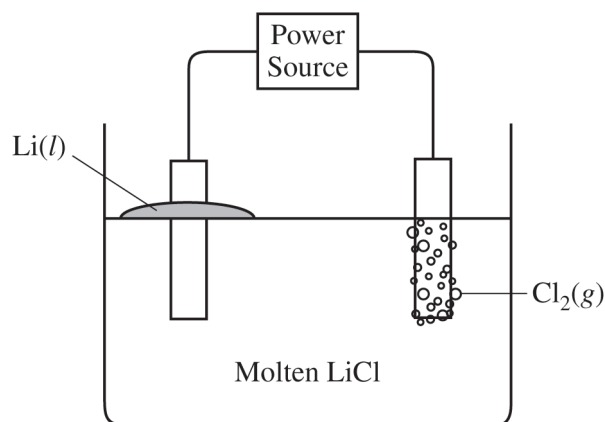
(d) An incomplete orbital energy diagram for the magnesium cation in the ground state is shown. Using arrows to represent electrons, complete the diagram with the correct number of electrons in the cation. The arrows for the 1*s* sublevel are already shown.



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6. Molten lithium chloride, $\text{LiCl}(l)$, is electrolyzed using an external power supply and inert electrodes, as represented in the following diagram. Liquid lithium metal and chlorine gas are produced.



The reduction potentials for the half-reactions associated with this process are shown in the following table.

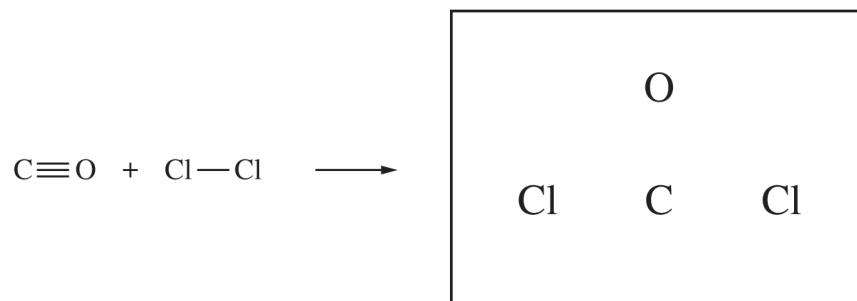
| Half-Reaction | E (V) |
|---|---------|
| $\text{Cl}_2 + 2 e^- \rightarrow 2 \text{Cl}^-$ | -1.36 |
| $\text{Li}^+ + e^- \rightarrow \text{Li}$ | -2.10 |

- (a) On the diagram, draw an arrow to show the direction of electron flow in the wire.
- (b) Use the half-reactions in the table to write the balanced net ionic equation for the reaction that occurs in the electrolytic cell.
- (c) Calculate the average current, in C/s, that must flow through the cell to produce 0.18 g of lithium metal in 3200. seconds.

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7. Phosgene gas (COCl_2) can be synthesized in the reaction represented by the following equation.



- (a) Complete the Lewis diagram for phosgene in which the formal charge on each atom is zero. Include all bonding and nonbonding valence electrons.
- (b) A student claims that the hybridization of the carbon atom is the same in CO and COCl_2 . Do you agree or disagree with the student's claim? Justify your answer in terms of the hybridization of the C atom in each structure.
- (c) When CO and Cl_2 are combined, no reaction is observed to occur. The reaction is initiated by exposing the reactants to ultraviolet light that has a frequency of $8.67 \times 10^{14} \text{ s}^{-1}$. Calculate the energy of 1.00 mol of photons at this frequency. Include units with your answer.

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DO NOT WRITE ON THIS PAGE.

STOP

END OF EXAM

**IF YOU FINISH BEFORE TIME IS CALLED,
YOU MAY CHECK YOUR WORK ON THIS SECTION.**

THE FOLLOWING INSTRUCTIONS APPLY TO THE COVERS OF THIS SECTION II: FREE RESPONSE BOOKLET. MAKE SURE YOU HAVE DONE THE FOLLOWING:

- **COMPLETED THE IDENTIFICATION INFORMATION AS REQUESTED ON THE FRONT AND BACK COVERS OF THIS FREE RESPONSE BOOKLET**
- **CHECKED THAT YOUR AP ID LABEL IS IN THE BOX ON THE FRONT COVER**

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