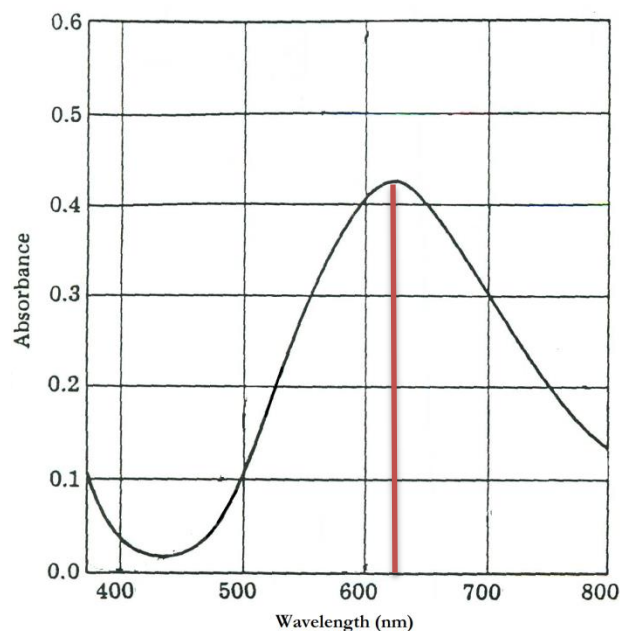
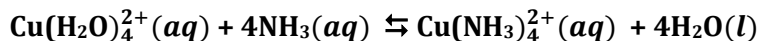


PART I: EQUILIBRIUM**Part A: Formation of a Complex Ion**

Anhydrous copper(II) sulfate is white, whereas hydrated copper(II) sulfate is blue. The structure of the hydrated compound is more accurately represented by the chemical formula $[\text{Cu}(\text{H}_2\text{O})_4]\text{SO}_4 \cdot \text{H}_2\text{O}$, where four of the water molecules are bound directly to the copper(II) ion and the fifth is a water of crystallization. When ammonia is added to a solution of the light blue copper(II) cation, a deep blue color is formed immediately. The blue color is due to ligand exchange between the water and the ammonia, as shown by the following equilibrium expression.



The absorption spectrum of the tetraamminecopper(II) cation, $\text{Cu}(\text{NH}_3)_4^{2+}$, is shown to the left, and it is the primary copper species in solution when up to 5M NH_3 was been achieved.

1. Identify the optimal wavelength of absorption of the tetraamminecopper(II) cation.

620 nm (± 5 nm)

2. Identify the color of the visible spectrum in which the cation absorbs the maximum amount of energy.

Red to orange

3. Explain why the tetraamminecopper(II) solution appears blue.

The solution is absorbing the red/orange wavelengths of visible light and all of the other colors pass through the solution; therefore, the eye would see a mixture of the remaining colors (i.e. blue). Blue would be seen since it is the complementary color to red-orange.

4. Write the mass action expression for this equilibrium process.

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}(\text{H}_2\text{O})_4^{2+}][\text{NH}_3]^4}$$

5. Explain how the addition of nitric acid will affect the equilibrium position in the formation of the tetraamminecopper(II) cation, as shown on the previous page.

The H⁺ ions react with the ammonia in solution decreasing its concentration. The equilibrium will therefore shift to the left, causing some of the tetraamminecopper(II) ion to be consumed and the solution to become lighter.

OR

The H⁺ ions break up the tetraamminecopper(II) complex causing the formation of NH₄⁺ and Cu²⁺ ions. The reaction mixture will reestablish a new equilibrium position based on the value of K_f since the concentrations of the reactants and products have changed.

6. The formation constant, K_f, for the tetraamminecopper(II) ion is 2.1 x 10¹³ at 298K. What is the concentration of Cu²⁺(aq) ions in a solution when 0.00150 mol of CuSO₄ is added to 1.00L of 1.25 M NH₃?

The K_f is huge; therefore, it can be assumed that all of the copper is used to form the tetramminecopper(II) ion. However, we now this not to be true as a small degree of dissociation will occur since an equilibrium position needs to be established.

| | | | | | | |
|---|---|---------------------------------|----------------------|--|---|---------------------------------|
| $\text{Cu}(\text{H}_2\text{O})_4^{2+}(\text{aq})$ | + | $4\text{NH}_3(\text{aq})$ | \rightleftharpoons | $\text{Cu}(\text{NH}_3)_4^{2+}(\text{aq})$ | + | $4\text{H}_2\text{O}(\text{l})$ |
| 0 | | 1.25 M - 0.00600 M | | 0.00150 M | | ---- |
| +x | | +4x | | -x | | ---- |
| x | | 1.25 - 0.00600 + 4x ≈ 1.25 M | | 0.00150 - x ≈ 0.00150 M | | ---- |

The initial concentration of the tetraamminecopper(II) ion will therefore be 0.00150 M. The initial concentration of the ammonia will be slightly less than the initial 1.25 M; however, since it is used in great excess, the concentration of the ammonia can be approximated to be essentially the same as the initial amount.

$$K_f = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}(\text{H}_2\text{O})_4^{2+}][\text{NH}_3]^4}$$

$$2.1 \times 10^{13} = \frac{[0.00150 \text{ M}]}{[x][1.25]^4}$$

$$[\text{Cu}^{2+}] = 2.9 \times 10^{-17} \text{ M}$$

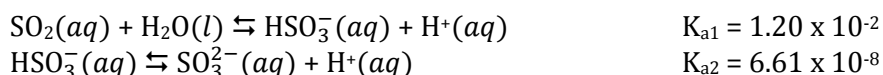
7. The formation constant, K_f , of tetraamminecadmium(II) is 1.3×10^7 at 298K. In which of the complex ions, $\text{Cu}(\text{NH}_3)_4^{2+}$ or $\text{Cd}(\text{NH}_3)_4^{2+}$, are the ammonia ligands attached through stronger coordinate covalent bonds to the center metal cation? Explain your answer.

The lower K_f value for tetraamminecadmium(II) indicates that a larger concentration of ammonia molecules is present in the equilibrium mixture. This implies that the degree of dissociation (the reverse reaction of formation) must be greater for the tetraamminecadmium(II), so the coordinate covalent bonds must be weaker in this complex. The tetraamminecopper(II) ion has the stronger coordinate covalent bonds.

Part B: Acid Rain

The pH value of pure water is 7.0, whereas natural rainwater is weakly acidic. This is caused by dissolution of atmospheric carbon dioxide. In many areas, however, rainwater is more acidic. This has many causes, some of which are natural and some of which derive from human activity. In the atmosphere, sulfur dioxide and nitrogen monoxide are oxidized to sulfur trioxide and nitrogen dioxide, respectively, which react with water to give sulfuric acid and nitric acid. The resulting so-called "acid rain" has an average pH value of 4.5. Values as low as 1.7 have, however, been reported.

Sulfur dioxide is a diprotic acid in aqueous solution. At 25°C, the acidity constants are



The solubility of sulfur dioxide gas at 25°C is 33.9 liters in one liter of water at a sulfur dioxide partial pressure of 0.987 atm. The pH of the saturated solution is 0.91.

8. Calculate the molar concentration of a saturated sulfur dioxide solution. Assume that the change in volume due to the dissolution of SO_2 is negligible.

$$\mathbf{PV = nRT}$$

$$\mathbf{n = \frac{PV}{RT} = \frac{(0.987 \text{ atm})(33.9 \text{ L})}{(0.08206 \text{ Latm/molK})(298 \text{ K})} = 1.37 \text{ mol sulfur dioxide}}$$

$$\mathbf{M = \frac{n}{V} = \frac{3.63 \text{ mol}}{1 \text{ L}} = 1.37 \text{ M}}$$

9. Calculate the percentage of bisulfite ions in a saturated solution of sulfur dioxide.

The second dissociation will not occur as readily since K_{a2} is much smaller than K_{a1} .

| | | | | | | |
|-------------------|---|-------------------------|----------------------|----------------------|---|------------------|
| $\text{SO}_2(aq)$ | + | $\text{H}_2\text{O}(l)$ | \rightleftharpoons | $\text{HSO}_3^-(aq)$ | + | $\text{H}^+(aq)$ |
| 1.37 M | | ----- | | 0 | | 0 |
| -x | | ----- | | +x | | x |
| 1.37 - x | | ----- | | x | | x |

One should not assume that the change in x will be negligible in this equilibrium system, so the quadratic equation is needed, if solved through the equilibrium method.

$$K_{a1} = \frac{x^2}{1.37 - x} = 1.20 \times 10^{-2}$$

$$x^2 = 1.20 \times 10^{-2}(1.37 - x)$$

$$x^2 = 0.0164 - 0.0120x$$

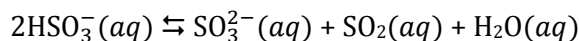
$$x^2 + 0.0120x - 0.0164 = 0$$

$$x = 0.122 \text{ M HSO}_3^-$$

$$\% \text{ comp} = \frac{0.122 \text{ M}}{1.37 \text{ M}} \times 100 = 8.91 \%$$

N.B. The equilibrium method is not needed. One can use the pH, since the $[\text{H}^+] \approx [\text{HSO}_3^-]$ in the saturated solution. $[\text{H}^+] = 10^{-0.91} = 0.123 \text{ M}$.

10. The dominant equilibrium in an aqueous solution of bisulfite ions is shown below:



Calculate the equilibrium constant for this equilibrium.

$$K = K_{a2} \times 1/K_{a1} = (6.61 \times 10^{-8})(1/1.20 \times 10^{-2})$$

$$K = 5.51 \times 10^{-6}$$

11. Calculate the pH of a 0.0100 M aqueous solution of sodium sulfite.

Sulfite is the conjugate base of the bisulfite ion. $K_b = K_w/K_{a2} = 1.51 \times 10^{-7}$

| | | | | | | |
|--------------------------------|---|--------------------------|----------------------|----------------------|---|-------------------|
| $\text{SO}_3^{2-}(aq)$ | + | $\text{H}_2\text{O}(aq)$ | \rightleftharpoons | $\text{HSO}_3^-(aq)$ | + | $\text{OH}^-(aq)$ |
| 0.0100 M | | ---- | | 0 | | 0 |
| -x | | ---- | | +x | | +x |
| 0.0100 - x ≈ 0.0100 | | ---- | | x | | x |

$$K_b = \frac{x^2}{0.0100} = 1.51 \times 10^{-7}$$

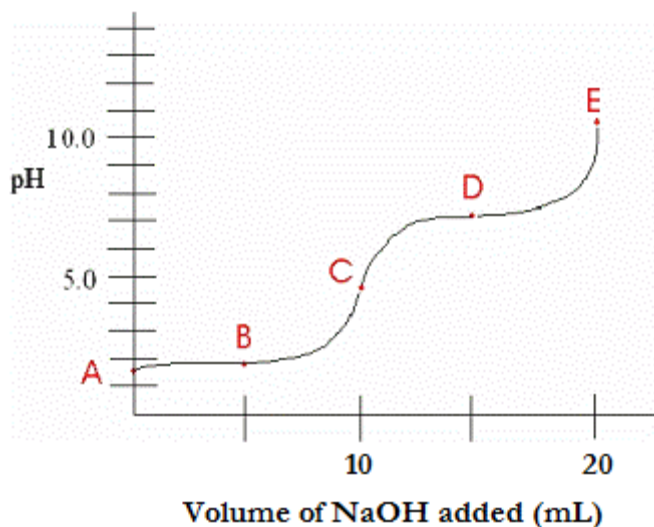
$$[\text{OH}^-] = 3.89 \times 10^{-5}$$

$$\text{pOH} = 4.41$$

$$\text{pH} = 14 - \text{pOH} = 9.59$$

Part C: Titration

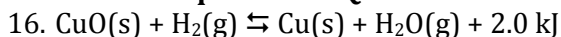
An unknown sample is titrated against a 0.40M NaOH solution. The titration curve is to the right is collected..



12. What type of titration does this curve represent?
- A weak monoprotic acid by a strong base.
 - A weak diprotic acid by a strong base.**
 - A weak triprotic acid by a strong base.
 - A weak diprotic base by a strong acid.
 - A strong monoprotic acid by a strong base.
13. If point B has a pH of 1.85 and point D has a pH of 7.19, what is the concentration of the major pH-determining species present at point C? **Species = H⁺ from first dissociation**
- 1.41×10^{-2} M
 - 3.02×10^{-5} M pH at C = $(pK_{a1} + pK_{a2})/2$ which is $(pt\ B + pt\ D)/2$**
 - 6.46×10^{-8} M
 - 6.21×10^{-10} M
14. If 20 mL of the 0.4 M titrant were added to reach point E, and the total volume at point E is 35 mL, what was the initial concentration of the unknown sample at point A?
- 0.800 M
 - 0.533 M
 - 0.267 M Requires 0.008 mol OH⁻ so 0.004 mol H₂A must be present in 15 mL**
 - 0.229 M
 - 0.114 M
15. A student is given a 0.10 M solution of the unknown sample. She uses 100 mL of the unknown sample and titrates it completely with 0.1 M NaOH. A similar-shaped titration curve, as shown above, is obtained. Calculate the pH at point E of this second titration.
- 4.09
 - 7.50
 - 8.66
 - 9.85 Will need 200 mL equimolar base and the pK_{b2} (from question 13)**
 - 10.1

Place the appropriate letter of the answer to the questions in the boxes below.

| | | | | | | | |
|-----|----------|-----|----------|-----|----------|-----|----------|
| 12. | B | 13. | B | 14. | C | 15. | D |
|-----|----------|-----|----------|-----|----------|-----|----------|

Part D: General Equilibrium Questions

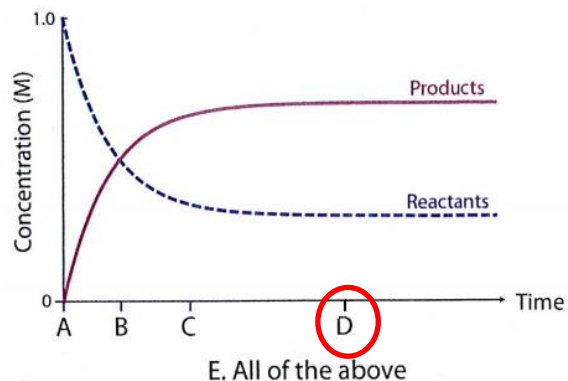
When the substances in the equation above are at equilibrium at pressure P and temperature T, the equilibrium can be shifted to favor the formation of the products by

- increasing the pressure by means of a moving piston at constant temperature
 - increasing the pressure by adding an inert gas such as argon
 - decreasing the temperature of the system**
 - allowing some gases to escape at constant pressure and temperature
 - adding a catalyst
17. Consider the following equilibrium system: $\text{C(s)} + \text{CO}_2\text{(g)} \rightleftharpoons 2\text{CO(g)}$
Given the data at constant volume below, which of the following statements about this equilibrium process is false?

| Temperature ($^{\circ}\text{C}$) | Percent CO(g) | Percent CO ₂ (g) |
|------------------------------------|---------------|-----------------------------|
| 850 | 93.77 | 6.32 |
| 950 | 98.68 | 1.32 |
| 1050 | 99.63 | 0.37 |
| 1200 | 99.94 | 0.06 |

- The reaction is endothermic.
 - The value of K is greater than 1 at all of the temperatures listed.
 - At 850 $^{\circ}\text{C}$, the value of K increases if the volume of the container is increased.**
 - The value of K at 1200 $^{\circ}\text{C}$ is larger than the value of K at 950 $^{\circ}\text{C}$.
 - None of the above statements are false.
18. The gaseous reaction $\text{N}_2\text{(g)} + 3\text{H}_2\text{(g)} \rightleftharpoons 2\text{NH}_3\text{(g)}$ is at equilibrium when the volume is suddenly doubled. Which is true of the reaction quotient Q relative to the equilibrium constant K at the instant that the volume changes?
- $Q = 0.25K$
 - $Q = 0.50K$
 - $Q = K$
 - $Q = 2K$
 - $Q = 4K$ plug $\frac{1}{2}$ concentration into mass action expression**

19. At which of the points to the right can the reaction be considered to be at equilibrium?



Place the appropriate letter of the answer to the questions in the boxes below.

| | | | | | | | |
|-----|----------|-----|----------|-----|----------|-----|----------|
| 16. | C | 17. | C | 18. | E | 19. | D |
|-----|----------|-----|----------|-----|----------|-----|----------|

Part E: Solubility of Calcium Hydroxide

20. Determine the solubility of calcium hydroxide under each of the following conditions. The solubility-product constant of calcium hydroxide is 5.00×10^{-6} and its molar mass is 74.1 g/mol. Show any calculations in the space which follows the table.

| | Pure water | 0.1 M $\text{Ca}(\text{NO}_3)_2$ | pH = 12.00 buffer |
|---------------------|------------|----------------------------------|----------------------|
| Solubility (g/L) | 0.800 | 0.262 | 3.71 |

$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2$$

- $K_{sp} = x(2x)^2 = 4x^3 = 5.00 \times 10^{-6}$
 $x = 0.0108 \text{ mol/L}$
 $(0.0108 \text{ mol/L})(74.1 \text{ g/mol}) = 0.800 \text{ g/L}$
- $K_{sp} = (.1)(2x)^2 = 5.00 \times 10^{-6}$
 $x = 0.00354 \text{ mol/L}$
 $(0.00354 \text{ mol/L})(74.1 \text{ g/mol}) = 0.262 \text{ g/L}$
- $K_{sp} = x(10^{-2})^2 = 5.00 \times 10^{-6}$
 $x = 0.050 \text{ M}$
 $(0.050 \text{ M})(74.1 \text{ g/L}) = 3.71 \text{ g/L}$

PART II: CHEMICAL REACTIONS & STOICHIOMETRY

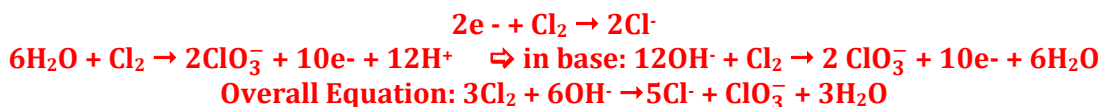
Part A: Potassium Chlorate

Chlorates and perchlorates are used in manufacturing to produce such products as matches, fireworks, and explosives. The first step in the production of potassium chlorate (KClO_3) involves the electrolysis of an aqueous solution of potassium chloride. At the anode, molecular chlorine is produced. At the cathode, hydroxide ions are produced.

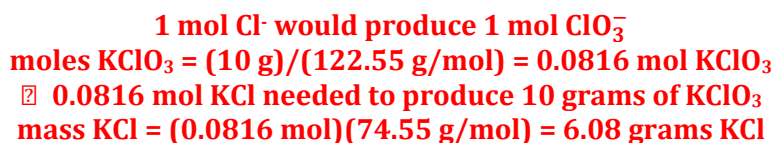
- Write a balanced net ionic equation for the two electrode reactions.



- The chlorine formed at the anode reacts with the hydroxide ions formed at the cathode to form chlorate ions. Write a balanced net ionic reaction for the formation of chlorate ions (and any other products) from molecular chlorine.

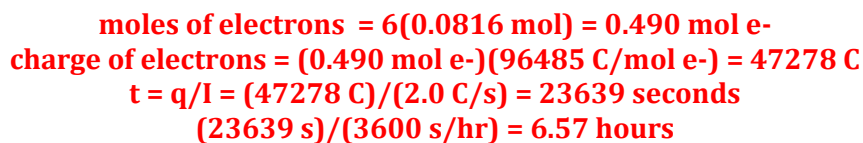


- Calculate the mass of potassium chloride needed to produce 10 grams of potassium chlorate.



- A student sets up an electrolytic cell with a saturated potassium chloride solution and supplies an average current of 2.0 A. How many hours will it take for the student to prepare 10 grams of potassium chlorate?

0.0816 moles ClO_3^- produced from the removal of 6 electrons (1 electron to oxidize initial chloride ion and 5 to oxidize the chlorine molecule to the chlorate ion)



TEAM NAME: _____ **KEY** _____

TEAM NUMBER: _____

Part B: Unknown Solutions

You have been provided four unknown solutions, each containing one of the following solutes:

- calcium nitrate
- sodium carbonate
- sulfuric acid
- sodium chloride

Perform an experiment in order to identify each of the unknown solutions. You have been provided only a pipette and a well plate to use for this portion of the examination.

5. Identify each of the solutions.

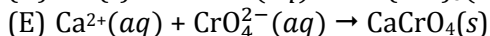
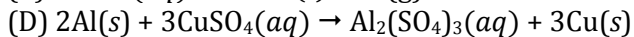
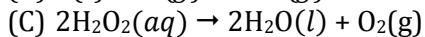
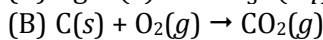
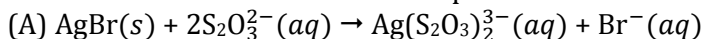
| |
|---|
| Solution A: Na₂CO₃ |
| Solution B: NaCl |
| Solution C: H₂SO₄ |
| Solution D: Ca(NO₃)₂ |

6. For any of the observed chemical reactions in your experiment, write the balanced net ionic equation and identify the driving force for each reaction. Please note that not *all* of the following boxes may be needed to answer the question.

| |
|---|
| Reaction #1: $2\text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2$ OR $\text{H}^+ + \text{CO}_3^{2-} \rightarrow \text{HCO}_3^-$ |
| Driving Force Reaction #1: Formation of a gas (removal of ions from solution) |
| Reaction #2: $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3$ |
| Driving Force Reaction #2: Formation of a precipitate (removal of ions from solution) |
| Reaction #3: $\text{Ca}^{2+} + \text{SO}_4^{2-} \rightarrow \text{CaSO}_4$ |
| Driving Force Reaction #3: Formation of a precipitate (removal of ions from solution) |
| Reaction #4: |
| Driving Force Reaction #4: |

Part C: Types of Chemical Reactions

Questions 7-13 refer to the reactions represented below. The choices may be used more than once.



7. A disproportionation reaction. **(simultaneously oxidized and reduced)**
8. A reaction in which the reaction rate could be increased in the presence of the enzyme catalase.
9. Both a synthesis reaction and a redox reaction.
10. A combustion reaction.
11. A Lewis acid-base reaction resulting in a linear coordination complex.
12. A precipitation reaction.
13. A reaction in which a strong reducing agent forces a cation in solution to react.
14. A reaction which has resulted in an increase of a greenhouse gas in the lower atmosphere.

| Place the appropriate letter of the answer to the questions in the boxes below. | | | |
|---|-----------------|-----------------|-----------------|
| 7. C | 8. C | 9. B | 10. B |
| 11. A | 12. E | 13. D | 14. B |

Part D: Unknown Barium Compound

A student is given a barium halide compound in which she does not know the identity of the halide ion. She dissolves 10.000-grams of the unknown barium compound in distilled water and then dropwise adds a solution of sodium sulfate to form a precipitate. She continues adding the sodium sulfate solution until no additional precipitate is observed. She filters and dries the precipitate, whose mass is determined to be 11.132-grams.

15. Determine the identity of the halide ion. Your answer must include all relevant calculations.



$$\text{moles of BaSO}_4 = (11.132 \text{ grams}) / (233.43 \text{ g/mol}) = 0.0477 \text{ mol BaSO}_4$$

0.0477 mol Ba²⁺ must have been initially present in the unknown compound

Since the substance contains a halide, the formula would be BaX₂, so the number of moles of barium equals the number of moles of the original compound

$$\text{molar mass of cmpd} = (10.00 \text{ g}) / (0.0477 \text{ mol}) = 209.6 \text{ g/mol}$$

$$\text{mass of two halides} = 209.6 - 137.33 = 72.3$$

$$\text{mass of one halide} = 72.3 / 2 = 36$$

The compound contains the chloride ion.

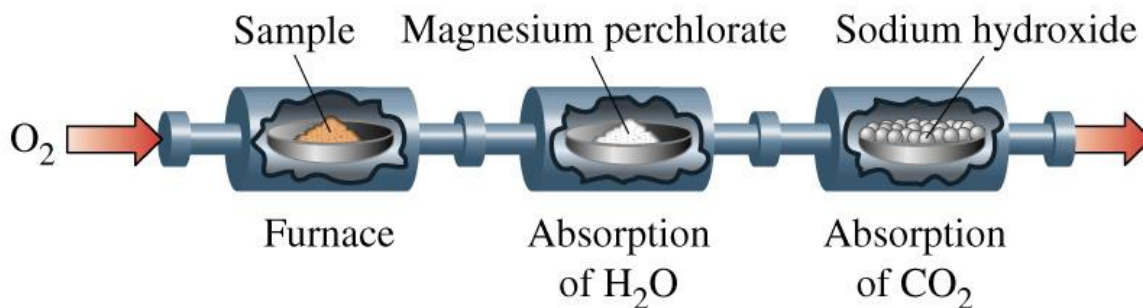
N.B. One can also determine the molecular mass by setting up a proportion between the two given masses and the molar masses since the same ratio will exist between the two barium-containing compounds.

Part E: Unknown Ester

A student prepares a fragrant ester in lab which presents a pineapple-like odor. In order to confirm the molecular formula of her ester, she performs the following two experiments.

Experiment #1: Combustion Analysis

The student places a 100.0-mg sample of the ester in a combustion chamber, as shown below.

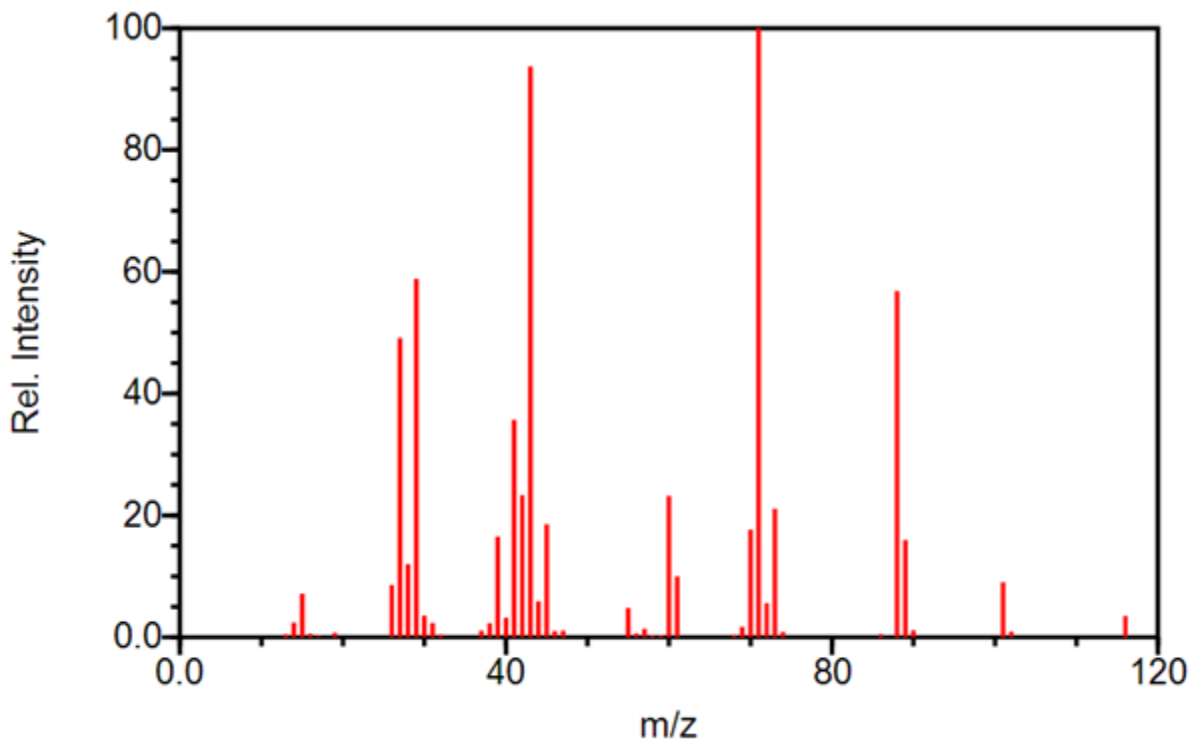


In excess oxygen, the sample is combusted completely. The masses of the magnesium perchlorate and sodium hydroxide sinks are given in the data table below.

| | |
|--|--------------|
| Initial Mass of Magnesium Perchlorate Chamber | 34.321 grams |
| Final Mass of Magnesium Perchlorate Chamber | 34.414 grams |
| Initial Mass of Sodium Hydroxide Chamber | 37.237 grams |
| Final Mass of Sodium Hydroxide Chamber | 37.464 grams |

Experiment #2: Mass Spectroscopy

The student obtained the following mass spectrum of her unknown ester sample.



NIST Chemistry WebBook (<http://webbook.nist.gov/chemistry>)

16. Calculate the number of moles of water absorbed by the magnesium chlorate.

$$34.414 \text{ g} - 34.321 \text{ g} = 0.093 \text{ grams of water}$$
$$\text{moles of H}_2\text{O} = (0.093 \text{ g}) / (18.02 \text{ g/mol}) = 0.00517 \text{ mol H}_2\text{O}$$

17. Calculate the number of moles of carbon dioxide absorbed by the sodium hydroxide.

$$37.464 \text{ g} - 37.237 \text{ g} = 0.227 \text{ grams of carbon dioxide}$$
$$\text{moles of CO}_2 = (0.227 \text{ g}) / (44.01 \text{ g/mol}) = 0.00516 \text{ mol CO}_2$$

18. Write a balanced chemical equation representing the reaction between the sodium hydroxide pellets and the carbon dioxide gas. **NET IONIC NOT NEEDED, BUT ACCEPTED**



19. Determine the empirical formula of the student's ester. Recall that esters contain carbon, hydrogen, and oxygen atoms.

$$(0.00517 \text{ mol H}_2\text{O}) \left(\frac{2 \text{ mol H}}{1 \text{ mol water}} \right) \left(\frac{1.008 \text{ g H}}{1 \text{ mol H}} \right) = 0.0104 \text{ grams H}$$

$$(0.00516 \text{ mol CO}_2) \left(\frac{1 \text{ mol C}}{1 \text{ mol CO}_2} \right) \left(\frac{12.01 \text{ g C}}{1 \text{ mol C}} \right) = 0.0620 \text{ grams C}$$

$$\text{mass of oxygen} = 0.1000 \text{ g} - (0.0104 \text{ g} + 0.0620 \text{ g}) = 0.0276 \text{ grams O}$$

$$\text{moles of O} = (0.0276 \text{ g}) / (16.00 \text{ g/mol}) = 0.00173 \text{ mol O}$$

$$\text{C: } (0.00516 \text{ mol C}) / 0.00173 = 3 \text{ mol C}$$

$$\text{H: } (0.01034 \text{ mol H}) / 0.00173 = 6 \text{ mol H}$$

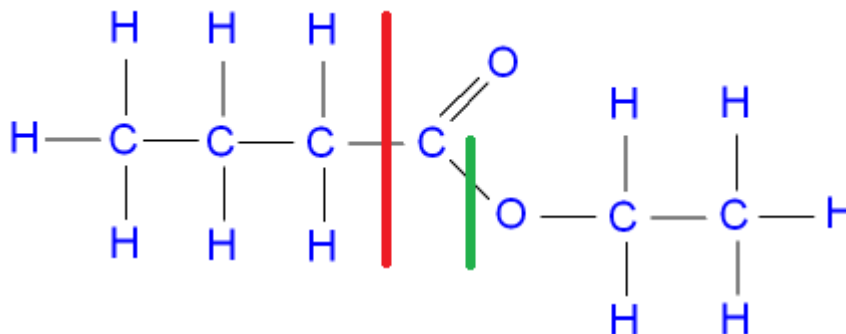
$$\text{O: } 0.00173 / 0.00173 = 1 \text{ mol O}$$

empirical formula: C₃H₆O

20. The student concludes that she has synthesized ethyl butanoate. Use evidence from the two experiments to support or to refute her claim.

The peak of highest mass to charge ratio is approximately 116; therefore, the unknown molecule would have a molecular mass of 116. Ethyl butanoate has the chemical formula C₆H₁₂O₂, which would have the same molecular mass seen from the mass spectrum and the same empirical formula shown in the combustion analysis.

N.B. The two strong peaks at 71 and 43 provide support for the correct structure of the ester as well. The analysis of the individual fragments is not needed for this question; it is only provided for further clarification of the mass spectrum provided. However, students should have been able to utilize the mass spectrum to determine the molecular mass of the unknown ester by looking for the most massive m/z fragment.



If bond broken along red line, peaks around 43 and 73 will be observed. If bond broken along green line, peaks around 45 and 71 will be observed. Both are observed in the mass spectrum provided.

