TEAM NAME: _____ TEAM NUMBER: _____

Islip Invitational 2013
Chemistry Lab Examination

Do not open this booklet until instructed to do so.
Goggles must be worn at all times during this examination.

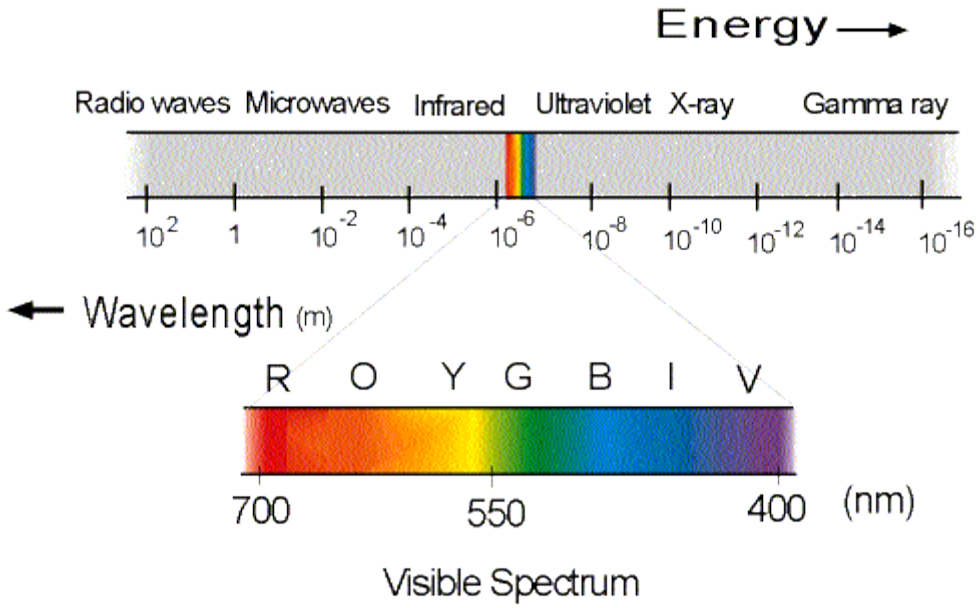
You are allowed to separate the packet and work in any order as long as the packet is stapled in the correct order when submitted to the event supervisor.

Please note that questions 5 & 6 of Part II require the team to perform an experiment. The total points from this section will serve as the first tiebreaker, if needed. Additional tiebreakers will be employed, as appropriate.

Potentially Helpful Information

$\mathcal{F}$ = 96,485 C/mol

$\mathcal{R}$ = 0.08206 L·atm/mol·K



Student Names: _____

_____

TEAM NUMBER: _____

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PERIODIC TABLE OF THE ELEMENTS

1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 16.00	9 F 19.00	10 Ne 20.179
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.938	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.02	89 †Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 § (269)	111 § (272)	112 § (277)						

§Not yet named

*Lanthanide Series	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
†Actinide Series	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

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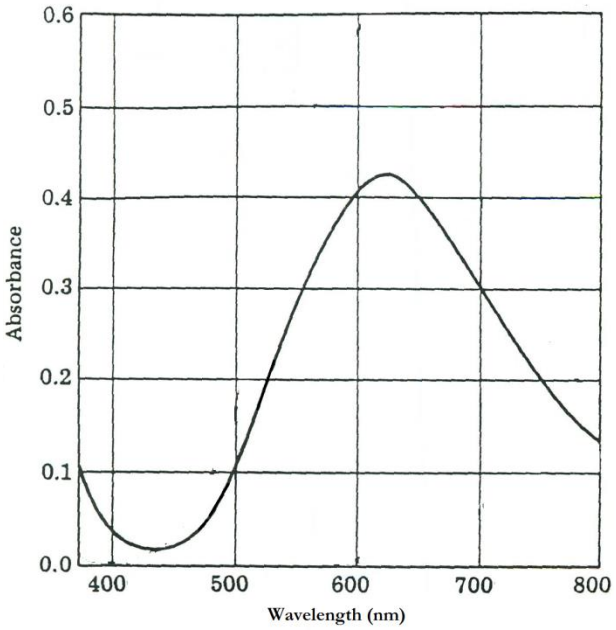
PART I: EQUILIBRIUM

Part A: Formation of a Complex Ion (15 points total)

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 $[Cu(H_2O)_4]SO_4 \bullet H_2O$, 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.

$$\mathbf{Cu(H_2O)_4^{2+}}(aq) + \mathbf{4NH_3}(aq) \leftrightarrows \mathbf{Cu(NH_3)_4^{2+}}(aq) + \mathbf{4H_2O}(l)$$



The absorption spectrum of the tetraamminecopper(II) cation, $Cu(NH_3)_4^{2+}$, 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.

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

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

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

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.

6. The formation constant, K_f, for the tetraamminecopper(II) ion is 2.1×10^{13} at 298K. What is the concentration of $Cu^{2+}(aq)$ ions in a solution when 0.00150 mol of $CuSO_4$ is added to 1.00L of 1.25 M NH_3?

7. The formation constant, K_f, of tetraamminecadmium(II) is 1.3×10^7 at 298K. In which of the complex ions, $Cu(NH_3)_4^{2+}$ or $Cd(NH_3)_4^{2+}$, are the ammonia ligands attached through stronger coordinate covalent bonds to the center metal cation? Explain your answer.

Part B: Acid Rain (13 points total)

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 25^0C, the acidity constants are

$$\mathbf{SO_2}(\boldsymbol{aq}) + \mathbf{H_2O}(\boldsymbol{l}) \leftrightarrows \mathbf{HSO_3^-}(\boldsymbol{aq}) + \mathbf{H^+}(\boldsymbol{aq}) \qquad \mathbf{K_{a1} = 1.20 \times 10^{-2}}$$

$$\mathbf{HSO_3^-}(\boldsymbol{aq}) \leftrightarrows \mathbf{SO_3^{2-}}(\boldsymbol{aq}) + \mathbf{H^+}(\boldsymbol{aq}) \qquad \mathbf{K_{a2} = 6.61 \times 10^{-8}}$$

The solubility of sulfur dioxide gas at 25^0C 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.

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

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

$$\mathbf{2HSO_3^-}(\boldsymbol{aq}) \leftrightarrows \mathbf{SO_3^{2-}}(\boldsymbol{aq}) + \mathbf{SO_2}(\boldsymbol{aq}) + \mathbf{H_2O}(\boldsymbol{aq})$$

Calculate the equilibrium constant for this equilibrium.

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

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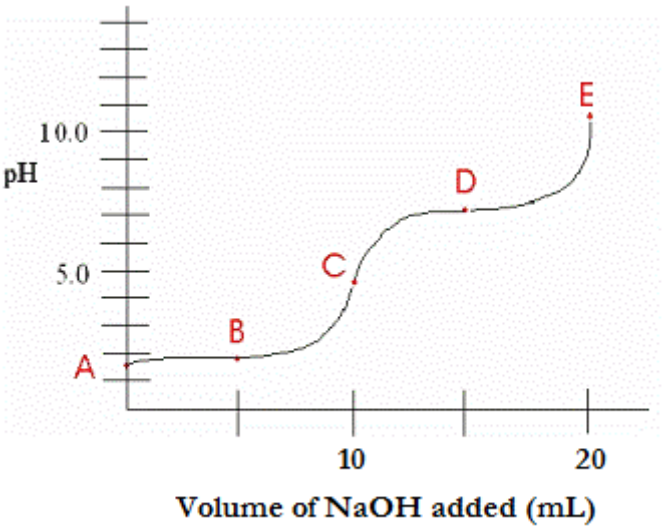
Part C: Titration (8 points total)
An unknown sample is titrated against a 0.40M NaOH solution. The titration curve is to the right is collected.



12. What type of titration does this curve represent?
    a. A weak monoprotic acid by a strong base.
    b. A weak diprotic acid by a strong base.
    c. A weak triprotic acid by a strong base.
    d. A weak diprotic base by a strong acid.
    e. 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?
    a. 1.41×10^{-2} M
    b. 3.02×10^{-5} M
    c. 6.46×10^{-8} M
    d. 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?
    a. 0.800 M
    b. 0.533 M
    c. 0.267 M
    d. 0.229 M
    e. 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.
    a. 4.09
    b. 7.50
    c. 8.66
    d. 9.85
    e. 10.1

Place the appropriate letter of the answer to the questions in the boxes below.			
12.	13.	14.	15.

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Part D: General Equilibrium Questions (8 points total)

16. **$CuO(s) + H_2(g) \leftrightarrows Cu(s) + H_2O(g) + 2.0\ kJ$**
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
    a. increasing the pressure by means of a moving piston at constant temperature
    b. increasing the pressure by adding an inert gas such as argon
    c. decreasing the temperature of the system
    d. allowing some gases to escape at constant pressure and temperature
    e. adding a catalyst

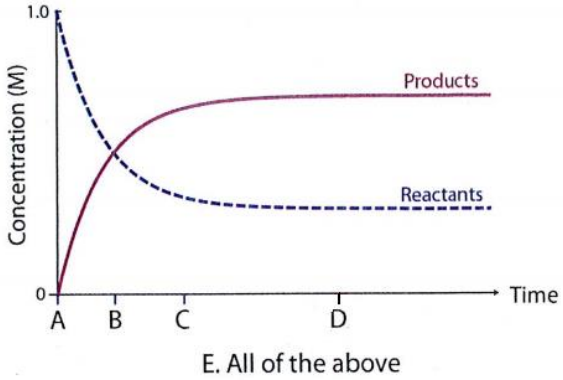
17. Consider the following equilibrium system: **$C(s) + CO_2(g) \leftrightarrows 2CO(g)$**
Given the data at constant volume below, which of the following statements about this equilibrium process is false?

Temperature (^{0}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

    a. The reaction is endothermic.
    b. The value of K is greater than 1 at all of the temperatures listed.
    c. At 850^{0}C, the value of K increases if the volume of the container is increased.
    d. The value of K at 1200^{0}C is larger than the value of K at 950^{0}C.
    e. None of the above statements are false.

18. The gaseous reaction **$N_2(g) + 3H_2(g) \leftrightarrows 2NH_3(g)$** 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?
    a. Q = 0.25K
    b. Q = 0.50K
    c. Q = K
    d. Q = 2K
    e. Q = 4K

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



E. All of the above

Place the appropriate letter of the answer to the questions in the boxes below.			
16.	17.	18.	19.

Part E: Solubility of Calcium Hydroxide (6 points total)

20. Determine the solubility of calcium hydroxide under each of the following conditions. The solubility-product constant of calcium hydroxide is 5.0×10^{-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 $Ca(NO_3)_2$**	**pH = 12.00 buffer**
Solubility (g/L)			

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PART II: CHEMICAL REACTIONS & STOICHIOMETRY

Part A: Potassium Chlorate (10 points total)

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.

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

Cathode:
Anode:

2. 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.

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

4. 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?

Part B: Unknown Solutions (14 points)
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:
Solution B:
Solution C:
Solution D:

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:
Driving Force Reaction #1:
Reaction #2:
Driving Force Reaction #2:
Reaction #3:
Driving Force Reaction #3:
Reaction #4:
Driving Force Reaction #4:

Part C: Types of Chemical Reactions (8 points total)

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

(A) $AgBr(s) + 2S_2O_3^{2-}(aq) \rightarrow Ag(S_2O_3)_2^{3-}(aq) + Br^-(aq)$
(B) $C(s) + O_2(g) \rightarrow CO_2(g)$
(C) $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$
(D) $2Al(s) + 3CuSO_4(aq) \rightarrow Al_2(SO_4)_3(aq) + 3Cu(s)$
(E) $Ca^{2+}(aq) + CrO_4^{2-}(aq) \rightarrow CaCrO_4(s)$

7. A disproportionation reaction.
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.	8.	9.	10.
11.	12.	13.	14.

Part D: Unknown Barium Compound (5 points total)

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.

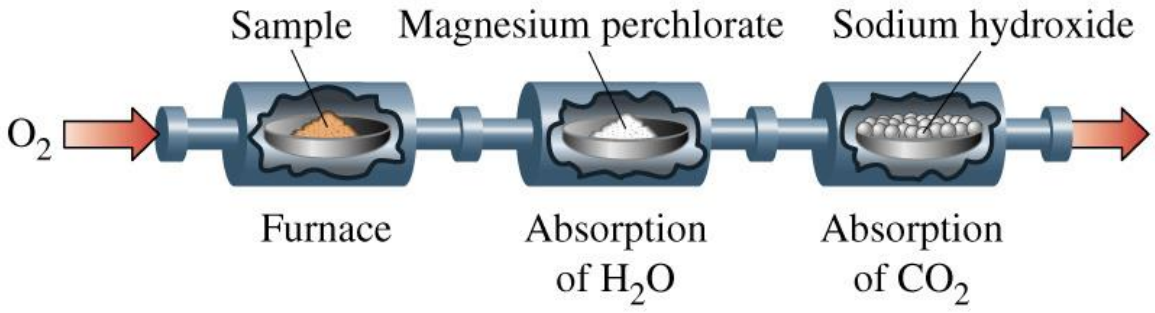
15. Determine the identity of the halide ion. Your answer must include all relevant calculations.

Part E: Unknown Ester (13 points total)

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 experiments.

Experiment #1: Combustion Analysis

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

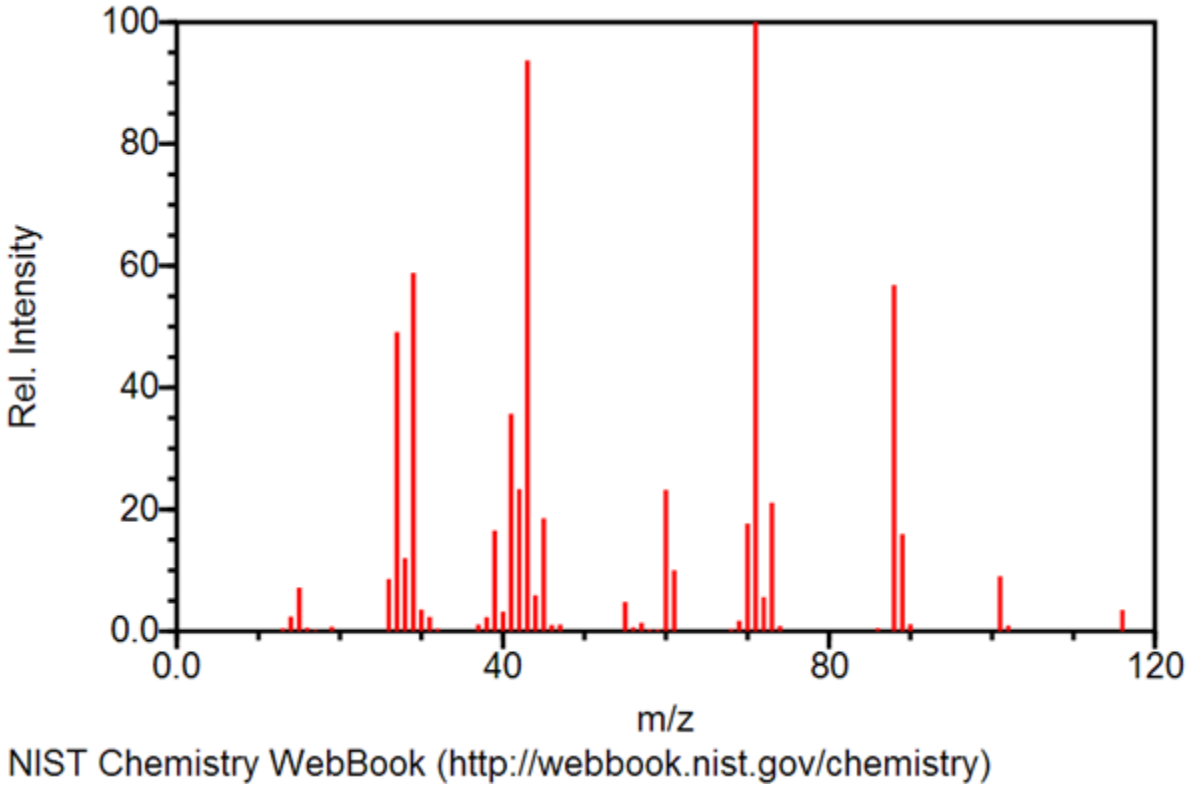


In excess oxygen, the sample is combusted completely. The masses of the magnesium perchlorate and sodium hydroxide sinks are given in the data table below.

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.



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

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

18. Write a balanced chemical equation representing the reaction between the sodium hydroxide pellets and the carbon dioxide gas.

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

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