Experiment 25B

FV 11/3/02

STRUCTURE AND FUNCTIONAL GROUPS: ORGANIC QUALITATIVE ANALYSIS[1]

MATERIALS: Small test tubes; plastic droppers; glass stirring rods; red and blue litmus paper; dropper bottles of conc. H_2SO_4, 5% $NaHCO_3$, 5% HCl, 5% NaOH, ethanolic $AgNO_3$, 1% $KMnO_4$, reagent-grade acetone, diethyl ether, chromic acid reagent and 2,4-DNP reagent.

PURPOSE: The purpose of this experiment is to introduce organic functional groups, and to reinforce concepts of bonding and structure of molecules, by having midshipmen deduce possible structures for unknowns through organic qualitative analysis.

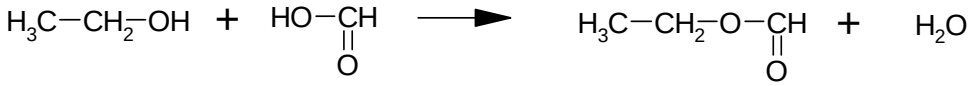
LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate proficiencies in the following areas:

1. Perform semi-micro solubility and chemical tests based on a qualitative analysis scheme supplied.
2. Deduce structural fragments by analysis of results of the qualitative analysis scheme (also known as a flow chart).
3. Draw structural formulas of compounds consistent with the observations from the qualitative analysis.
4. Clearly and logically justify the proposed structures based on experimental evidence.

DISCUSSION:

Principles: Organic chemistry is often described as the "chemistry of carbon". Each carbon atom forms a total of four bonds. If the remaining bonds (those not coupled to another carbon) involve hydrogen atoms, we obtain the hydrocarbons such as propane (C_3H_8) or octane (C_8H_{18}) which are familiar as fuels, or the "plastic" polyethylene, $-(-CH_2-)_n-$, a very long chain polymer where n might be 1000 or more. The length of the carbon chain has an effect on the properties of the material because these molecules interact by London dispersion forces, which increase in strength as the molecule gets larger. For example, propane is a gas, octane is a liquid, and polyethylene is a solid at room temperature. Still, the chemistry (i.e., the chemical reactions) of hydrocarbons is rather limited, in spite of the wide range of chain lengths that are possible. Carbon-carbon double and triple bonds, and bonds to elements like oxygen, nitrogen, sulfur or the halogens, provide for the huge array of chemical and physical properties that is most notable about organic chemistry.

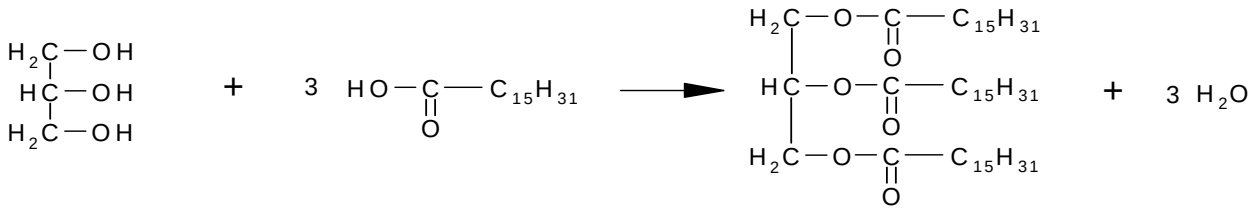
The reactivity of organic compounds is attributed to the bonding arrangements of these groups of bonded atoms within molecules. Such a site of reactivity is called a functional group. There are perhaps twenty-five major functional groups, but we will only consider a few of the most common – sometimes so common that their names have become part of everyday language. Some examples are carboxylic acids, alcohols, esters (as in polyester garments), and ethers (used as an early anesthetic). Members of a functional group often have distinctive features which are readily recognizable. For example, organic acids tend to have a pungent odor (such as vinegar); amines, which are organic bases analogous to ammonia, tend to have a fishy or ammonia-like smell, and esters frequently have a fruity aroma. (Not coincidentally, the natural or artificial flavorings or fragrances of bananas, pineapples, pears, etc. are esters.) Each of the functional groups also has a very characteristic chemistry, regardless of the rest of the molecule – when a compound of that class is in the presence of some particular other reactants, it will usually undergo the same kind of reaction. For example, ethyl alcohol reacts with formic acid to make the ester ethyl formate (which has the scent of rum).



ethanol (an alcohol) — formic acid (a carboxylic acid) — ethyl formate (an ester)

Similarly, a more complicated alcohol like glycerol reacts with a more complicated carboxylic acid like palmitic acid to make another ester, tripalmitin. Glycerol esters are also known as triglycerides, which are biological fats.

[1]adapted from J.H. Cooley and R.V. Williams, *J. Chem. Educ.* **76**, 1117 (1999).



glycerol (an alcohol) palmitic acid (a carboxylic acid) tripalmitin (an ester)

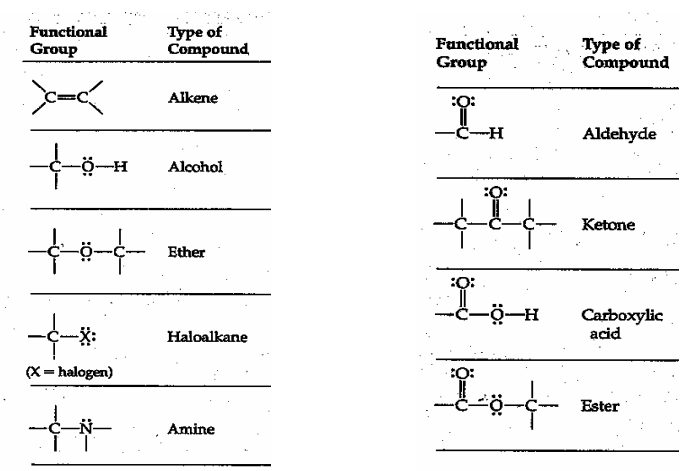
In each case, an acid plus an alcohol produces an ester (plus water). Such characteristic reaction behavior can be used to *identify* the presence of a particular functional group in an unknown compound.

The process of using the known chemical behavior of functional groups to identify an organic compound is called organic qualitative analysis. The word "qualitative" implies that we are not measuring amounts, but instead are monitoring the nature of the materials. Qualitative analysis is a very common procedure; in fact it was the only such process to determine structure before the advent of sophisticated spectroscopic instruments. It is still widely used today – in atmospheric monitoring of confined spaces using "Draeger tubes", and in field tests for alcohol and narcotics, to name a few instances.

The tests in this experiment include solubility tests and chemical reaction tests. Solubility is a good clue to structure, because "like dissolves like". Polar molecules will be soluble in water, which is polar, but not soluble in a hydrocarbon solvent (like octane, which is nonpolar). In most cases, the polarity of an organic molecule is due to the presence of a polar functional group. However, it is possible for a molecule with a polar group to be insoluble in water if it is more 'hydrocarbon-like' than 'water-like'. For example, one polar alcohol group (-OH) on the end of a very long chain hydrocarbon will not provide enough intermolecular attraction with water molecules to overcome the repulsion of the hydrocarbon part. So, in some cases, we can narrow down the identity of a compound not only by the presence of a functional group, but also by the relative size of the molecule.

The chemical tests are more specific than solubility tests, but some of them will still give a positive response to more than one functional group. Note also that, for some functional groups, <u>no</u> single test provides a quick and characteristic product. Such groups can only be identified by deductions based on solubility and the *absence* of positive indications in other functional group tests. The flow charts which accompany this experiment were constructed with such "interferences" and limitations in mind. However, it is always a good idea to do a test on a known compound at the same time that you work with the unknown. Such a process makes clear how a "positive" response to the test will appear.

The goal of this experiment is to use solubility and chemical tests on some unknown organic compounds, and to deduce features about the structures of the molecules from the results of such tests. The possible functional groups include those listed below:



When you know what functional groups are present (and, in some cases, the relative size of the molecule), you should be able to draw a structure that is *consistent with* your observations. Note that there will likely be <u>many</u> such structures that can be drawn for any set of observations, but they will necessarily be members of the same chemical "family" (all esters, for example). To ascertain the exact identity of the unknown would require much more testing than can be done in the limited time available.

PROCEDURE:

Midshipmen will work in pairs; each pair will be given two unknowns, labeled A and B. Record the physical appearance and characteristics of the material such as color, phase, viscosity, odor, etc. first. (*Never smell an unknown compound directly!* Hold the open tube away from your face, and use your hand to gently waft the vapors towards your nose.) Then proceed with the solubility and chemical tests, following the appropriate flow charts. Keep one plastic dropper available for use with each unknown; do not use that dropper for any other material. The testing scheme for unknown A is given in Flow Chart I on p. E25B-5; the possible testing schemes for unknown B appear in Flow Chart II and Flow Chart III, pp. E25B-6,7. For each test, follow the directions given below. Record your observations of the unknown on the attached data sheets. Use the results of the tests to deduce the functional group of your unknown. Known samples for each functional group will be available in bottles marked "Alcohol Standard", "Ketone Standard", etc. When you think you have determined the functional group of your unknown, take a standard from the same category and carry it through the same steps as your unknown to confirm your results.

A Note on Safety: Some of the materials used in this lab are flammable (e.g., ether) or corrosive (e.g., chromic acid solution); some waste materials are incompatible with others (e.g., aqueous vs. organic solutions). Pay careful attention to the directions for each test, including disposal of waste material from the tests. Waste from the chromic acid test and the potassium permanganate test should ONLY be discarded in the Chromic Acid Waste container in the hood. Wastes from ALL other tests should be discarded in the Organic Waste container in the hood. Use the heating bath only in the hood. Wash your hands with soap and water at the end of the lab.

Part A. Tests for Unknown A

1. Record your unknown number and physical characteristics of the unknown. Start with the flow chart on p. E25B-5 to determine which tests to do. Record complete observations of your unknown for each test. If you are unsure whether your unknown showed a positive or negative response to a test, try the test with a known (standard) sample to help you decide. The specific directions for each test are given below.

Water solubility test: To a test tube containing 10 drops of distilled water, add 2 drops of the unknown. Observe closely as you add the sample. Agitate the mixture to ensure mixing. If the resulting mixture is homogeneous, the unknown was soluble; cloudy or unmixed (immiscible) liquid layers or oily droplets on the sides of the test tube indicate insolubility. *Discard waste in the "Organic Waste" container.*

H_2SO_4 solubility test: To a test tube containing 10 drops of concentrated H_2SO_4, add 2 drops of the unknown. Observe closely as you add the sample. Agitate the mixture (with care!) to ensure mixing. If the resulting mixture is homogeneous, the unknown was soluble; cloudy or unmixed (immiscible) liquid layers or oily droplets on the sides of the test tube indicate insolubility. *Discard waste in the "Organic Waste" container.*

Ether solubility test: To a test tube containing 10 drops of diethyl ether, add 2 drops of the unknown. Observe closely as you add the sample. Agitate the mixture to ensure mixing. If the resulting mixture is homogeneous, the unknown was soluble; cloudy or unmixed (immiscible) liquid layers or oily droplets on the sides of the test tube indicate insolubility. *Discard waste in the "Organic Waste" container.*

Silver nitrate ($AgNO_3$) test: To a test tube containing 4 drops of ethanolic $AgNO_3$ reagent solution, add 1 drop of unknown. A precipitate or milky appearance that forms within 2 minutes is a positive test for an alkyl bromide or iodide. If no precipitate forms within 2 minutes, use a water bath (*in the hood*) to heat the mixture to boiling. A precipitate of AgCl is indicative of an alkyl chloride. *Discard waste in the "Organic Waste" container.*

Chromic acid (CrO_3/H_2SO_4) test: Dissolve 1 drop of unknown in 10 drops of reagent grade acetone. To this sample solution, add 1 small drop of chromic acid reagent solution. Agitate the mixture. Formation of a green color (liquid or precipitate) within 5 seconds of addition of the orange-yellow reagent represents a positive indication. (A positive indication for aldehydes may show only a color change rather than a precipitate.) *Chromic acid solution is hazardous. Discard all waste material from this test in the "Chromic Acid Waste" container.*

Potassium permanganate ($KMnO_4$) test: Do this test only if you get a negative result for the Chromic acid test. Dissolve 1 drop of unknown in 10 drops of reagent grade acetone, and add 1 drop 1% aqueous $KMnO_4$ solution with shaking. Formation of a brown precipitate is a positive indication of an alkene. (This may develop slowly for some compounds; give it 1-2 minutes to react.) *Discard waste in the "Chromic Acid Waste" container.*

Part B. Tests for Unknown B

1. Record your unknown number and physical characteristics of the unknown. Start with the flow chart on p. E25B-6 to determine which tests to do. Record complete observations of your unknown for each test. If you are unsure whether your unknown showed a positive or negative response to a test, try the test with a known (standard) sample to help you decide. The specific directions for each test are given below.

Water solubility test: To a test tube containing 10 drops of distilled water, add 2 drops of the unknown. Observe closely as you add the sample. Agitate the mixture to ensure mixing. If the resulting mixture is homogeneous, the unknown was soluble; cloudy or unmixed (immiscible) liquid layers or oily droplets on the sides of the test tube indicate insolubility. *Discard waste in the "Organic Waste" container*.

pH test: Place one strip of Alkacid test paper ("pH paper")on a clean paper towel. Lightly dampen the test strip with distilled water. Dip a clean glass stirring rod in the unknown sample. Apply 1-2 drops of the sample to the test strip and observe the result. Determine the pH range by comparison of the test strip color to the indicator standard colors on the label of the test strip dispenser. Do not confuse an apparent darkening when the strip becomes wet for a color change.

5% $NaHCO_3$ solubility/reactivity test: To a test tube containing 10 drops of 5% $NaHCO_3$, add 2 drops of the unknown. Observe closely as you add the sample. Agitate the mixture to ensure mixing. If bubbles develop, the unknown was soluble or reacted. *Discard waste in the "Organic Waste" container*.

2,4-DNP test: Dissolve 2 drops of the unknown in 10 drops of ethanol, and add 15 drops of 2,4-dinitrophenylhydrazine (2,4-DNP) reagent solution. Mix thoroughly and let stand for a few minutes. A yellow to red precipitate is a positive test. *Discard waste in the "Organic Waste" container*.

5% HCl solubility/reactivity test: To a test tube containing 10 drops of 5% HCl, add 2 drops of the unknown. Observe closely as you add the sample. Agitate the mixture (with care!) to ensure mixing. Cloudy or unmixed (immiscible) liquid layers or oily droplets on the sides of the test tube indicate insolubility. *Discard waste in the "Organic Waste" container*.

5% NaOH solubility/reactivity test: To a test tube containing 10 drops of 5% NaOH, add 2 drops of the unknown. Observe closely as you add the sample. Agitate the mixture (with care!) to ensure mixing. If solid forms or the liquid remains uniform, the unknown was soluble or reacted; immiscible liquids or oily droplets on the sides of the test tube indicate insolubility. *Discard waste in the "Organic Waste" container*.

Clean Up:

1. Discard wastes as described in the directions for each test.

2. *DO NOT WASH or rinse the unknown vials with anything*! Replace the caps to their proper vials, and return the unwashed unknown vials to your instructor.

3. Clean your test tubes, using a wire brush to remove any precipitates.

4. Return all standard samples and test reagents to their original sources.

5. Wipe down your work area of the lab bench with a damp sponge.

Name _____ Section _____

Partner _____ Date _____

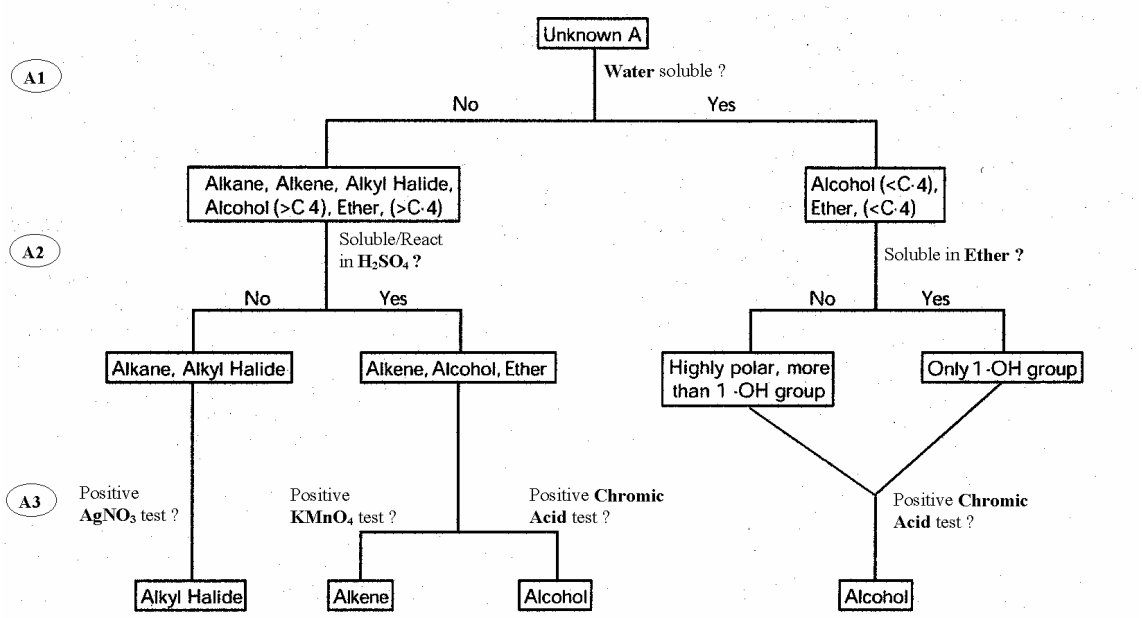
DATA SECTION

Experiment 25B

Unknown number, Sample A _____

Physical properties: _____

On the flowchart below, use a pencil to highlight the path you followed through the analysis of your unknown. On the lines below, identify the tests you performed, and your observations.



Flow Chart I
For Alkane, Alkene, Alkyl Halide, Alcohol, and Ether

Test A1 Identity: _Water Solubility Test__ Observations: _____

_____

_____

Test A2 Identity: _____ Observations: _____

_____

_____

Test A3 Identity: _____ Observations: _____

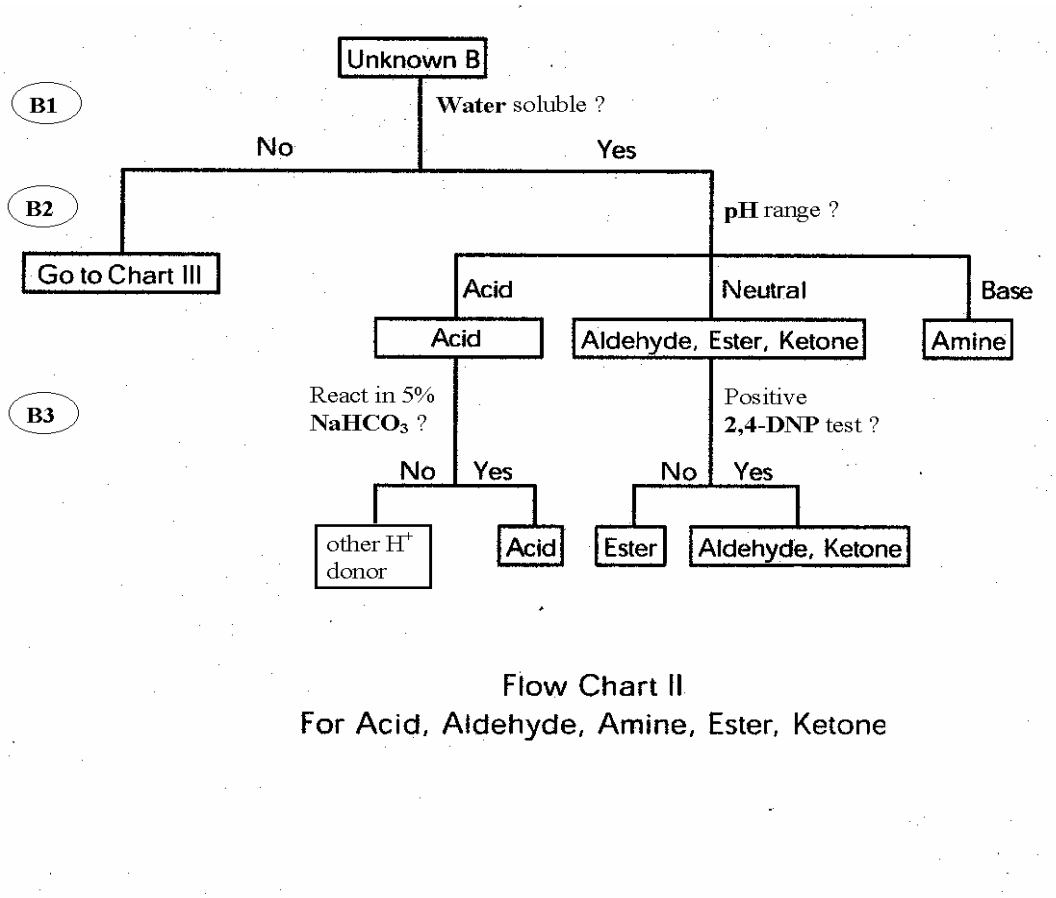
_____

_____

Unknown number, Sample B _____

Physical properties: _____

On the flowchart below, use a pencil to highlight the path you followed through the analysis of your unknown. On the lines below, identify the tests you performed, and your observations.



Flow Chart II
For Acid, Aldehyde, Amine, Ester, Ketone

Test B1 Identity: _Water solubility test___ Observations: _____

_____

_____

Test B2 Identity: ___ pH range test_____ Observations: _____

_____

_____

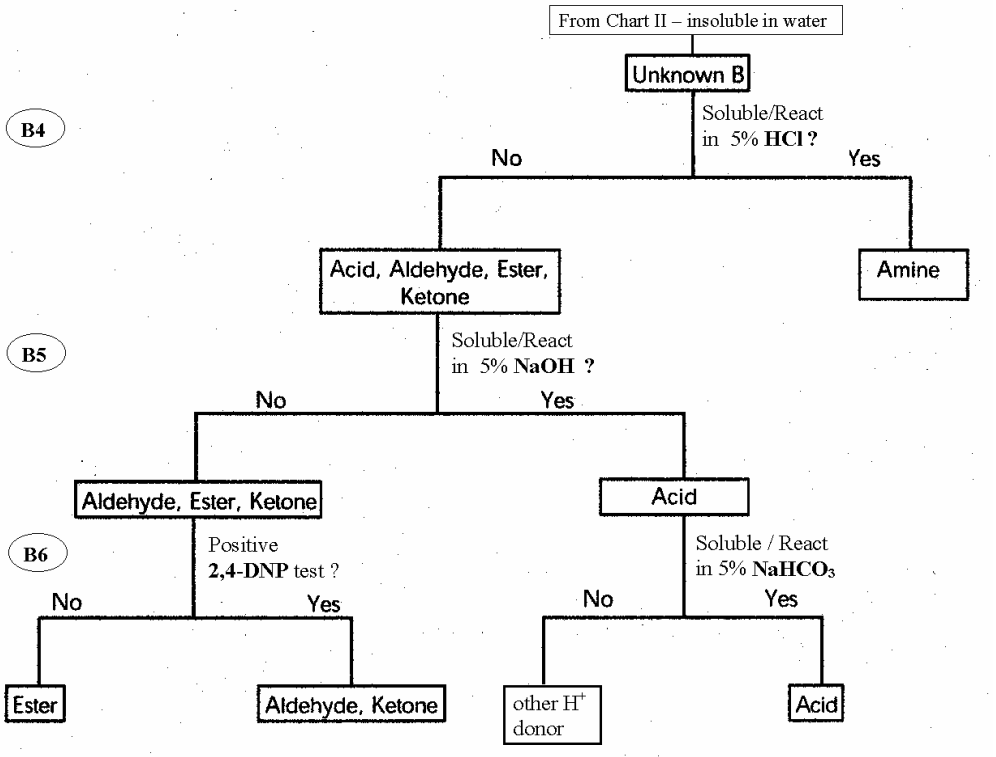
Test B3 Identity: _____ Observations: _____

_____

_____

Unknown number, Sample B _____

On the flowchart below, use a pencil to highlight the path you followed through the analysis of your unknown. On the lines below, identify the tests you performed, and your observations.



Flow Chart III
For Water-Insoluble Acid, Aldehyde, Amine, Ester

Test B4 Identity: __5% HCl test_____ Observations: _____

_____

_____

Test B5 Identity: ___5% NaOH test_____ Observations: _____

_____

_____

Test B6 Identity: _____ Observations: _____

_____

_____

DATA TREATMENT
Experiment 25B

Unknown A.

Unknown number _____

(A.1) According to your tests, what functional group is present in your unknown A? Explain your reasoning.

(A.2) Draw a complete chemical structure (including lone pair electrons) for a compound that is *consistent with* your observations for unknown A.

Unknown B.

Unknown number _____

(B.1) According to your tests, what functional group is present in your unknown B? Explain your reasoning.

(B.2) Draw a chemical structure (including lone pair electrons) for a compound that is *consistent with* your observations for unknown B.

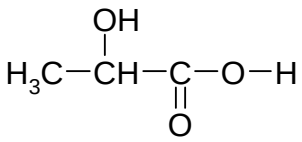
QUESTIONS
Experiment 25B

1. Consider the chemical structures of the various functional groups when you answer these questions.

a. In Flow Chart III, carboxylic acids, aldehydes, esters and ketones all behave the same when subjected to the 5% HCl solubility/reactivity test. What structural features are similar among these four functional groups? How do their structures differ?

b. In Flow Chart III, the 5% NaOH solubility/reactivity test can distinguish carboxylic acids from the other groups mentioned above (aldehydes, esters and ketones). What type of reaction is occurring here for carboxylic acids? Why do aldehydes, esters and ketones not participate in this type of reaction?

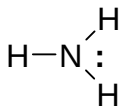
2. a. Write a chemical reaction that shows lactic acid, $C_3H_6O_3$, reacting with OH^-. Be sure to show the structure of the lactate ion product, including both resonance forms. (Lactic acid is a compound produced in the muscles as you exercise; it is also formed in milk when it turns sour.)



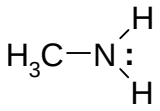
2. b. Lactic acid has more than one functional group. What are the two functional groups in this compound?

2. c. Could two molecules of lactic acid react to form an ester? What would be the structure of that ester? (Hint: see reactions in the discussion section.)

3. Methylamine, CH_3-NH_2, is a weak organic base, related to ammonia, NH_3. For each of these bases, write net ionic equations that describe their neutralization with HCl solution. Be sure to show the structures of the products.



ammonia



methylamine