Chem 220a - Organic Chemistry

Problem Set 1

Chapters 1 and 2

Due: Monday, September 16, 2002

John Dalton

(1766-1844)

John Dalton's formulation of an Atomic Theory in the first decade of the 19th century provided a theoretical basis for understanding chemical behavior. In addition to defining the Law of Multiple Proportions, he also formulated the Rule of Greatest Simplicity, which held that water was a binary compound, OH. (Note: Dalton did not use our modern symbols, which came to us from Berzelius, but rather circles that were distinguishable from one another.) Dalton established the combining masses of H to O in water as ~1:6. This ratio was refined later to 1:8. The Rule of Greatest Simplicity, which was at odds with Gay-Lussac's Law Combining Volumes of Gases, did not lead to a correct formulation for the atomic composition of water. Moreover, although there was agreement regarding the combining masses of atoms in the first half of the nineteenth century, there was disagreement as to the unit mass of the common atoms encountered in organic chemistry: hydrogen (1), carbon (2x6 or 1x12), oxygen (2x8 or 1x16). Since hydrogen was the lightest of the elements, it was assigned a mass of one, a notion that is unrelated to today's mass of hydrogen owing to the presence of a single proton in the hydrogen nucleus. Berzelius's proposal of a mass scale based upon O = 100 would have worked as well.

For a Brief History of Organic Chemistry (PowerPoint), click here.

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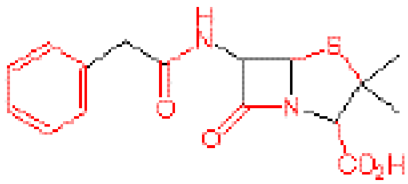
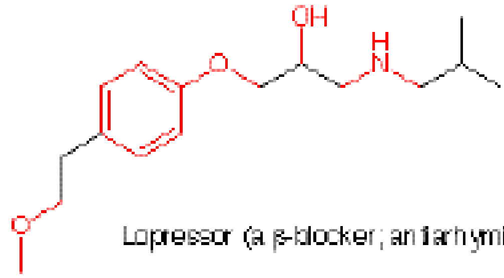
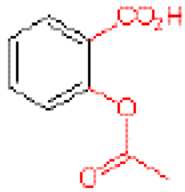
1. Circle and name the functional groups (in red) in each of the following compounds. The inside front cover of your text has a list of functional groups.



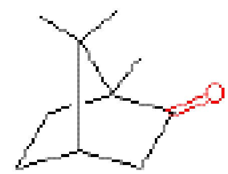
Penicillin G (antibiotic)



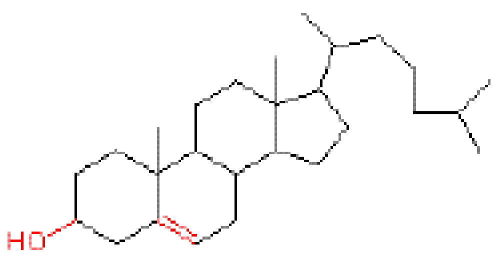
Lopressor (a β-blocker; antiarhymia)



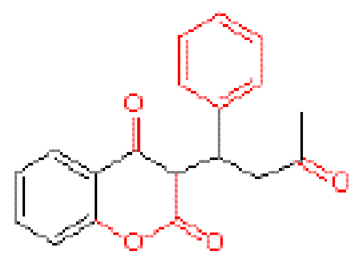
Aspirin (acetylsalicylic acid)
(antiinflammatory, antipyretic, analgesic)



camphor (a terpene)



Cholesterol (a steroid)



Coumadin (warfarin, anticoagulant)

2. In the structure of cholesterol (problem #1), how many primary sp^3 carbons (methyl groups) are present? How many secondary sp^3 carbons (methylene groups)? How many tertiary sp^3 carbons (one hydrogen attached)? How many quaternary sp^3 carbons (no hydrogens attached)? What is the molecular formula of cholesterol?

3. For each of the following acids or bases, identify the corresponding conjugate base or acid.

a) $NaNH_2$ (sodamide)

b) acetic acid

c) NaOH

d) CH_3OH

e) CH_3Li

4. Arrange the acids and conjugate acids #3 in order of decreasing acidity (increasing pKa).

5. The palindromic year 2002 is not only the sesquicentennial of Frankland's studies on valence but also Williamson's landmark work on the structure of ether. Williamson prepared unsymmetrical ethers such as $C_5H_{11}OC_2H_5$ (n-amyl ethyl ether; N.B.: amyl is a common name for a 5-carbon chain). Data from Williamson's paper [*Journal of the Chemical Society*, **1852**, *4*, 229] is shown below. For the ether in question, Williamson derived the empirical and molecular formula $C_7H_{16}O$.

a)Using Williamson's calculated values, determine the atomic masses of C, H, and O that he employed. Assume H =1.00)

b) Using the masses in a), calculate the experimental percentages of C, H, and O based upon the data presented: mass of sample, CO_2, and H_2O. The amount of oxygen is determined by difference.What experimental values do you get? Compare your values with the published values.

c) Using the masses of a) and your percentages in b), compute the empirical formula (assume it is the molecular formula) of the ether. Is there a problem reaching the conclusion that the ether contains 16 hydrogens?

d) Use the ideal gas law to show that d=PM/RT, where d = vapor density and M = molecular weight. Use the experimental vapor density [How many times heavier a given volume of vapor is compared with air.] of the ether and the density of air (you should know the composition of air from general chemistry) to show that the molecular and empirical formulas are the same. All measurements are at the same temperature and pressure.

0·2350 grm. yielded :
0·624 „ of carbonic acid, and
0·276 „ of water ;

or in 100 parts.

	Experiment.	Calculation.	Difference.
Carbon	72·42	72·41	0·01 +
Hydrogen	13·99	13·79	0·20 +
Oxygen	13·59	13·80	0·21 −

Its formula is therefore $\begin{matrix} C_2 H_5 \\ C_5 H_{11} \end{matrix}$ O, or empirically $C_7 H_{16} O$.

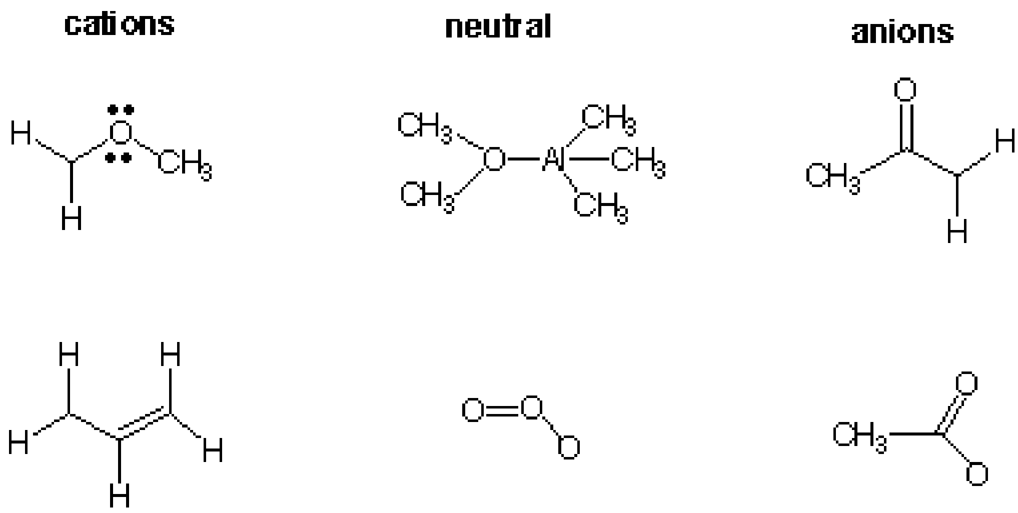
The density of its vapour was found to be :

By Experiment.	Calculation.	Difference.
4·042	4·031	0·011

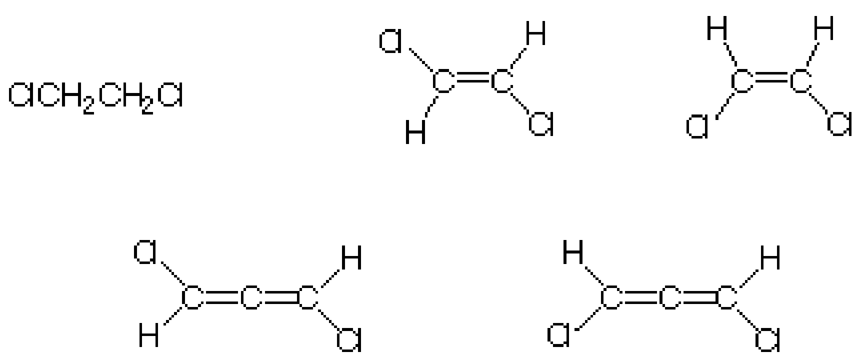
6. a) Draw Lewis structures for the species shown below with all the appropriate electrons and charges.

b) For those structures that are resonance stabilized, draw the two canonical resonance structures. Use the formulas below, not Lewis structures.

c) For the anions, which one is the stronger base? Explain briefly.



7. Which of the following compounds have a net dipole moment? Explain and illustrate.



8. Draw a molecular orbital diagram for the last two structures in #7. Are they identical or are they different. If they are different, in what way are they different?