

# Chemistry 125 Third Examination Answers November 13, 2001

Third Exam: Mean 79.1 (1/3 of grades > 85 ; 2/3 > 79)

Sum of 3 Exams: Mean 219.4 (1/3 of grades > 240 ; 2/3 > 215)

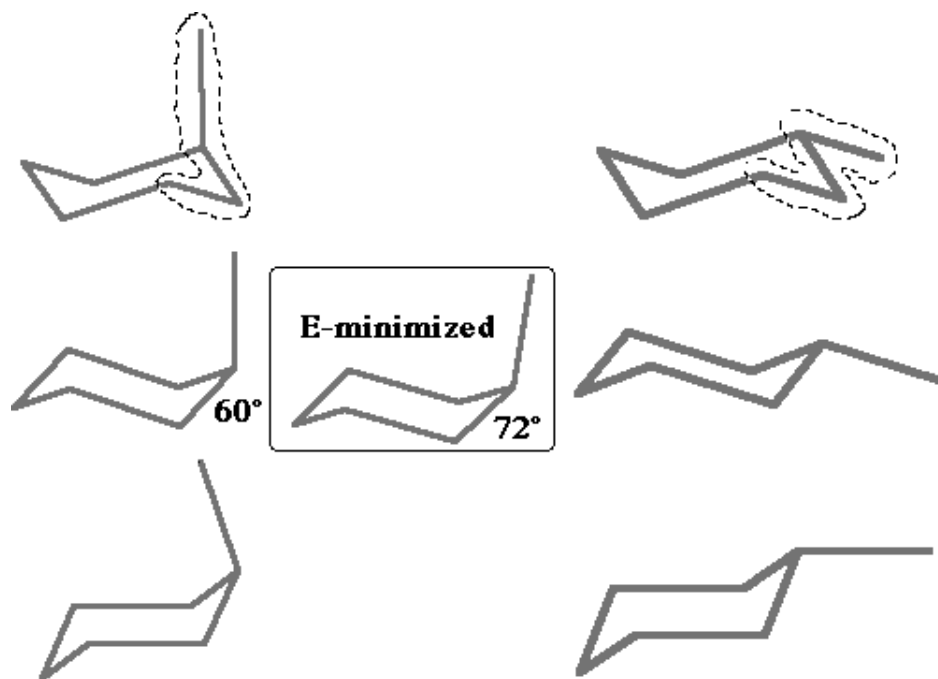
Half of the credit for the semester is based on the final exam, so there is still plenty of opportunity to improve (or slip) dramatically, but to help see where you stand at this point here are the boundaries between letter grades that I would assign on the basis of three hour exams: A 235 A- 220 B+ 200 B 175 B- 150 C+ 125 C- 105

## 1. Methylcyclohexane.

A. (3 minutes) Draw **accurate** representations of the arrangement of the carbon atoms in two conformational isomers of methylcyclohexane and name them. Both isomers should have the chair conformation. [You may omit hydrogens.]

Here we show each conventional conformer in three different views (as well as an axial conformer with its energy minimized by Chem3D). You were expected to draw only one pair. Whatever the view, opposite bonds are parallel to one another within the ring, and the equatorial bond is parallel to next-adjacent ring bonds. The axial bond is perpendicular to the planes containing three non-adjacent ring carbons in the conventional view.

[splayed out a bit in the E-minimized structure - note 72° torsional angle. Conventional views were expected.] It is conventional to view rings from slightly above, as if they are tipped toward the viewer at the top.



I. name AXIAL

II. name EQUATORIAL

N.B. EquAatorial (as in Equator) not EquIatorial.

B. (2 minutes) In each of the structures above circle a chain of four consecutive carbon atoms that includes the methyl group and give the name for the conformation of these two four-carbon chains as if they stood alone as **butane**.

I. name GAUCHE

II. name ANTI

C. (3 minutes) Estimate the energy difference between the two isomers of methyl cyclohexane (kcal/mole). Explain the basis for your estimate.

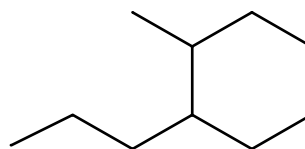
The energy difference between gauche and anti conformers of butane is 0.9 kcal/mole. The axial conformer of methylcyclohexane contains **TWO** gauche butanes where the equatorial conformer has two anti butanes, so the difference between the methylcyclohexanes should be  $2 \times 0.9 = 1.8$  kcal/mole. In fact it is 1.7 kcal/mole by experiment (or 1.77 by Chem3D). Not bad for a crude theory.

D. (3 minutes) Estimate the equilibrium ratio of these isomers of methylcyclohexane (**I/II**) at **room temperature and at 30K**.

The Boltzmann factor gives the equilibrium constant as  $e^{(-\Delta E/RT)}$ , where  $\Delta E$  is the difference in energy between the two species in equilibrium. At room temperature (300 K) this is  $10^{(-3/4 \Delta E)}$ . At 30K T in the denominator would be 1/10 as large so the Boltzmann factor would be  $10^{(-30/4 \Delta E)}$ . The constants would be  $\sim 10^{(3/4 \times 1.8)} = 10^{1.35} \sim 20$  and  $10^{(30/4 \times 1.8)} = 10^{13.5} \sim 3 \times 10^{13}$ .

[The cube root of 10 is about 2 and the square root about 3. The approximations in the theory do not justify higher precision in taking the square root.]

2. (5 min) Give the systematic (IUPAC) name of the compound to the right AND state at least **four principles** that you had to observe in composing the correct name.



Name: **4-Ethyl-3-methylheptane**

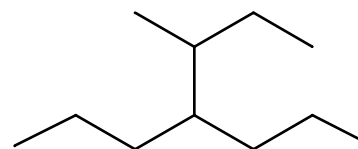
Principles: **Longest straight chain** as root (7 carbons)

**Greek numerical root** for main chain (*heptane*)

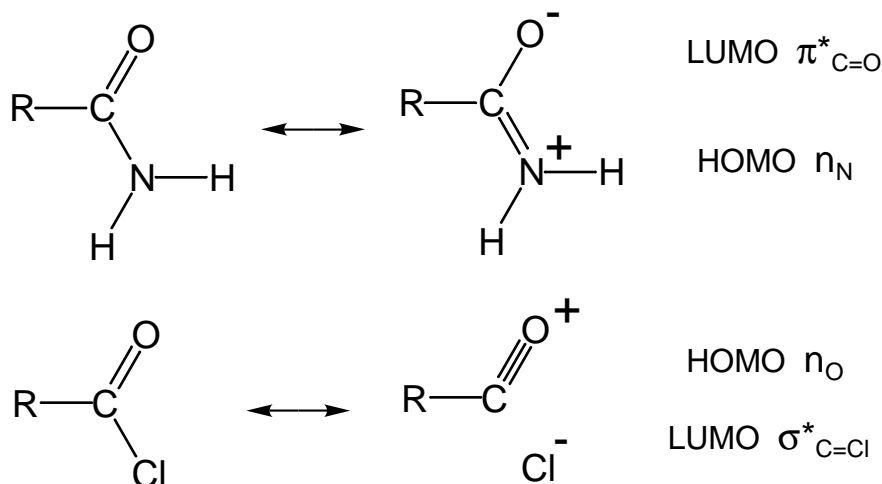
**Alphabetical arrangement** of substituent names (*ethyl* before *methyl*)

Number main chain to give **smallest number at first difference**

[Note: I made a "typo" in drawing the structure. I had intended to draw the structure to the right, which would have been tricky because there are two 7-carbon chains, and one would be forced to choose the less obvious one in order to have the **maximum number of substituents**, which would have been a more sensible "principle" than using a Greek number to name the main chain.]



3. (10 min) **Draw two** important resonance structures of an amide ( $\text{RCONH}_2$ ) **and two** of an acid chloride ( $\text{RCOCl}$ ) to **explain** why their carbonyl IR stretching frequencies differ from that of an aldehyde ( $\text{RCOH}$ ). Next to each charge-separated resonance structure **name the HOMO and the LUMO** whose mixing gave rise to the charge separation. [Hint: relevant generic frequencies, in no particular order, are  $1800$ ,  $1725$ , and  $1690 \text{ cm}^{-1}$ .]



Because of its partial single-bond character (addition of electrons to the antibonding  $\pi^*$  orbital), the carbonyl bond of an amide is weakened and vibrates at a lower frequency ( $1690 \text{ cm}^{-1}$ ) than does that in an aldehyde ( $1725 \text{ cm}^{-1}$ ).

Because of its partial triple-bond character (overlap of O unshared pair with the  $\sigma^*$  orbital of C-Cl), the carbonyl bond of an acid chloride is strengthened and vibrates at a higher frequency ( $1800 \text{ cm}^{-1}$ ) than does that in an aldehyde.

4. (8 min) Sketch **ONE** of the following pieces of apparatus, and explain how it worked (labels would help) and what information it provided:

Lavoisier/Laplace calorimeter

Liebig combustion apparatus

Chupka/Inghram graphite oven.

**Diagrams of these pieces of apparatus are available on the following web pages:**

<http://classes.yale.edu/chem125a/125/history99/2Pre1800/Lavoisier/Instruments/calorimeter.html>

<http://classes.yale.edu/chem125a/125/history99/4RadicalsTypes/Analysis/Liebiganal.html#liebig>

<http://classes.yale.edu/chem125a/125/Thermochemistry/carbonatoms.htm>

Here are some **key features** that you should have mentioned:

**Lavoisier/Laplace calorimeter:**

Provided the heat liberated from an oil by combustion

Oil-burning lamp to supply heat to be measured

Inner can containing ice completely surrounding lamp and separated from it by wire mesh. (Ice must be at 0°C at the beginning of the experiment, so that all heat from lamp melts the ice, rather than warming it.)

Outer can and lid containing ice to shield inner can from heat in the environment (i.e. all melting of ice in inner can must come from the lamp's heat)

Drain from inner can to allow measuring the amount of water generated by melting its ice.

Air supply/exhaust tubes to provide O<sub>2</sub> to support combustion and to exhaust CO<sub>2</sub> product. The supply tube must pass through the outer ice to cool it to 0°C before it enters the combustion volume so as not to bring heat into the sample area. Exhaust tube must pass through ice to be melted so that it leaves this area at 0°C and does not remove heat from the lamp before it is measured.

**Liebig combustion apparatus:**

Measured the weight (mass) of carbon and oxygen contained in a sample by conversion to H<sub>2</sub>O and CO<sub>2</sub>.

Trough containing coals to heat combustion tube

Combustion tube containing sample to be burned mixed with oxidizing agent (CuO)

Tube containing CaCl<sub>2</sub> to absorb H<sub>2</sub>O formed in combustion

"Five-bulb" apparatus containing KOH to absorb CO<sub>2</sub> formed in combustion

A second drying tube beyond the 5-bulb apparatus to collect water lost from this apparatus when there was a strong flow of gas (from formation of nitrogen gas by a nitrogen-containing sample)

The tubes are connect to one another with pieces of rubber tubing to allow easy disassembly for weighing before and after the gas is absorbed.

At the conclusion of the combustion the tube was cooled and the remote tip of the combustion tube was cracked off. Gentle suction at the other end of the "combustion train" pulled the last of the combustion gases into the absorption tubes.

**Chupka/Inghram graphite oven:**

Measured the vapor pressure of carbon atoms in equilibrium with graphite at 2000-2500 K in order to determine the heat of formation of the carbon atom.

Central tantalum oven lined with graphite and pierced by a hole that is very small (1/1500) compared with its surface area, so that gases within the oven are very nearly at equilibrium with the oven walls. (Tantalum the only element with a higher mp and lower vapor pressure than graphite, and it is easily machined.)

Surrounding tungsten filaments from which electrons may be boiled and accelerated by a 1000 volt potential difference to collide with the tantalum oven and heat it to the required temperature.

Tantalum heat shield around the oven to prevent it from excessive loss of radiant heat.

A hole drilled through the tantalum shield and a quartz window to allow viewing the color of the oven so as to determine its temperature.

An electron beam to convert particles exiting the oven into ions.

A mass spectrometer to separate the ions by mass and thus to distinguish carbon atoms from higher aggregates of carbon or other species.

A detector to count the ions.

5. (10 min) Choose **TWO** of the following three concepts. For **each** of these two provide **experimental** evidence **both for and against** its validity. [In all you should mention four experiments.]

Dualism is useful for understanding organic chemistry

Lavoisier's Acid/Base Theory

The proper model of cyclohexane has the carbons in a single plane

#### Dualism:

*For:* persistence of the  $C_7H_5O$  (benzoyl) grouping in a series of compounds produced by chemical transformations from oil of bitter almonds. The persistence suggested that such a "radical" played the role in organic chemistry that elements played in inorganic chemistry. These reactions were regarded as double decomposition reactions of the type that had been observed in inorganic chemistry and involved changing partners with attraction of opposite charges.

*Against:* reaction of acetic acid with chlorine (under illumination) replaced a positive element (H) by a negative one (Cl) and changed the acetyl radical  $C_2H_3O$  into the trichloroacetyl radical  $C_2Cl_3O$ . This showed that organic radicals were not truly the analogues of unchangeable elements they were supposed to be.

#### Lavoisier Acid/Base Theory:

*For:* reaction of elements such as sulfur, carbon, and phosphorus with oxygen generated the corresponding acids. Organic chemistry was supposed to involve compound "organized" radicals to form acids such as benzoic, lactic, and tartaric.

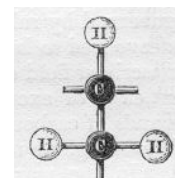
*Against:* If all acids were formed by reacting an elemental radical with oxygen, there should be a muriatic radical that is converted by oxygen to muriatic acid. Ultimately this acid (HCl) was found to be free of oxygen. So it was not true that all atoms were formed by oxidizing radicals.

#### Planar Cyclohexane:

*For:* Only one isomer was known for such monosubstituted cyclohexanes as cyclohexanecarboxylic acid and methylcyclohexane. Non-planar carbon skeletons should make more isomers possible, for example axial and equatorial isomers of substituted chair cyclohexanes.

*Against:* When the arrangement of carbon atoms in diamond was determined by x-ray diffraction in 1918, Mohr (who had not actually done the determination) noticed that they were arranged in the pattern predicted by Sachse for chair cyclohexane. (Note that Sachse's work on cyclohexane was completely theoretical and speculative, not experimental.)

6. (6 min) The picture on the right shows a model used at the conclusion of a 19th century chemistry lecture. **Explain what the model was intended to show.** Give the **date** of the lecture within 10 years. Explain **how this type of model differed** from the type used by Paternó to explain isomerism in the dihaloethanes.



The model was intended to show the **valence** and linking (constitution) of the atoms, and the unsatisfied valences on the top carbon were used to explain the **reactivity** of the "olefiant" gas (ethene) with  $Cl_2$  to give the "oil of Dutch chemists"  $C_2H_4Cl_2$ . (The stand beneath the bottom hydrogen ball was just a stand to hold the model up.)

The lecture was presented by August Hofmann in 1865.

The carbons in Hofmann's models had all four bonds of carbon in a single plane, while those of Paternó had the bonds pointing toward the vertices of a tetrahedron centered on the carbon atom (models of Kekulé). When interpreted as depicting the arrangement of atoms in three dimensions Hofmann's would predict two isomers of a disubstituted methane, while Paternó's would predict a single isomer. Paternó used his models to predict two conformational isomers of 1,2-disubstituted ethanes.

