Chemistry 125 First Semester Final Examination

December 21, 2000

	Average	1/3 Scores greater than	2/3 Scores greater than
Final Exam	235	251	228
Semester Total	461	488	452

1 . (4 min) Write the quantum-mechanical formula for kinetic energy of a particle in one dimension (**NOT** Kinetic E = Total E - Potential E) :

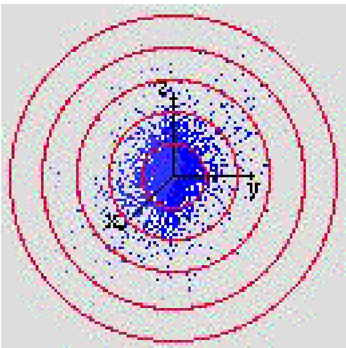
$$KE = \frac{-h^2}{8\pi^2} \times \frac{1}{m} \times \frac{d^2\psi / dx^2}{\psi}$$

Use this kinetic energy formula to **explain** what kind of **potential and total energy** would give a wave function with the shape of an exponential decay **$\Psi = Ce^{-cx}$**, where C and c are constants):

$d^2\Psi/dx^2 = Cc^2e^{-cx}$, thus $(d^2\Psi/dx^2)/ = c^2$, a constant, and the Kinetic Energy is a negative constant times this constant. This would be true for a potential energy that is constant and greater than the total energy.

2. (7 min) A science education website allows high school students to investigate quantum mechanics with the computer. It generates a cloud diagram of electron density from a *1s* orbital by putting 5000 sample dots on the screen in a density that reflects the probability of finding the electron in corresponding regions of 3D space. The student can then press a few keys to count up the electron "probability" dots in concentric shells 50 pm thick and study the electron density distribution.

By pushing buttons I got this figure showing the black probability dots, the 5 shells (the innermost ball is hard to see in black and white) and x,y,z coordinate axes. There was also a table giving the *"Distance Range (pm)"* (inner and outer shell radii) and the *"Electron Density (points)"* that the computer counted in each shell. Let's suppose the count was correct. Here are the results:



Distance Range (pm)	0-50	50-100	100-150	150-200	200-250	Total
Elect. Density (points)	1553	2229	931	233	54	5000

(a) Write the formula that describes a *1s* orbital :

$\psi_{1s} = Ce^{-cr}$, where r is the electron-nucleus distance.

(b) How does this formula relate to Question 1 and the potential energy of a 1-electron atom?

This looks just like the formula in Question 1, except that the x in one-dimensional space is replaced by *r* in 3D space. So it looks a lot like a situation with a constant potential energy higher than the total energy, which is for practical purposes the case for a bound electron far from the nucleus (where 1/*r* is no longer changing significantly, having become practically zero).

[Incidentally note that far from the nucleus along the *x* axis the curvature of the *1s* orbital with respect to *y* and with respect to *z* is practically zero, so it really is practically a one-dimensional problem with curvature only with respect to *r* (*i.e. x*). Near the nucleus Ψ is more curved perpendicular to the radial direction.]

(c) Knowing the formula for an orbital, how do you calculate its electron probability density?

By squaring the value of the orbital.

(d) Explain the mistake in the caption for the second row of data from the instructional web site.

The 1s orbital and its square, the electron density, are obviously maximum at the nucleus, but the table shows the *"Elect. Density(points)"* maximum in the second shell. The reason is that the number of electron "points" in a shell is **not** the electron density, it is the electron density *times the volume of the shell*. The volume of a shell of a given thickness (here 50 pm) increasing with increasing radius of the shell.

3 . (40 min) For each of the eight 20-year periods between 1780 and 1920 cite one major discovery that was important to the developing theory of organic chemistry. In each case **describe the new fact or theory** and try to include: an **experiment or technique** involved , the **name** the discoverer, and **notation** the discoverer used. [Do not use Planck.]

It is not practical to write an answer key for this question. The scoring was 10 points per period:
3 pts. for a major discovery in the proper time period (or at least in the proper sequence)
4 pts. for description of the experimental results or technique
2 pts. for relevant notation
1 pt. for name of the discoverer
Below are given reasonable discoveries for each period - details available from web pages.

1780-1799: Lavoisier combustion analysis and/or calorimetry and/or oxygen theory of acids; Scheele isolation of pure organic acids, new elements, and oxygen)

1800-1819: Dalton proposal of atoms (through meteorology); Berzelius improvement of combustion analysis and of atomic weights, discovery of new elements (through electrolysis - and proposal of dualism), coining of modern element symbols (with superscripts for ratios).

1820-1839: Wöhler discovery of isomerism and destruction of vitalism via urea synthesis; Liebig and Wöhler discovery of benzoyl radical (and radical-dualism theory); also extension of Berzelius work above, and beginning of Dumas Type theory below.

1840-1859: French (Dumas/Gerhardt) halogenation reactions and type theory; Couper/Kekulé tetravalence of carbon and valence in general. (Earnshaw's theorem - though it is not strictly organic)

1860-1879: Hermann's correlation of heat of combustion with molecular structure; Koerner's proof of the equivalence of positions in benzene; van't Hoff's stereochemistry based on tetrahedral carbon.

1880-1899: Baeyer's strain theory for reactivity; Sachse's unstrained chair and boat conformations of cyclohexane; Fischer's system for correlating molecular configurations based on D-glyceraldehyde. Thomson's discovery of the electron is a little less strictly organic.

1900-1919: Lewis's cubic octet and shared pair bonding; Mohr's vindication of Sachse's chair conformation of cyclohexane based on a published (not by Mohr) structure of diamond.

1920-1939: Schrödinger's discovery of quantum wave mechanics to explain atomic structure. Kohler's confirmation of van't Hoff's prediction of allene chirality

Bijvoet's determination of absolute configuration and Barton's conformational analysis did not come on the scene until about 1950, Bürgi and Dunitz analysis of attack on the C=O group was 25 years later still, and scanning probe microscopy came within the last 15-20 years.

4 . (4 min) List **six** sources of strain (or steric) energy evaluated by the molecular mechanics program in *Chem 3D*.

Stretch	Bend
Stretch-bend	Torsion
1,4 van der Waals	non-1,4 van der Waals

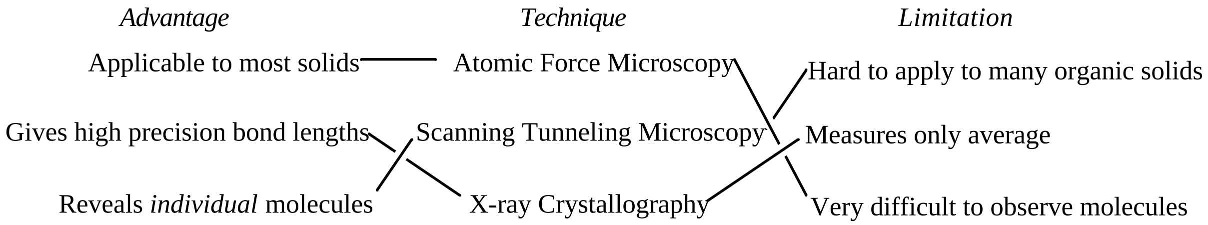
5 . (3 min) **Explain** why bond stretching energy is usually rather small in a strained molecule.

Because it is usually easier to remove strain by distortions that provide less resistance (like bending or torsion). A simple mechanical analogy is that stretching a pair of springs in series puts more energy into the weaker spring, because the stiffer one does not stretch.

6. (4 min) Demonstrate using **experimental evidence** (a picture may help) that the calculation of van derWaals energy by Molecular Mechanics programs (like *Chem 3D*) is oversimplified.

Molecular Mechanics programs usually calculate van der Waals energy by assuming particular van der Waals atomic radii, thus implicitly assuming that there **is** a van der Waals radius - that the non-bonded atom-atom interaction potential is independent of direction. Positions of bromine atoms with respect to neighboring Br-C bonds in molecular crystals shows that intermolecular Br…Br distances are shorter along the C-Br axis than at a substantial angle from it. (see web page)

7. (5 min) **Draw straight lines** to connect each technique in the central column with its advantage in the left column and its limitation in the right column. Then **pick one case and explain** the source of its limitation.



Difficult to observe molecules with AFM because the tip of the probe that "feels" the surface has a radius of curvature that is 10 to 100 times larger that the size of an individual organic molecule.

STM hard to apply to many organic solids because it detects contact with the surface by electrical conductivity and many organic solids are not conductive.

X-ray crystallography measures only an average structure because the diffraction in any given allowed direction comes from scattering by all of the atoms in the crystal with coresponding atoms in every repeating "unit cell" of the structure scattering in phase with one another. Thus the scattering would not be sensitive to misorientation of a single molecule in the crystal.

8. (4 min) Describe **experimental** evidence that contrasts the electron distribution in double bonds with that in single bonds.

Electron "difference" (or "deformation") density plots, generated by subtracting the density expected for spherical atoms from experimental total electron densities (from X-ray diffraction), show the shift of electron density that is associated with bonding. A section of such a plot perpendicular to a single (or triple) bond shows concentric circles of electron density increasing as one approaches the axis of the bond. A corresponding section perpendicular to a double bond shows concentric ellipsoids elongated in the direction perpendicular to the plane of the six atoms including the C=C in the double bond and their substituents.

9. (6 min) Describe a **set of experiments** that would establish the **heat of formation** of benzene assuming nothing can be looked up in the chemical literature. Assume all necessary instruments and pure compounds are available.

In a combustion calorimeter measure the heat liberated by combustion of a given mass of benzene and that liberated by combustion of a mass of graphite and of hydrogen gas (the standard states of the elements) corresponding to the amount of these elements contained in the benzene. The benzene will liberate a smaller amount of heat and the difference is its heat of formation from the elements.

10. (4 min) Explain in statistical terms how entropy influences the equilibrium between chair and "boat" cyclohexane.

The "boat" form of cyclohexane is much more flexible that the chair form and includes about seven times as many structures as the chair. Thus there is a statistical factor of about seven in favor of the boat that partially cancels the Boltzmann factor that favors the chair because of its lower heat content.

11. (5 min) What is "Equipartition of Energy", and what role did it play in Planck's discovery of energy quantization (100 years and 1 week ago today)? (**IRRELEVANT TO FALL 2001)**

Equipartition of energy is the concept that at equilibrium every "degree of freedom" of an atom or molecule must have the same average energy. This was shown to be the most likely distribution by Boltzmann's statistical analysis assuming that energy could be added to the "degrees of freedom" in increments of arbitrary size. Planck found that he could fit the observed spectrum of heated objects by assuming a Boltzmann like distribution with the difference that the energy increments in vibrational degrees of freedom could only be of sizes proportional to the frequency of the oscillator. The large energy increments in high-frequency oscillators are statistically unlikely to be realized, since "focussing" the energy this way cuts down on the number of ways energy can be distributed elsewhere in the sample.

12. (3 min) Suppose at some instant it were possible to prepare a pure sample of ***gauche*** **butane** (maybe Snape and Granger could do it). At room temperature **how long would it take (in seconds)** for the sample to become mostly *anti*-butane?

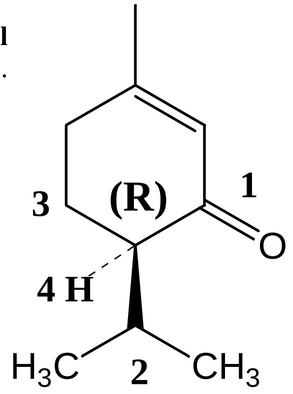
The energy barrier between *gauche* and *anti* butane is about 2.9 kcal/mole above the *gauche* energy minimum (and about 3.8 kcal/mole above the *anti* minimum). The room temperature rate constant is related to the energy of activation by the equation:

$$k \approx 10^{13}\,\text{sec}^{-1} \times 10^{-\frac{3}{4}\Delta H^{*}} \approx 10^{13-2}\,\text{sec}^{-1} = 10^{11}\,\text{sec}^{-1}$$

The time for interconversion is about 1/k (actually the half-life is 0.69/k), so about 10^{-11} sec.

13. ***d*-Piperitone**, which has the odor of peppermint, is a chiral molecule.

a. (8 min) Label its structure on the right with **relevant priority numbers**, and then **label the absolute configuration of its stereogenic center** with the appropriate symbol.



What other two types of stereochemical symbols might be used in naming this enantiomer of piperitone?

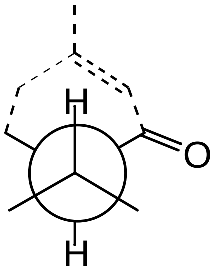
Genetic (D or L)
Phenomenological (+ ; not - , since it is *d-)*

Explain which of these two other systems would have the **more unambiguous** significance:

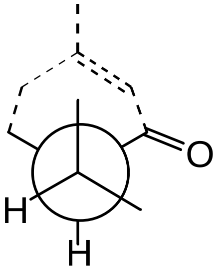
+ means it rotates light to the right which is unambiguous (though not directly related to the absolute configuration in any easily predictable way).

D or L means whether is could be constructed from D- or L-glyceraldehyde. It is not at all clear how the synthesis would work, so this system is ambiguous.

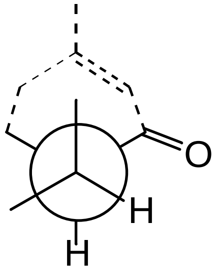
b. (3 min) In the space below **complete three Newman Projections *A*, *B*, and *C*** to show different conformational isomers for rotation of the isopropyl group about the bond that appears as a wedge in the structure of Piperitone above.



A __0__



B __0.58__



C __0.85__

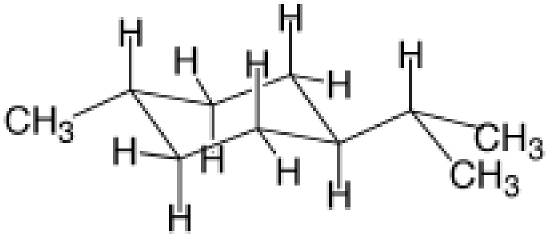
Enter 0, 1, or 2 in each cell of the following table to indicate for each conformation the number of each kind of interaction between methyl groups on the front carbon of the Newman Projections and CH_2 or C=O groups on the back carbon (ignore dashed atoms)

CH_3 Interactions	**A**	**B**	**C**
CH_2 *gauche*	1	1	2
CH_2 *anti*	1	1	0
C=O *gauche*	1	2	1
C=O *anti*	1	0	1

c. (6 min) In the space to the right **draw a chair** structure for

***trans*-1-methyl-4-(1-methylethyl)cyclohexane**

with the 1-methyl group **equatorial**. **Use a convention that shows clearly the location of all carbon and hydrogen atoms** except hydrogens of the methyl groups (which you may write as CH_3).



[Although the shape of the cyclohexane ring is not just the same as that of the cyclohexenone ring of piperitone, this structure should help convince you that the isopropyl group in piperitone will not have substantial steric interaction with the atoms joined by dashed lines in Newman Projections ***A-C***.]

d. (5 min) From the **A-values** in cyclohexane for CH_3 (1.7 kcal/mole) and acetyl, $CH_3C=O$, (1.17 kcal/mole). **Estimate** (within 0.1 kcal/mole) the *gauche-anti* energy differences for CH_3CH_2-CH_2-CH_3 and CH_3CH_2-CH_2-$COCH_3$.

The axial-equatorial energy difference in kcal/mole (A) is roughly twice the difference between *gauche* and *anti* (because conversion from equatorial to axial converts two *anti* conformations to *gauche* ones).
Thus the *gauche-anti* energy difference for the methyl group is about 0.85 kcal/mole, and that for the acetyl group is about 0.58 kcal/mole.

e. (8 min) Use your values from **13d** and the table in **13b** on the **page 6** to estimate differences in energy between the conformations shown by Newman projections ***A***, ***B***, and ***C***. **On page 6 write 0** beneath the Newman structure of the lowest-energy conformer **and the appropriate relative energies** beneath the other two.

Going from A to B converts an *anti* methyl interaction to a *gauche* one (costing 0.85 kcal/mole). Other interactions cancel.
Going from A to C converts and *anti* acetyl interaction to a *gauche* one (costing 0.58 kcal/mole)

Use these relative energy values to **estimate the equilibrium constant** between lowest- and highest-energy Newman structures **at room temperature** and **at 30 Kelvin** (1/10 of room temperature).

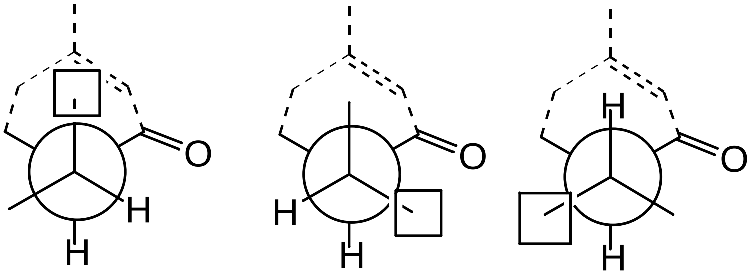
At room temperature the Boltzmann factor $e^{-\Delta H/RT}$ is the same as $10^{-3/4\,\Delta H}$ (with ΔH in kcal/mole). So the equilibrium constant for A going to C at room temperature would be $10^{-.75x0.85} = 10^{-.64}$ (or about 0.2). At 1/10 of room temperature the exponent would be 10 times as large yielding $10^{-30/4\,\Delta H}$, or about $10^{-7.5\Delta H}$. So the equilibrium constant for A going to C would be $10^{-7.5x0.85} = 10^{-6.4}$, fewer than 1 in a million molecules would have conformation C.

f. (4 min) On the multiple choice form below **darken two spots** to indicate both the **configurational** relationship between the **two methyls** of isopropyl in your Newman structure ***A***, and the **type of reagent** that could in principle distinguish between such methyl groups:

The methyls are **configurationally diastereotopic** and thus could be differentiated by **any** type of reagent. [The reason they are diastereotopic rather than enantiotopic is because there is a genuine stereogenic center in the molecule. It happens to be on the carbon next to the carbon to which they are attached, but the distinction would apply wherever in the molecule the stereogenic center was located.]

g. (4 min) **Put a square around one** of the isopropyl methyl groups in your Newman structure ***A*** on p. 6, and write

its systematic **configurational name** here: __________Pro-R__________



[Note that in assigning priorities the boxed group is given a higher priority than the other group it was formerly tied with, but NOT a higher priority that groups that were ahead of it before promotion.]

h. (4 min) Although one might imagine that a natural source would yield a single enantiomer of piperitone, it is racemic when isolated from oil of eucalyptus. Explain how one might hope to resolve such a liquid by chromatography.

Somehow the enantiomers to be separated must be involved in different diastereomeric interactions. This could be either with a chiral resolved stationary solid phase or with a chiral resolved moving solvent phase.

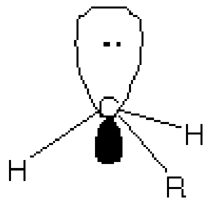
Perhaps during handling the "natural" piperitone had been racemized when a base temporarily removed a proton from the stereogenic carbon next to its carbonyl group, generating a carbon anion, which might become planar rather than pyramidal. Return of the proton could then generate either enantiomer of piperitone. *(See next page for relevant question)*

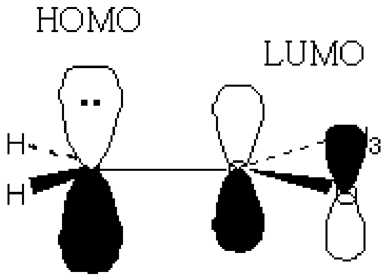
h'. (6 min) At first glance one would expect an anionic carbon to be pyramidal, like NH_3. **Explain** in terms of **orbital energies** why $\mathbf{NH_3}$ is pyramidal and $\mathbf{BH_3}$ is planar.

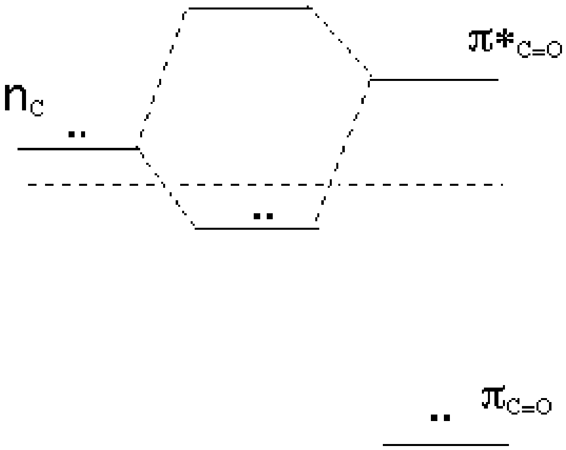
In either case the X-H bonding electrons would be lowest in energy with *sp*^{2} hybridization (planar XH_3), but in NH_3 there is another pair of electrons (the unshared pair) that would have to be in a pure *p* orbital if the hybridization were *sp*^{2}. By going to a pyramidal structure this pair of electrons gains stability (more *s*-character) at the expense of the bonding electrons. It is reasonable to do this because the nitrogen orbital is the sole "home" of the unshared pair, whereas is houses only about half of the bonding pair. That is you remove stabilization from one electron to give it to two electrons. There is of course a limit to this where the loss of overlap (and the repulsion between the hydrogen nuclei) becomes intolerable.

i. (10 min) But a carbon anion attached to a carbonyl group, such as $^-CH_2$-(C=O)-CH_3, might be special both in stability and in stereochemical structure compared to a generic $^-CH_2R$ anion. Explain this in terms of **HOMO/LUMO** interaction (show **shapes AND energies** of mixing orbitals).

A generic $^-CH_2R$ anion should have the unshared pair in a hybridized orbital with even more *s*-character than in NH_3, because the bonding pairs of the C-H bonds spend less time on C than those in the N-H bonds do.

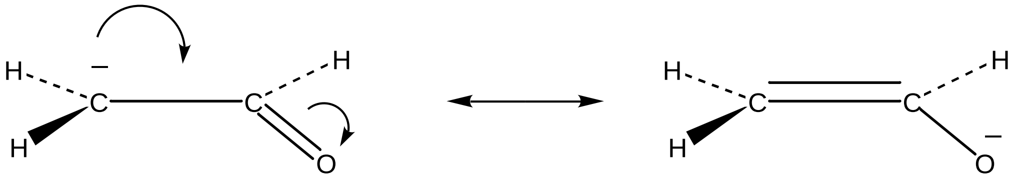






But the unshared pair of electrons on the anionic carbon is unusually high in energy (higher that the pair of N, because of the lower nuclear charge), and the adjacent carbonyl group in the "enolate" anion provides a low LUMO ($\pi^*_{C=O}$) that can stabilize carbon's unshared pair. It can overlap with the orbital of the carbon's unshared pair only to the extent that the pair is housed in a *p*-orbital on carbon (the *s*-orbital is orthogonal to the π^* orbital of the carbonyl group). Thus this particular carbon anion should be planar with its *p*-orbital parallel to the *p*-orbitals of the carbonyl group for maximum overlap.

j. (3 min) Answer the preceding question (**i**) again by drawing resonance structures.



Since resonance structures have the same nuclear arrangement , planarity of the double bond in the right resonance form requires planarity of the "anionic" carbon in the left one.

k. *(3 bonus points)* Explain in orbital terms how the existence of an additional C=C double bond in piperitone might influence the ability of the C=O group to stabilize an adjacent carbon anion.

The LUMO of the C=O group is already being used to stabilize the HOMO of the adjacent C=C bond. This mixing raises the energy of the resulting LUMO and gives it poorer energy match for stabilizing the unshared pair of the carbon anion. (Alternatively you could say that stabilization of the carbon anion by the C=O LUMO makes the LUMO higher in energy and less able to stabilize the π electrons of C=C. Either way there is reduced stabilization for the planar form as compared to what was available without the C=C.)