Chemistry 125 First Semester Final Examination

December 21, 2000

Name ____________________

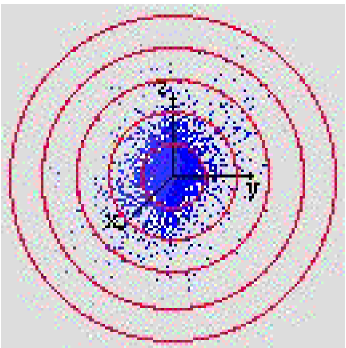
This exam is budgeted for 150 minutes, but you may have 180 minutes to finish it. Good Luck.

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

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 $\mathbf{\Psi = Ce^{-cx}}$, where C and c are constants):

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 :

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

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

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

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.]

1780-1799

1800-1819

1820-1839

1840-1859

1860-1879

1880-1899

1900-1919

1920-1939

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

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

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

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.

Advantage	*Technique*	*Limitation*
Applicable to most solids	Atomic Force Microscopy	Hard to apply to many organic solids
Gives high precision bond lengths	Scanning Tunneling Microscopy	Measures only average structures
Reveals *individual* molecules	X-ray Crystallography	Very difficult to observe molecules

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

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.

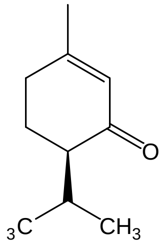
10. (4 min) Explain in statistical terms how entropy influences the equilibrium between chair and "boat" cyclohexane.

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 CHEM 125 FALL 2001)**

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?

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

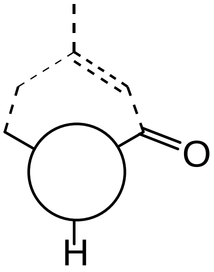
a. (8 min) Label its structure on the right with **relevant priority numbers**, and then **label the absolute configuration of its stereogenic center** with the appropriate symbol.



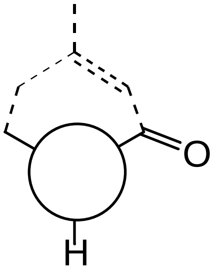
What other two types of stereochemical symbols might be used in naming this enantiomer of piperitone?

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

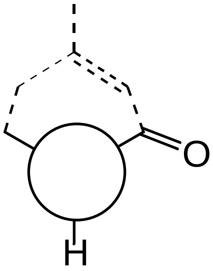
b. (3 min) In the space below **complete three Newman Projections *A*, *B*, and *C*** to show different conformational isomers for rotation of the isopropyl group about the bond that appears as a wedge in the structure of Piperitone above.



A ____



B ____



C ____

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*			
CH_2 *anti*			
C=O *gauche*			
C=O *anti*			

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).

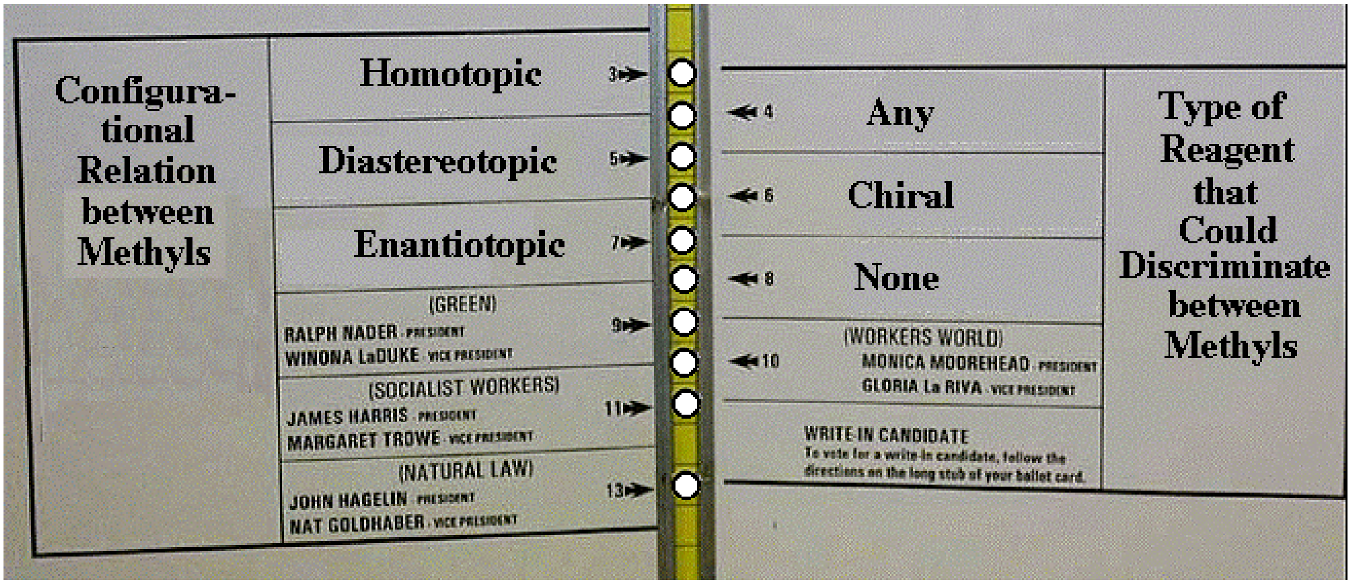
[Although the shape of the cyclohexane ring is not just the same as that of the cyclohexenone ring of piperitone, this structure should help convince you that the isopropyl group in piperitone will not have substantial steric interaction with the atoms joined by dashed lines in Newman Projections ***A*-*C***.]

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-$COCH_3$.

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.

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).

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:



Configurational Relation between Methyls

Homotopic 3➔ ○

Diastereotopic 5➔ ○

Enantiotopic 7➔ ○

(GREEN)
RALPH NADER - PRESIDENT
WINONA LaDUKE - VICE PRESIDENT
9➔ ○

(SOCIALIST WORKERS)
JAMES HARRIS - PRESIDENT
MARGARET TROWE - VICE PRESIDENT
11➔ ○

(NATURAL LAW)
JOHN HAGELIN - PRESIDENT
NAT GOLDHABER - VICE PRESIDENT
13➔ ○

Type of Reagent that Could Discriminate between Methyls

○ ◄4 Any

○ ◄6 Chiral

○ ◄8 None

○ ◄10 (WORKERS WORLD)
MONICA MOOREHEAD - PRESIDENT
GLORIA La RIVA - VICE PRESIDENT

WRITE-IN CANDIDATE
To vote for a write-in candidate, follow the directions on the long stub of your ballot card.

g. (4 min) **Circle one** of the isopropyl methyl groups in your Newman Structure ***A***, and give it a systematic **configurational name**.

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

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 **NH_3** is pyramidal and **BH_3** is planar.

i. (13 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).

Explain again by drawing resonance structures.