Chemistry 125 — First Semester — Name _____

December 16, 2005 — Final Examination

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

1. (52 minutes). ANSWER **13** OF THE FOLLOWING **16** in a blue book. Only the first 13 answers will be graded.

Cite **experimental** evidence that was used to support each of the following chemical principles for the **first** (or nearly the first) time. If the original proposal was hypothetical, cite the experimental evidence that first confirmed it.

Answers (4 min each) need not be detailed, just outline the evidence. Where relevant, try to identify the **specific** molecules studied.

   a) The bond dissociation energy of CO is 257.3 kcal/mole (or maybe 227.3 kcal/mole).
   b) The heat of atomization of graphite is 171 kcal/mole.
   c) The atoms in organic molecules are held together by electrical (dualistic) forces.
   d) The atoms in organic molecules are **not** held together by electrical forces.
   e) The van der Waals shape of atoms is not always spherical.
   f) The substituents in "meta" disubstituted benzenes are on the 1st and 3rd atoms of the hexagonal ring.
   g) The bonds of a tetravalent saturated carbon do not lie in a single plane.
   h) The bonds from a tetravalent saturated carbon atom make a specific preferred angle.
   i) Cyclohexane is planar.
   j) Cyclohexane is not planar.
   k) The properties of molecules are not solely dependent on the number of atoms of the various elements present.
   l) Double bonds have elliptical cross sections.
   m) Carbon is the central atom in methane and holds the four hydrogen atoms to itself.
   n) Long chain compounds adsorbed on graphite lie flat and as straight and parallel as possible.
   o) Some bonds do not involve substantial increase in internuclear electron density relative to the component atoms.
   p) There is a 3 kcal/mole barrier to rotation about the C-C bond in ethane.

2. (5 min) Use the relation of **wave function shape** to potential and total energy to explain why electron energy is sometimes quantized and sometimes not quantized.

3.   (6 min) What **key assumption** did Boltzmann make in applying statistics to the distribution of energy within a set of molecules, **and** how did it lead to the general **shape** of the distribution for a single "degree of freedom"?

4.   (5 min) One may report the energy of a molecule as heat of combustion, as heat of formation, or as heat of atomization. Explain which of these is best suited for developing a simple, practical scheme for relating energy to structural theory.

5.   (8 min) Use the following heats of formation to establish strain energies for the five compounds:

	ΔH_f (kcal/mole)
cyclopropane	+13
cyclobutane	+7
cyclopentane	-20
cyclohexane	-30
cycloheptane	-28

6. (5 min) Explain how cyclohexane distorts from idealized angles in order to minimize its energy. **Repeat** for one of the other molecules in the previous question.

7. (5 min) Explain how it is that "correlation energy" and "strain energy" may be considered to be analogous concepts.

8.   A) (4 min) Draw accurate structures for axial **and** equatorial methylcyclohexane in the chair conformation.

                    Axial   Equatorial

B) (3 min) Use your drawings in part A to illustrate a pair of atoms that are homotopic (**H**), a pair that are enantiotopic (**E**), and a pair that are diastereotopic (**D**), all in terms of configuration. (Draw three lines connecting the pairs, label H,E,D)

C) (5 min) Use your knowledge of the conformational energy of butane to estimate a numerical equilibrium constant between axial and equatorial methylcyclohexane. Explain your thinking briefly.
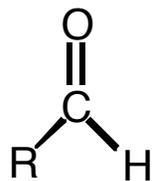
9.   (7 min) Draw a Fischer projection **and** a Newman projection for **each** of the following two isomers of tartaric

(1R,2R) tartaric acid   mesotartaric acid

Fischer

Newman

10.   (4 min) In terms of the mechanism of pharmacological action of the proton pump inhibitor omeprazole, what was the reason for AstraZeneca to worry that a "chiral switch" to enhance potency would not be successful?

11.   (6 min) Briefly describe the three different methods AstraZeneca used to prepare esomeprazole as a single enantiomer.
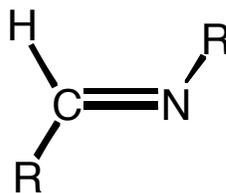
12. (2 min) Name the functional group in each of the following molecules (I-IV, which are the subjects of Questions 12-16)
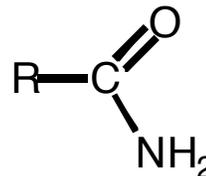
$$\underset{\textbf{I}}{\overset{\displaystyle O}{\underset{R\diagup\ \diagdown H}{\|}C}}
\qquad
\underset{\textbf{II}}{R\!-\!NH_2}
\qquad
\underset{\textbf{III}}{\overset{H}{\underset{R}{}}C\!=\!N\!-\!R}
\qquad
\underset{\textbf{IV}}{R\!-\!\overset{O}{\underset{NH_2}{}}C}$$

13. (6 min) Identify the HOMOs and LUMOs of I-III above, **and explain why** each is particularly high or low energy.

	I	**II**	**III**
HOMO			
LUMO			

14. (5 min) Use **curved arrows** to show how molecule **I** could react with molecule **II** to give an "aminol" (both an alcohol and an amine). Several steps are necessary.

15. (5 min) Use **curved arrows** to show how the aminol product of the previous question could give molecule **III**.

**16.**   **A)** (1 min) Explain why molecule III is more easily protonated (more basic) than molecule I.

B) (6 min) **Explain** why, despite the above, molecule **IV** is preferentially **protonated on its oxygen** atom rather than on its nitrogen, **and** how this property is related to **the resistance to rotation** about the C-N bond in molecule IV in its unprotonated and protonated forms.

17. A novel experimental technique reveals the **shape and relative signs of the HOMO** of the N_2 molecule. The figure on the right shows a slice through this HOMO as measured experimentally in this way.

   To interpret the Å scale, <u>**NOTE that the N-N distance in N_2 is 1.09Å**</u>

[The original figure is colored with the dark central blob shades of blue and the flanking "eyes" shades of red to denote opposite signs of the wave function. The lighter surrounding features are probably insignificant beacause of experimental error.]

   The lower graph, with the same horizontal scale, plots the MO wave function ψ along the Y = 0 line of the upper graph.   The dashed line is experimental, and the solid line is the result of an MO calculation.
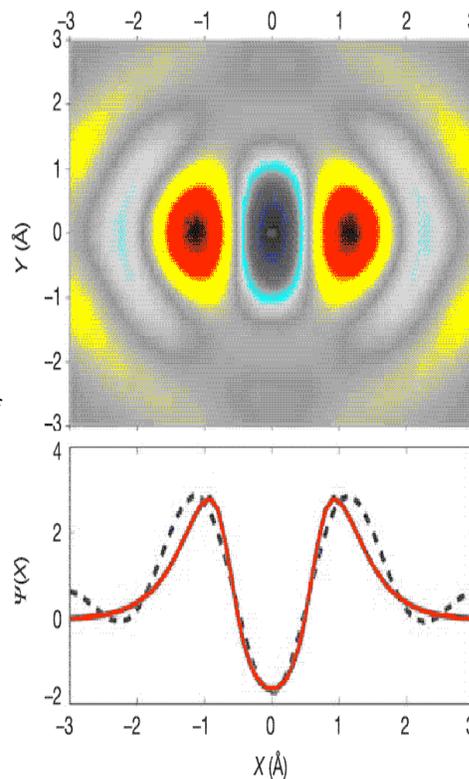
A) (4 min) Why cannot **x-ray** diffraction provide a similar graph showing the shape and signs of the HOMO?   (Give two reasons, but ignore the difficulty of preparing a crystal of N_2).

B) (2 min) Explain which **atomic orbitals** of nitrogen seem to dominate in making up this MO?

C) (4 min) At the extremes of the lower plot, the calculated (solid) wave function seems to approach Ψ=0 exponentially, while the experimental (dashed) curve has extra wiggles. Explain which behavior makes more sense in terms of reasonable kinetic and potential energy for an electron in this molecule.

d) (4 min) Given this shape of the HOMO, **explain where in the top figure** you would expect H^+ to add to N_2, **and** whether protonation should make the N–N distance **longer or shorter**.