Chemistry 125 First Semester Final Examination Name _______________

December 15, 1999

The exam budgets 150 minutes, but you may have 180 minutes to finish it. Good answers can fit in the space provided.

1. (36 minutes) Give as specific an example as you can for each of 8 of the following 11 items. Make your answers as brief and clear as possible, but try to make them **specific** - e.g. real molecules, real numbers. Continue on the back of this page. **OMIT 3.** ONLY YOUR FIRST 8 ANSWERS WILL BE GRADED Write your answers on this page and the next, using the backs if necessary.

a) Operation of the reactivity-selectivity principle.

b) A situation in which one should use average bond energies rather than bond dissociation energies.

c) An experimental technique that reveals the position of *individual* atoms (not average positions)

d) A pair of conformational enantiomers that do not racemize at room temperature.

e) The source of radical theory in organic chemistry in the early 19th century.

f) Determination of the heat of formation of an atom.

g) Evidence that cyclopropane rings have bent bonds.

h) Two cases where work with tartaric acid isomers contributed in a fundamental way to organic chemistry

i) A case of stabilization due to "resonance"

j) An experiment by Lavoisier involving an organic substance.

k) A type of isomerism that was predicted long before it was observed.

2. (6 min) What does it mean to solve a problem in quantum mechanics? That is, what are you given, and what do you have to find? [You might want to illustrate your answer with an example such as the hydrogen atom]

3. (5 minutes) Draw "3-isopropyl-5,5-dimethyloctane" and give the correct constitutional **and configurational** name to what you have drawn.

4. (3 minutes) How does one identify a first order reaction experimentally?

5. (6 minutes) Explain how the rate at which A is converting to B might be zero-order in A for high concentration of A and first-order in A for lower concentrations?

6. Free Radical Halogenation

A. (4 minutes) Draw the mechanism for the propagation "machine" of free-radical chlorination and use it to show where the structure of the product is determined.

B. (3 minutes) The rate of free-radical chlorination depends on the rate of initiation, but the relationship is not usually linear (i.e. doubling the initiation rate does not double the rate of product formation). Explain.

C. (4 minutes) The yield of isomeric alkyl halides from free-radical chlorination of suitable alkanes can be understood in terms of primary (RCH_2-H), secondary (R_2CH-H) and tertiary (R_3C-H) bond dissociation energies (BDEs), where R is an alkyl group. Values for the 1°, 2°, 3° BDEs vary smoothly from 101 to 98 to 96 kcal/mole, respectively. Provide an explanation for these differences in terms of bonding theory.

D. (4 minutes) Use the BDEs for primary and tertiary C-H bonds to predict the EQUILIBRIUM CONSTANT between isobutyl [$(CH_3)_2CHCH_2$] and t-butyl [$(CH_3)_3C$] radicals at room temperature.

E. (5 minutes) When 2-methylpropane reacts with Cl_2, the relative yields of t-butyl chloride and isobutyl chloride are 36% and 64%. Show how to use these values to reckon the relative reactivity of primary and tertiary C–H bonds.

F. (7 minutes) Use the Hammond Postulate to relate the ratio you calculated in Question E to the equilibrium constant you calculated in Question D, **AND** to explain how things would be different in the case of bromination rather than chlorination.

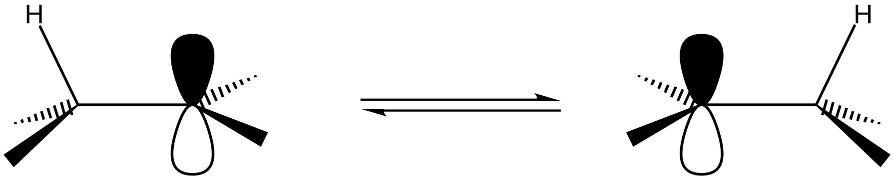
G. (6 minutes) One could imagine chlorinating propene ($CH_2=CH-CH_3$) to give either 1-chloropropene ($ClCH=CH-CH_3$) or 3-chloropropene ($CH_2=CH-CH_2Cl$). Use the following heats of formation (kcal/mole) to calculate or estimate relevant **BDE** values, **and** then use these values to predict the **relative yield** of these two potential products.

molecule	$CH_2=CH_2$	12.5	$CH_2=CH-CH_3$	4.9
radical	$CH_2=CH$	71.5	$CH_2=CH-CH_2$	40.9
	H	52.1		

H. (4 minutes) Rationalize the BDE of CH_2=CH–H (called a vinylic bond) relative to that of a normal primary C–H in terms of bonding theory.

I. (6 minutes) Rationalize the BDE of CH_2=CH-CH_2–H (called an allylic bond) relative to that of a normal primary C–H in terms of bonding theory. In this case consider orbital energy both for the orginal C-H bond and for the resulting radical.

J. (8 minutes) We will soon see that positively charged reaction intermediates often rearrange as shown below, whereas the corresponding free radicals rarely rearrange. Rationalize this difference in terms of the orbital mixing that goes on as the "migrating" hydrogen shifts from left to right. It would help to talk about overlap and orbital occupancy.



K. (4 minutes) Explain the analogy between the behavior of the cation in Question J and the reason that BH_3 dimerizes.

Most of our insight about organic chemistry comes not from measuring a property of an individual molecule, but rather from following the trend in how a property changes through a series of related molecules. One good example is the monotonic trend in BDEs in Question 6C above. **Questions 7 to 9** provide additional example of this style of thinking in cases where the trend is not monotonic.

7. (5 minutes) The A-value that expresses the conformational preference for monohalogenated cyclohexanes does not follow a monotonic trend as one goes from F to Cl to Br to I. How can one rationalize this behavior.

8. (7 minutes) We have belabored why chair cyclohexane is less strained than cyclopentane, but why is it less strained than cycloheptane? Baeyer had predicted that the difference would be due to bond bending, but according to Chem3D only 1/3 of the 6-8 kcal of additional strain in cycloheptane is due to bond bending. **You may examine the models** of chair cyclohexane and cycloheptane to answer the following questions.

What are the sources of extra strain in cycloheptane?

Why should there be **any** bond bending strain in cycloheptane? (there is practically none in chair cyclohexane)

Explain what would you predict for the relative entropy of cycloheptane and chair cyclohexane?

9. (7 minutes) As shown below, the entropy of XH_3 molecules (in cal/moleK) does not follow a uniform trend upon increasing the mass of X from B to C to N. Explain how entropy is related to the concept of a potential energy surface and vibrational quantum states, **and** rationalize the fact that the entropy of CH_3 is higher than that of either of its neighbors.

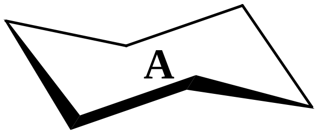
BH_3 44.9 CH_3 46.4 NH_3 46.1

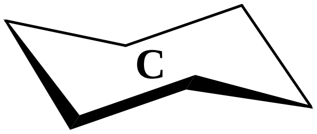
10. (8 minutes) For the uninitiated tunneling is one of the most puzzling concepts in chemistry. We hoped to demystify it by becoming familiar with one-dimensional quantum mechanics through *Erwin Meets Goldilocks.* Explain what it is about quantum mechanics that makes tunneling through a barrier in a double minimum potential no more curious than the probability distribution for the lowest energy level in a parabolic (harmonic oscillator) potential. Diagrams would help.

11. (12 minutes) Complete the structures below to show the two chair forms of trans- and of cis-1,3-dimethylcyclohexane. You need not draw hydrogens, but draw the directions of the bonds to methyl precisely.

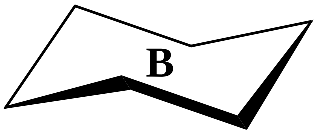
trans-1,3 cis-1,3

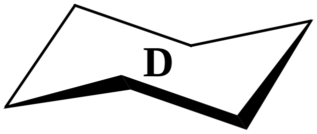
chair 1





chair 2





Taking the energy of A to be 0, assign values for the energies of B, C, and D (kcal/mole, give a phrase of explanation for each to be eligible for partial credit)

B __________

C __________

D __________

In the line below, **circle the structures which are chiral** (configurationally or conformationally)

A **B** **C** **D**

In the line below, **circle the structures with conformationally diasteriotopic methyls**

A **B** **C** **D**

In the line below, **circle the structures with configurationally homotopic methyls**

A **B** **C** **D**

In the line below, **circle the structures with methyls that could probably be discriminated by free radical bromination in a real experiment (not just a thought experiment)**

A **B** **C** **D**

In the line below, **circle the structures with methyls that could probably be discriminated by an enzyme in a real experiment (not just a thought experiment)**

A **B** **C** **D**