Chemistry 125　First Semester　Name _____
## December 19, 2003　Final Examination

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

1 . (30 minutes) Describe evidence to support FIVE (5 ONLY) of the following eight assertions. The more specific your evidence and explanation, the better.

a)　b-form DNA is a double helix with major and minor grooves.

b)　An organic compound can be chiral without possessing a stereogenic carbon.

c)　An enzyme can distinguish between enantiotopic hydrogens.

d)　NH_3 is pyramidal in its minimum-energy structure.

e)　Some cycloalkane rings with more than 5 carbon atoms are strained.

f)　The mathematical expressions used for van der Waals repulsion in molecular mechanics calculations are inadequate.

g)　Ladenburg's prism structure is no better than Kekulé's ring structure for discussing isomerism in disubstituted benzenes.

**h)**　Covalent bonds result from sharing electrons.

Question 1 (continued)

2 . (7 min) If Legos had been available in the 1860s, someone would almost certainly have used them as molecular models.

a) **Draw** a Crum-Brown style "Kekulé" structure (lines for bonds) of the molecule whose Lego model is shown on the right, and **name the functional group** it contains.
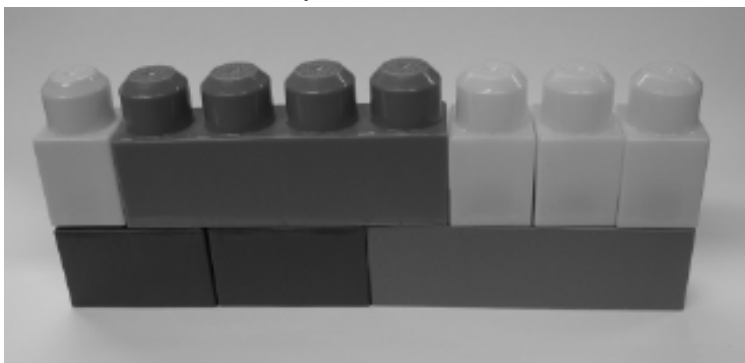
b) **Name** the individual who might have used these models, **and explain the experimental basis** on which one might choose between his molecular structures and those of Crum-Brown using evidence that would have been available to 19th Century chemists.

3. The figure on the right shows pentane in a conformation that would result
from replacing a CH_2 group in an **idealized** cyclohexane structure by two
hydrogen atoms.
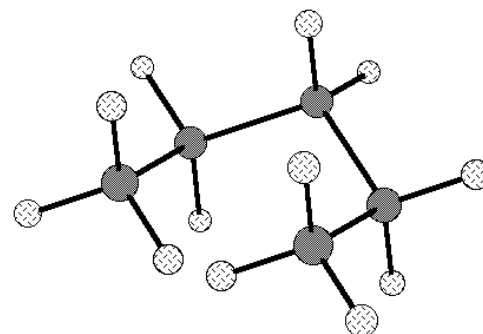
  a) (5 min) The two methyl groups might also be regarded as the axial
methyls of a chair 1,3-dimethylcyclohexane in which two other hydrogen
atoms of the structure shown are replaced by a chain of 3 CH_2 groups. **On
the figure draw additional bonds to** show the proper position and
orientation of these 9 new carbon and hydrogen atoms and **complete the
chair structure of 1,3-dimethylcyclohexane with the
existing methyl groups in axial positions.**

  b) (5 min) For the pentane structure shown in the figure, Chem3D
calculates a total strain energy of 242.5 kcal/mole. Chem 3D breaks this
total strain energy down into 6 classes, one of which is bond stretching.
Three of these values are near zero, one is 4.5 kcal/mole and one is 237.3
kcal/mole. Complete the first two lines of the table below with names of
the strain energy classes and the corresponding energy values for the
idealized structure above.

Type of energy	Bond Stretching					
idealized pentane	0 (kcal/mole)					
minimized pentane						

  c) (6 min) Chem3D finds the local energy minimum nearest in structure to the figure above whose total strain energy is only
6.0 kcal/mole. After this adjustment in structure **two** components of the strain energy are positive, but less than 0.3
kcal/mole, one is actually favorable (**-0.7**), the others are **1.3, 1.9, and 3.1 kcal/mole**. Make an educated guess as to
which of these strain energy component is which, and **enter the 6 values in the appropriate column of third row
of the table above**.   [To be eligible for partial credit give a brief explanation of your energy assignments.]

4. (12 min) Describe three completely different approaches for isolating a single enantiomer from a racemic sample. (The more specific your answer, the better. Real examples are best.)

5. (6 min) In what way are the **electron density functions** for one-electron atoms and the **Boltzmann factor** for equilibrium distribution of energy mathematically analogous? [write mathematical functions]

How is the role of **nuclear charge** in the density function case **analogous to temperature** in the equilibrium case?

6. The photo on the right shows chemists at the German
University of Göttingen in 1863. The arrow points to
Professor Friedrich Wöhler.

a) (7 min) Name **one** of the two important
development in organic chemical theory about
30 years earlier that was due, at least in part, to
Wöhler. Mention the **implications** of this
contribution and the **experiment** on which it
was based.

b) (7 min) On the right is a detail from the
photo above showing the apparatus
displayed on the lecture bench.
Presumably what looks like a rank of
organ pipes (arrow) is a set of Bunsen
burners. Explain what this apparatus is
used for in general, and specifically what
the three white devices in the white box
on the right are and what they do.

7. (6 min) Interpret **one** of the following two statements (CHOOSE ONE ONLY):

"It is the change from an ordered arrangement to a disordered arrangement which is the source of the irreversibility."

**or**   "Entropy becomes increasingly important as temperature increases."

8. (8 min) This plot shows the amount of energy radiated at different wavelengths by a surface heated to 1650 K. **What feature** of this curve was most difficult to understand, and **how was it finally explained**?

IRRELEVANT FOR 2004

$\mathcal{E} = f(\lambda).$

$\mathcal{T} = 1650°abs.$

$\lambda \longrightarrow$
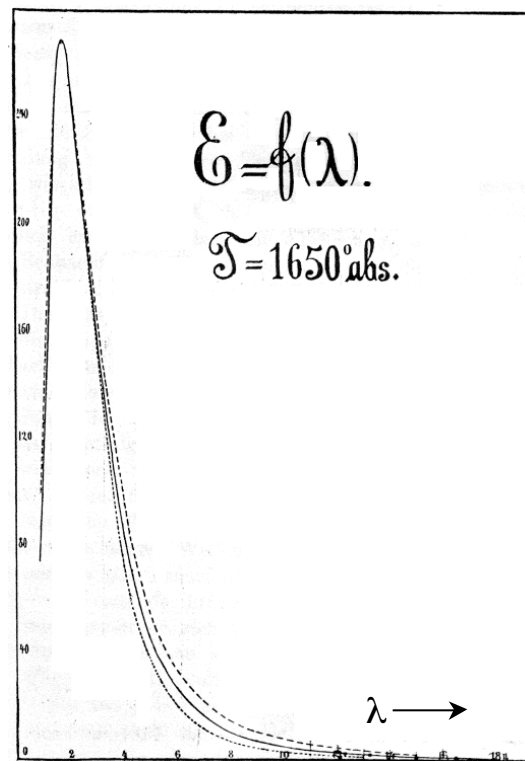
9. (5 min) Under what conditions should the lowest energy orbital of an isolated hydrogen atom be a hybrid orbital, rather than a $1s$ orbital. Explain.

10. (4 min) Explain the curious shape of this histogram showing the
frequency of occurrence of different bond lengths between nitrogen
atoms and aromatic carbon atoms.

1.31   1.46

$d_{N-C_{Ar}}(\mathring{A})$
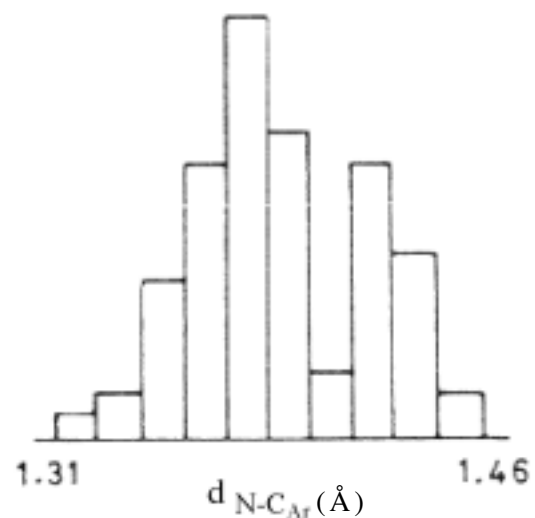
11. (7 min) What is the magnitude of the average C-H bond energy in CH_4? _____ **kcal/mole**

How much do the four successive bond dissociation energies of bonds in CH_4 differ from this ABE? (**circle correct value**)

$\pm0.5\%$ $\pm5\%$ $\pm15\%$ $\pm50\%$ by a factor of two

Identify **five actual experiments** which, taken together, allow one to determine the average C-H bond energy in CH_4.

1 2 . Methylene (CH_2) appeared in a Disney comic book about 50
years ago. Donald Duck, who had just been struck on the head,
had the idea of mixing CH_2 with NH_4^+. The absence of the
positive charge on nitrogen must be a typo.

a) (2 min) Why should NH_4 normally have a positive charge?
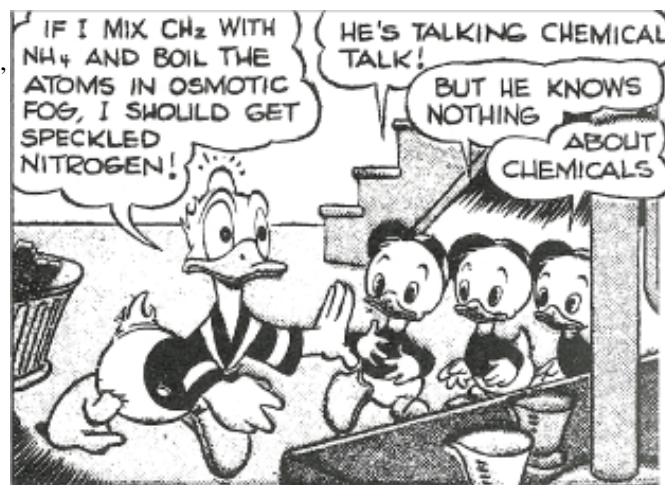
b) (5 min) If an extra electron were added to NH_4^+ to give a neutral molecule, **what orbital** might it go into and what
influence would presence of this additional electron have on the **structure** of the molecule? [For purposes of this
question you may consider MOs to be composed of two or fewer AOs.]

c) (7 min) The name "methylene" for the radical CH_2 had been coineda little more that a century before the Donald Duck
reference by a famous French chemist. The name came from Greek meaning "daughter of the spirit of wood." **Name**
the French chemist, explain the meaning of **"daughter of the spirit of wood,"** and write two or three sentences
explaining what **experiments** ultimately led this chemist to abandon the radical theory of organic chemistry.

d) (7 min) Assume that CH_2 should have the structure expected for the CH_3^+ cation with one proton missing. **Discuss** the **factors** determining the **hybridization** of the carbon atom in :CH_2 **and** the nature of its **HOMO** and **LUMO**. **Draw** these orbitals.

I am not certain what the results of Donald Duck's experiment was, but I can imagine two ways that :CH_2 might react with NH_4^+ to give the same ultimate product.

e) (7 min) One would be a **two-step** reaction in which the first step gives two small molecules which subsequently react with one another to give a single molecule. Propose such a two-step process and **explain both steps** in terms of HOMO/LUMO interactions.

f) (7 min) The other possibility for the Donald Duck reaction would be a **one-step process** in which two orbitals of CH_2 react simultaneously with two orbitals of NH_4^+ to generate the ultimate product directly. To explain this process **draw two identical pictures of CH_2 adjacent to NH_4^+** appropriately arranged for this one-step reaction to occur. On one of these pictures show the **HOMO of CH_2 interacting with the LUMO of NH_4^+**. On the other show the **LUMO of CH_2 interacting with the HOMO of NH_4^+.**