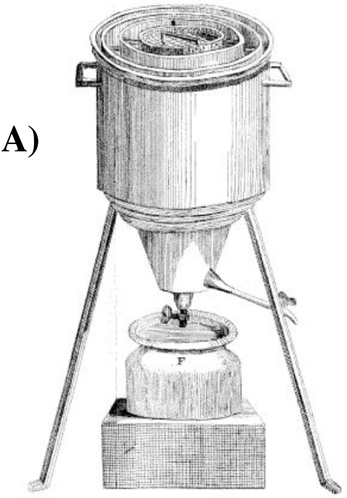
Chemistry 125 First Semester Name ___________________

**December 19, 2007** Final Examination

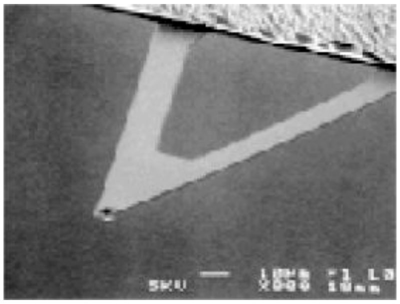
This exam is budgeted for 150 minutes, but you may have 180 minutes to finish it. Good Luck.

**1.** (10 min) Explain briefly how each of two **(2 only)** of the following 4 pieces of apparatus are (or were) used and for what purpose.

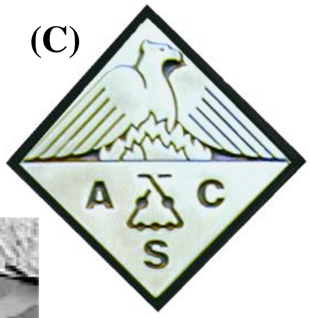
**(A)**



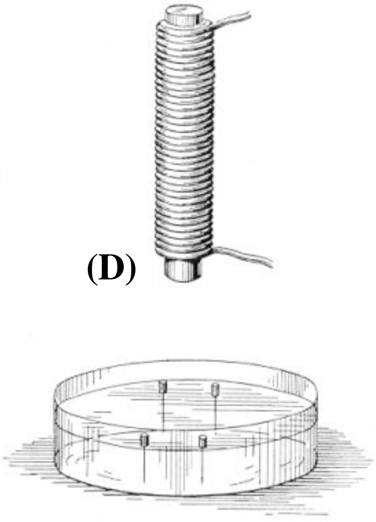
**(B)**



**(C)**



**(D)**



**2.** (9 min) (Write your answer on the Back of this sheet) Choose **any reaction process that involves several steps** and draw a mechanism using curved arrows to show every electron (pair) shift involved (*e.g.* alkene + $Cl_2$ → dichloroalkane; **or** alkane + $Cl_2$ → alkyl chloride + HCl; **or** $NH_3$ + $Cl_2$ → $NH_2Cl$ + $NH_4Cl$; **or whatever**). No discussion of HOMOs and LUMOs required, but draw the arrows carefully.

**3.** (6 min) Explain what two **(2 only)** of the following three formulas are meant to express.

**(A)**

$$K\,e^{-\rho/2}$$

$$\rho \equiv \frac{2Z}{na_o}\,r$$

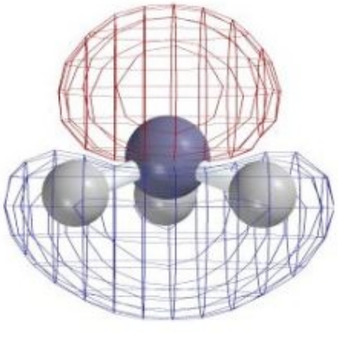
**(B)**

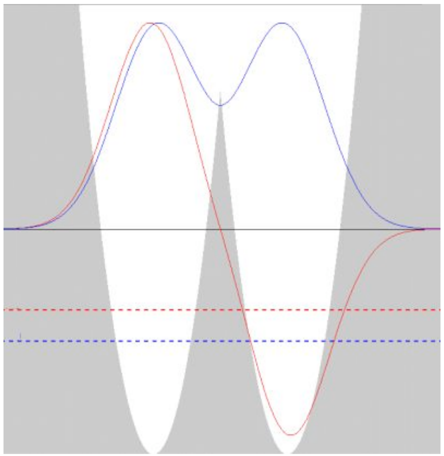
$$\psi_a(r_1,\theta_1,\phi_1) \times \psi_b(r_2,\theta_2,\phi_2)$$

**(C)**

$$\frac{\geq 1}{2}\left(AO_A{}^2 + AO_B{}^2 - 2\,AO_A\,AO_B\right)$$

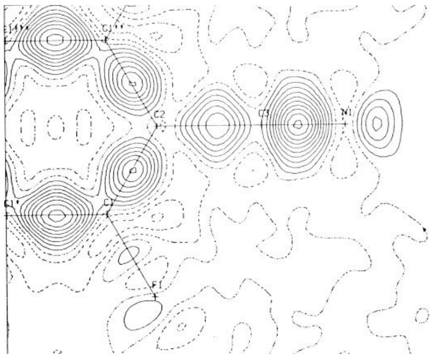
**4.** (8 min) Explain the significance of these two figures.



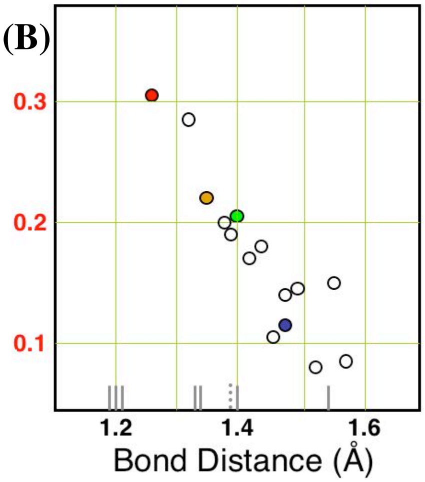


**5.** (10 min) Tell a brief story about two **(2 only)** of the following three figures.

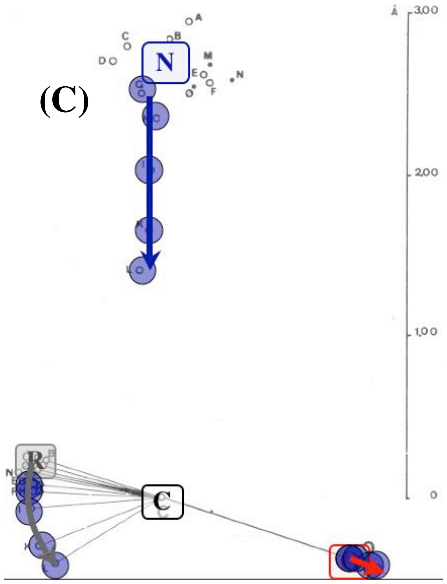
**(A)**



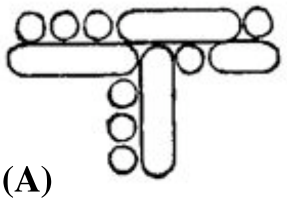
**(B)**



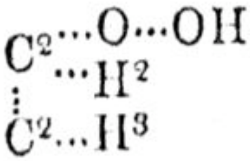
**(C)**



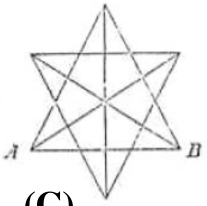
**6.** (15 min) Tell how each of three **(3 only)** of the following five played a role in 19th century organic chemistry.



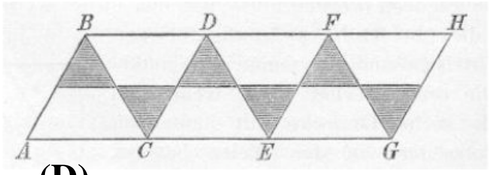
**(A)**



**(B)**



**(C)**

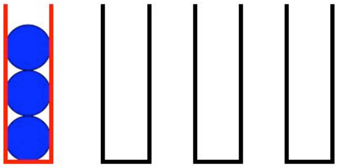


**(D)**

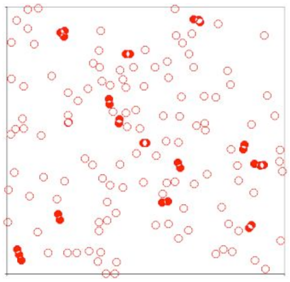
**(E)** $\overset{+}{NH_4}\,\overset{-}{Cl} + \overset{+}{Ag}\,\overset{-}{OCN} \longrightarrow \overset{+}{NH_4}\,\overset{-}{OCN} + \overset{+}{Ag}\,\overset{-}{Cl}$

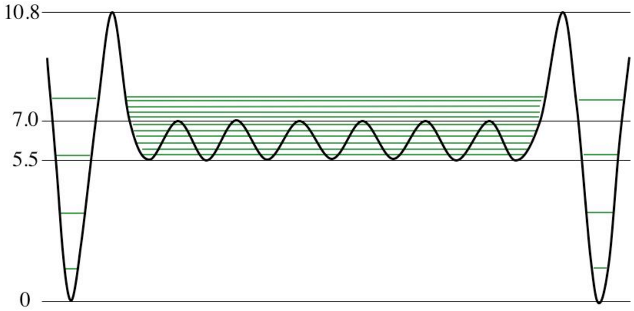
**7.** (10 min) Tell how each of two **(2 only)** of the following four figures relates to thermodynamics or kinetics.

**(A)**



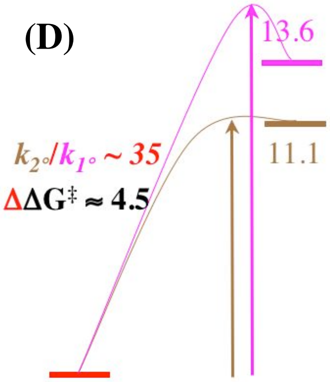
**(B)**





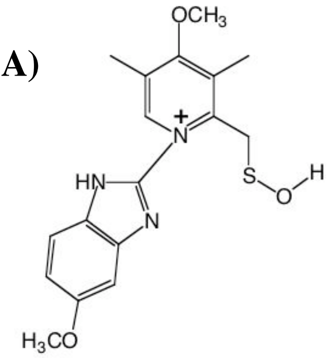
**(C)**

**(D)**

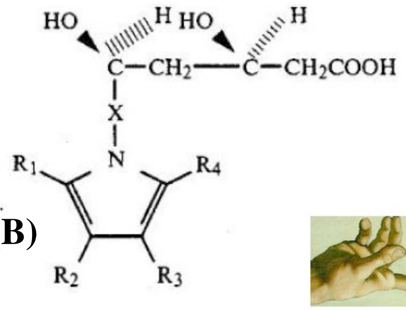


**8.** (10 min) Tell how each of two **(2 only)** of the following four figures relates to questions of stereochemistry.

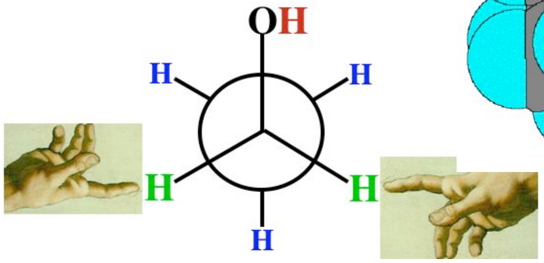
**(A)**



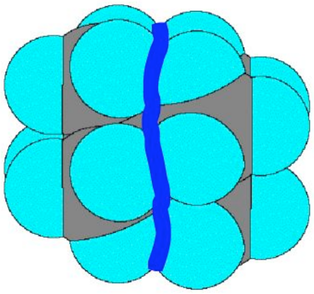
**(B)**



**(C)**



**(D)**



**9.** (4 min) Why is HBr the only hydrogen halide that can add to alkenes by a radical-chain mechanism?

**10.** (12 min) Describe briefly three different methods that were used to prepare a single-enantiomer samples of omeprazole.

**11.** (5 min) **Draw** a structure of cyclohexane in the **chair conformation** showing clearly the orientation of the axial and equatorial hydrogen atoms.

**12.** (6 min) Suppose that the conversion of your chair to a boat conformation went through a transition state in which one carbon atom becomes **coplanar with the four carbons atoms nearest to it**. **Explain** why you might expect two components of strain energy (as calculated by molecular mechanics) to increase upon this deformation, and why another component might decrease.

**13.** (7 min) If you were in charge of public health, how would you have designed tests for the efficacy of esomeprazole (Nexium) that would be different from those that were actually conducted? Why were such tests not conducted?

# Measures of Bond Strength

One way to measure bond strength is by Average Bond Energy, another is by Bond Dissociation Energy, a third is by the stretching frequency of the bond as observed by Infrared Spectroscopy, a fourth is by Bond Length.

## 14. Average Bond Energy

(5 min) What is the **purpose** of compiling **Average Bond Energies**, and why do they differ from Bond Dissociation Energies? (an example would help)

## 15. Bond Dissociation Energy

The following table presents recent values of **Bond Dissociation Energies** involving the hydrocarbon radicals named in the first row.

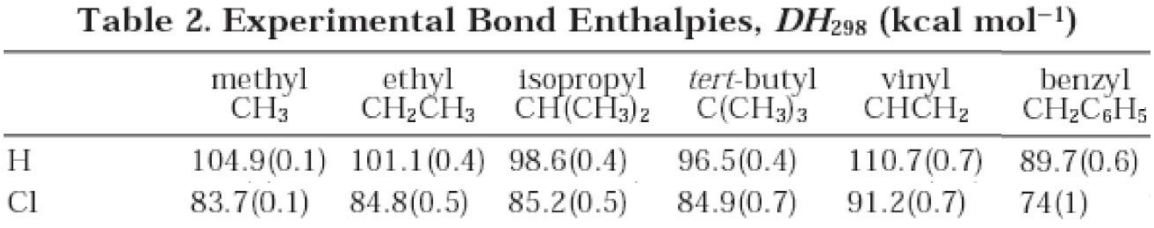


**Table 2. Experimental Bond Enthalpies, $DH_{298}$ (kcal mol$^{-1}$)**

| | methyl<br>$CH_3$ | ethyl<br>$CH_2CH_3$ | isopropyl<br>$CH(CH_3)_2$ | *tert*-butyl<br>$C(CH_3)_3$ | vinyl<br>$CHCH_2$ | benzyl<br>$CH_2C_6H_5$ |
|---|---|---|---|---|---|---|
| H | 104.9(0.1) | 101.1(0.4) | 98.6(0.4) | 96.5(0.4) | 110.7(0.7) | 89.7(0.6) |
| Cl | 83.7(0.1) | 84.8(0.5) | 85.2(0.5) | 84.9(0.7) | 91.2(0.7) | 74(1) |

**A)** (4 min) One of the hydrocarbon radicals is unusually stable. Which radical is it, and why is it stable?

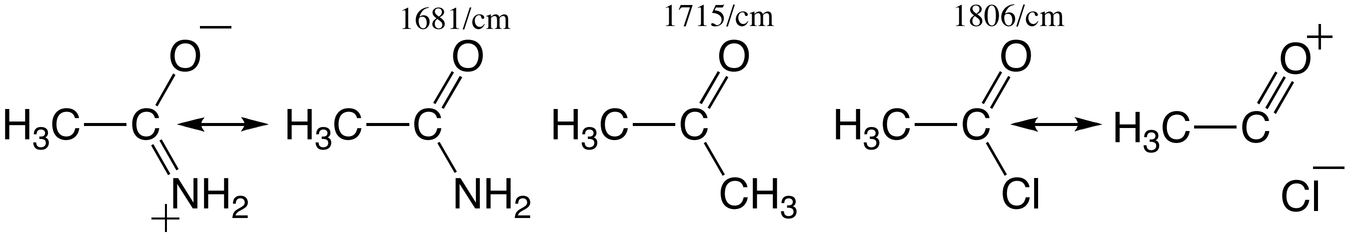
**B)** (5 min) One of the hydrocarbon radicals forms unusually strong bonds. Which radical is it, and why are its bonds so strong?

**C)** (5 min) Despite what many textbooks say, the other radicals do not form a series whose members are increasingly stabilized by substitution. Explain how these data prove that these textbooks are in error.

**D)** (5 min) Explain in terms of theory why hyperconjugation could be an explanation for special stability of more highly substituted carbon cations even if the greater stability of radicals is illusory. *i.e*. Why might hyperconjugation be more important for carbon cations that for carbon radicals?

## 16. IR Spectroscopy

Stronger springs have higher vibration frequency. By this criterion the C=O bond in a ketone (1715/cm) is stronger than the C=O bond in an acetamide (1681/cm) but weaker that the C=O bond in acetyl chloride (1806/cm). It has been suggested that these differences can be explained in terms of ionic resonance structures that give the C=O bond in the amide "single bond character" and the C=O bond in the chloride "triple bond character".



**A)** (5 min) Explain **in terms of intramolecular HOMO/LUMO mixing** why the single-bond amide resonance structure is sensible.

**B)** (5 min) Explain **in terms of intramolecular HOMO/LUMO mixing** why the triple-bond chloride resonance structure is sensible.

## 17. (4 min) Bond Length

In the 1987 survey of the Cambridge Structural Database the C=O distance in 551 esters was 1.196Å (±0.01), while the C=O distances in 378 amides was significantly longer, 1.231Å(±0.01). **Explain** this difference in terms of orbital mixing.