Chemistry 125 First Semester Name ____________________
December 17, 2002 Final Examination

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

1. (5 min) **What amount** of hybridization occurs in the atomic orbitals that form the bond in a hydrogen molecule?

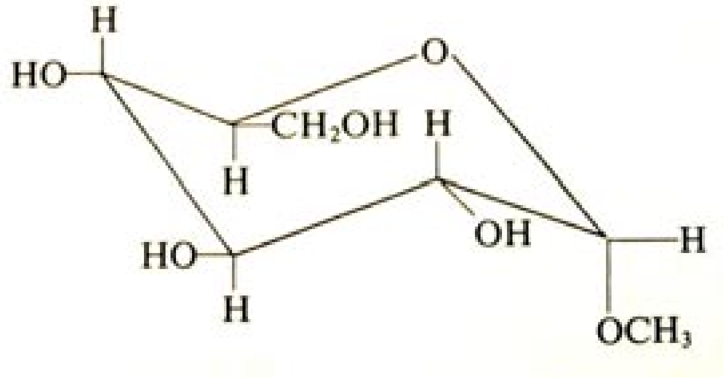
Why does the hydrogen AO hybridize?

Why is hybridization more important in C-C bonds?

What C hybridization gives the **best overlap** at normal C-C bonding distances?

2. (3 min) Yale organic chemistry students 35 years ago studied from a text that showed this figure of the chair conformation of a sugar derivative.

On the figure **redraw** any bonds that need to be adjusted by 15° or more to give a more realistic view of the positions of the substituents on the ring.

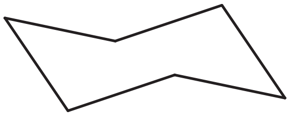


3. **a)** (4 min) Reactions with favorable equilibrium constants (K > 1) usually occur with a release of heat. **Explain** why this is so with reference to the **Boltzmann** factor (don't derive the factor, just use it).

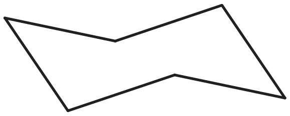
b) (4 min) However, there are first-aid cold packs with two chambers, one containing water, the other ammonium nitrate. When the pack is squeezed, and contents of the two chambers mixed, **a dissolution proceeds that absorbs heat**. **WITHOUT** considering details of whatever change in bonding might occur, **explain using thermodynamic concepts** how it can be favorable for ammonium nitrate to dissolve, even though it absorbs heat.

4. Using Chem 3D one can estimate strain energies for the **two** lowest energy chair conformations of **methylcyclohexane**, the **two** lowest energy chair conformations of ***cis*-1,3-dimethylcyclohexane**, and the lowest energy chair conformation of ***trans*-1,3-dimethylcyclohexane**.

a) (6 min) **Draw lines** indicating bonds to methyl groups on the following cyclohexane skeletons to show which of these five structures has the indicated strain energy (in kcal/mole).



6.9



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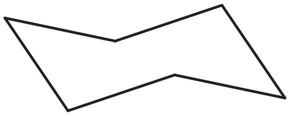

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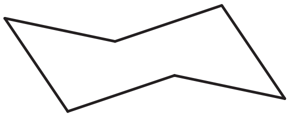
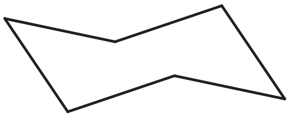


9.0



12.5

b) (3 min) In the scheme above draw **circles** around two methyl groups that are **conformationally diastereotopic**, and **squares** around two methyl groups that are **configurationally enantiotopic**.

(Only one pair of each is necessary – two circles and two squares)

c) (6 min) **Explain** how some of the energies above relate to the difference in strain energy between the most and the least strained conformational isomers of n-pentane.

[Consider *gauche* and *anti* conformation about the two central C-C bonds of pentane]

5. (6 min) Indicate circumstances that might give rise to each of **TWO** of the following three reaction-order phenomena:

zeroth order **half** order **pseudo first** order

6 . Quantum mechanics deals in the kinetic and potential energies of a system. Although it is possible to solve the Schrödinger equation for any old form of the potential energy (*e.g.* harmonic oscillator or Morse potential), there is in fact just one fundamental force law involved in the quantum mechanics of electrons in atoms or molecules.

a) (2 min) **Name** the fundamental source of electron's potential energy and write a **formula** that expresses it.

b) (3 min) Given this formula, how did **Earnshaw's theorem** make it impossible for an atom to have a static "structure" in terms of classical physics.

c) (2 min) Quantum mechanics made atomic structure possible by reformulating kinetic energy. Write the quantum-mechanical **formula for kinetic energy** (in one dimension) and express in words what the formula says.

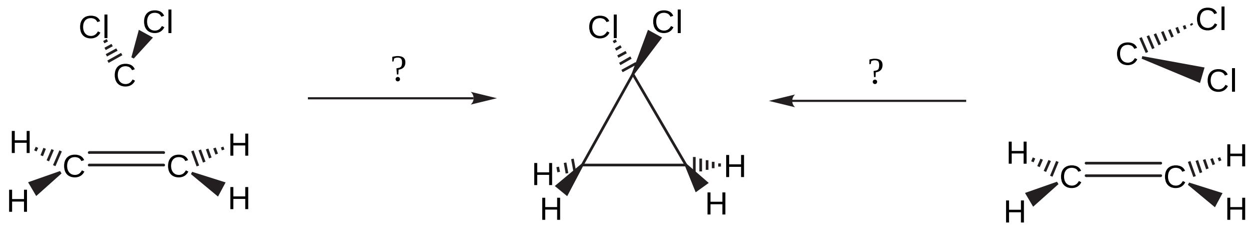
7 . We have considered trivalent carbon (e.g. $\cdot CH_3$) as a reactive intermediate. Next semester we will briefly consider divalent $:CX_2$ intermediates as well. They are called carbenes.

a) (6 min) One can wonder whether the geometry of $:CH_2$ should be linear ($\angle HCH = 180°$) or bent. Suppose the preferred angle is 100° (the value measured by spectroscopy for $:CCl_2$). Use this angle to **discuss** the **factors** determining the **hybridization** of the carbon atom in $:CH_2$ **and** the nature of its **HOMO** and **LUMO**. **Draw** these orbitals.

b) (2 min) **Explain** whether the **HOMO** of $:CH_2$ should be more or less reactive that that of NH_3, **and** whether the **LUMO** should be more or less reactive than that of BH_3.

Question 7 cont.

c) (6 min) A characteristic reaction of :CCl_2 is addition to an alkene to form a dichlorocyclopropane. **Discuss the orbital mixing** occurring at the transition state for this addition to decide whether it would be better for CCl_2 to approach ethene **"head-on"**, as shown at the left **or "sideways"**, as shown at the right.

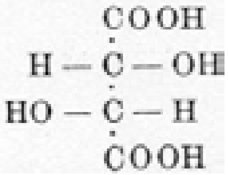


d) (6 min) Use plausible **resonance structures** and orbital-mixing **energy diagrams** to predict relative reactivities of the three CX_2 molecules where X is H, or F, or OCH_3.

8. (6 min) Describe the **experimental** (**NOT theoretical**) **basis** for **ONE** of the following claims. Be **specific.**

The favored path for attack of a HOMO nucleophile on a carbonyl group is not along a line perpendicular to the C=O bond.

Molecular mechanics calculation of bromine-bromine repulsion in organic molecules should be taken with a grain of salt.



9. No substance played a more central role in the development of organic chemistry generally, and stereochemistry in particular, than **tartaric acid** (2,3-dihydroxybutanedioic acid).
Its monopotassium salt deposits on the inside of wine casks, and when recrystallized is called "cream of tartar." The salt was called tartarum already in the 13th Century.

a) (5 min) The structure of **L-(+)-tartaric acid** shown above is taken from the 1891 paper that first proposed this type of drawing for depicting stereochemistry. **Explain** what "**L**" and "**(+)**" mean in this name, **and** give the correct absolute (**CIP**) descriptor for the configuration shown by this structure.

b) (10 min) Here are three years we mentioned in class in which tartaric acid played a role in the development of non-stereochemical organic theory: **1789, 1830, 1858**. Choose **TWO** of these three dates and explain, in a few sentences each, what the development was in which tartaric acid played a role.

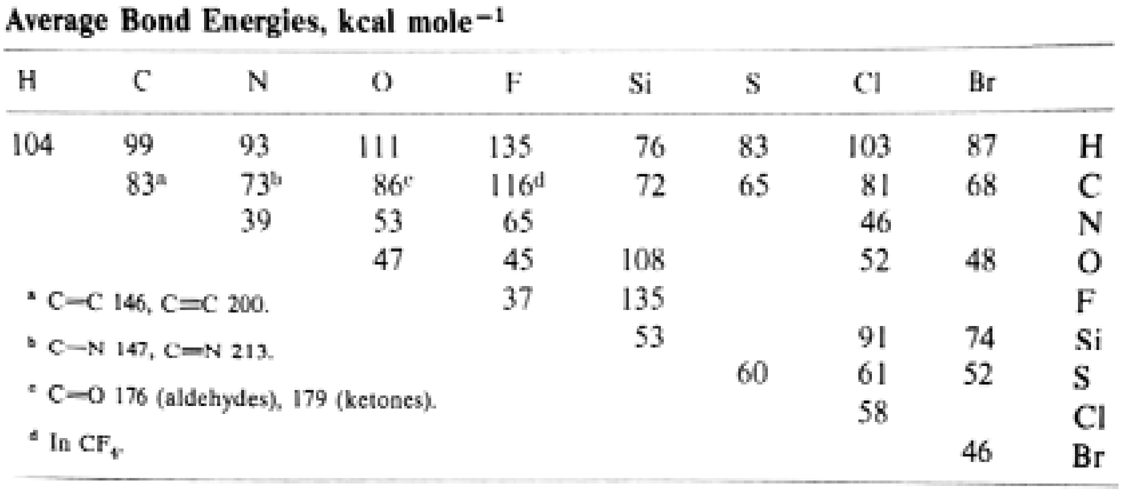
c) (15 min) Here are four years we mentioned in class in which tartaric acid played a role in the development of organic **stereochemistry**: **1848, 1857, 1877, 1949**. Choose **THREE** of these four dates and explain, in a few sentences each, what the development was in which tartaric acid played a role. [Continue on next page]
[We didn't mention 1857, which was the year of the second discovery by the individual who made the 1848 discovery.]

9c cont.

d) (6 min) Consider the two H atoms **bound to carbon** in L-(+)-tartaric acid, and the two H atoms **bound to carbon** in *meso*-tartaric acid. In the “topicity” column of the following table **enter the name of the configurational topicity** relationship between the indicated H atoms. Put an **“X”** in each box where the indicated reagent **could *in principle* discriminate** between them:

H-Pair	Topicity Name	Br Atom?	Dehydrogenase Enzyme?	No Possible Reagent?
two Hs of L-(+)				
two Hs of *meso*				
H of L-(+) and H of *meso*				

10. (8 min) Consider the energy of the lowest allowed level for an electron in a double-minimum potential (for example, H_2^+) as the distance between the minima (the protons) changes. Would you agree with the claim that significant bonding occurs only when tunneling becomes rapid? **Why**? [A proper answer must mention what determines the rate of tunneling.]



Average Bond Energies, kcal mole^{-1}

H	C	N	O	F	Si	S	Cl	Br	
104	99	93	111	135	76	83	103	87	**H**
	83[a]	73[b]	86[c]	116[d]	72	65	81	68	**C**
		39	53	65			46		**N**
			47	45	108		52	48	**O**
				37	135				**F**
					53		91	74	**Si**
						60	61	52	**S**
							58		**Cl**
								46	**Br**

[a] C═C 146, C≡C 200.

[b] C═N 147, C≡N 213.

[c] C═O 176 (aldehydes), 179 (ketones).

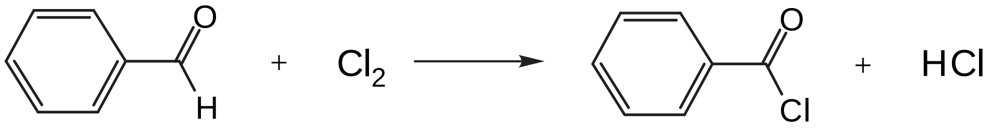
[d] In CF_4.

11. It was found in 1832 that the oil of bitter almonds (benzaldehyde) reacted with chlorine to replace H by Cl.

a) (4 min) **What theory** did this observation engender in 1832?

What subsequent line of research in the 1840s cast doubt on the correctness of this theory?

b) (5 min) Use the data in the table above to **estimate the equilibrium constant** for this double decomposition:



c) (5 min) Use a **cyclic diagram** to show the radical-chain **propagation** steps that would be involved in this transformation. [You may abbreviate the benzene ring by "Ph".]

Question 11 cont.

d) (4 min) **Which** propagation step in 11c do you think should be slower? **Why**?
Why might you worry about using the **numbers in the table** above for estimating its rate?

e) (2 min) Suggest plausible **initiation** and **termination** steps for this process

12. (8 min) Give the key reasoning behind **one** of the following arguments (complete details are not required):

Clerk-Maxwell's derivation of the distribution of translational energy among atoms
Boltzmann's derivation of the distribution of energy among molecular "degrees of freedom"
Planck's explanation of why "black body radiation" passes through a maximum with decreasing wavelength.

13. (8 min) The website (www.blacklightpower.com) of a startup company in Cranbury, NJ, claims invention of a promising new source of abundant, clean energy in the following words:

> *Blacklight Power cells generate energy through a chemical process (BlackLight Process), which the Company believes causes the electrons of hydrogen atoms to drop to lower orbits, thus releasing energy in excess of the energy required to start the process.*

The idea seems to be that they can start with H atoms in their lowest previously known energy state, and make them release energy by falling to a still lower energy state, previously unknown, presumably one where the electron is nearer to the nucleus on average.

From what you know of how quantum mechanics works, construct an argument that such a process may, or may not, be possible.