Chemistry 124 Second Examination Name _____

October 19, 2009

The exam budgets 50 minutes, but you may have 60 minutes to finish it. Good answers can fit in the space provided. Question values correspond to alloted time. Don't waste too much time on cheap questions.

Read each question carefully to see what it asks for (bold face is used to help highlight key points).
Make sure you are answering the question, not just saying something vaguely relevant to its topic.

1. (5 min) Explain why the bonding combination of two orbitals is more favorable energetically than the antibonding combination. Discuss **both potential and kinetic energies**.

2. (5 min) **Sketch** the most important **orbital interactions** involved in dimerization of two BH_3 molecules, and comment on the **energies** of the orbitals that interact.

3. (5 min) Rationalize the observed geometry of the **CF_3** radical in terms of the factors that determine orbital **hybridization**. (You do NOT need to describe the ESR experiment or its interpretation.)

4. (6 min) Draw the three reactions involved in oxidation of NH_3 by Cl_2 to give hydrazinium hydrochloride (NH_2NH_3Cl). Draw **curved arrows** carefully, AND very briefly explain how the three reactions are **analogous** in HOMO/LUMO terms.

5. (4 minutes) Draw lines to match each of the following mixings of **valence orbitals of two adjacent carbon atoms** with the appropriate overlap integral at the **normal distance of a C=C double bond**. [No explanations required]

s with s	0.00
s with p (pi)	0.22
s with p (sigma)	0.33
p with p (pi)	0.46
p with p (sigma)	0.50
sp with sp (sigma)	0.68
sp^3 with sp^3 (sigma)	0.82

6. (6 min) Describe "**correlation energy**" touching briefly on the following points: **(a)** how it relates to the energy of **self-consistent-field orbitals**; **(b)** the **direction** of its influence on electronic energy; and **(c)** the extent to which it might be **negligible**.

7. An article in the November 2009 issue of *Clinical Infectious Diseases* suggests that some fatalities during the 1918-19 influenza pandemic were caused by overprescription of the first artifical "wonder drug", asprin (acetylsalicylic acid). Bayer had lost patent protection in February 1917. Many other manufacturers had jumped in to manufacture and market the drug that was being prescribed in what are now know to be toxic doses.

(a) (2 min) How does salicylic acid relate to the "Doctrine of Sympathies" of Paracelsus?

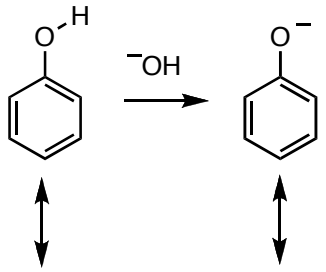
Salicylic acid was (and is) cheap to make using the "Kolbe" synthesis, which had been developed in 1860. It involves treating phenol (hydroxybenzene) with NaOH and CO_2.

(b) (4 min) **Name** the HOMO and the LUMO involved in reaction shown below between phenol and hydroxide. Say **what factors** (if any) make them *unusually* high or low. [Save resonance for Part c.]

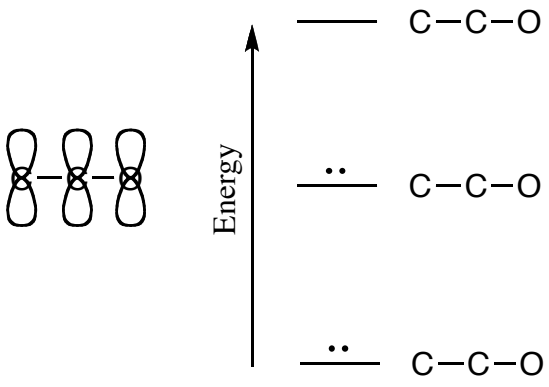
HOMO:

LUMO:

(c) (6 min) Consider "resonance" involving **only the closest double bond** of the benzene ring (*i.e.* treat phenol as an enol) **both** in phenol and in the "phenoxide" anion product. **DRAW** the resonance structures below each structure **AND EXPLAIN** in terms of "HOMO/LUMO" mixing of localized orbitals whether this resonance should favor or disfavor formation of phenoxide as shown.



(d) (6 min) The pi orbitals of the enolate anion are made from the parallel atomic *2p* orbitals of the C, C, and O atoms shown below left. Over the letters on the right **sketch the three MOs** a computer would make from these three AOs with appropriate relative sizes and signs for the AOs in each MO. [A few words of explanation might help]



(e) (1 min; **note the small credit**, don't waste time on this challenging question unless you have answered the others as well as possible and become bored)

Draw structures with **curved arrows** to complete the Kolbe reaction, and explain **why** it is favorable to proceed from the phenolate to the salicylate.