Chemistry 125 Third Examination Answers **November 11, 2005**

Scores	Average	1/3 >	2/3>
this exam	78.0	84	77
Σ 3 exams	221.8	236	210

Congratulations, you did well on this exam. Half the semester grade is still pending but the current borders for letter grades would be: A (246) A- (228) B+ (211) B (196) B- (179) C+ (162) C (150) C-

1. (4 min) Give succinct definitions for each of the following terms:
"constitutional isomers"

Molecules with the same composition (elements and numbers of atoms) but different nature and/or sequence of bonds.

"diastereomers"

Molecules with the same constitution but completely different arrangement in space (*i.e.* not mirror images).

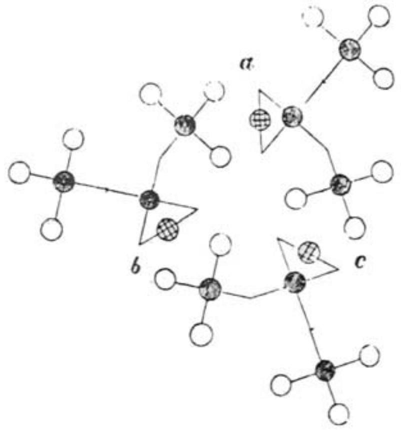
2. (6 min) Good theory rationalizes existing observation and makes testable predictions of new observatons.
Give a specific example of each for van't Hoff's theory of stereochemistry. (TWO EXAMPLES altogether)

Van't Hoff **cited existing evidence** for a number of optically active compounds, all of which had at least one "asymmetric" carbon (with four different substituents) in their structure, *e.g.* lactic acids, tartaric acids, aspartic acid, amyl alcohol, glucose, malic acid, and most of their derivatives (but not those lacking an asymmetric carbon).

He also **predicted** the optical activity of substituted "allenes" ($R_1R_2C{=}C{=}CR_1R_2$ or $R_1R_2C{=}C{=}CR_3R_4$), which was not confirmed experimentally until 1935.

3. (3 min) How did Kekule show that the methyl groups in "mesitylene" must be in the 1, 3, and 5 positions?

He proposed that its preparation from three molecules of acetone involved loss of three molecules of water and joining the surviving carbon atoms with double bonds. The resulting compound must have methyl groups on every other carbon atom of the benzene ring.



4. (4 min) How did Koerner demonstrate that the position of OH in hydroxybenzoic acid is equivalent to that of COOH?

Beginning with "Arppe's nitroaniline," the relative of hydroxy benzoic acid with NH_2 in place of OH and NO_2 in place of COOH, he replaced the NH_2 by Cl and the NO_2 by Br. In another sample of Arppe's nitroaniline he replaced the NH_2 by Br and the NO_2 by Cl. These two bromochlorobenzenes were identical, thus the positions the halogens occupy must be equivalent.

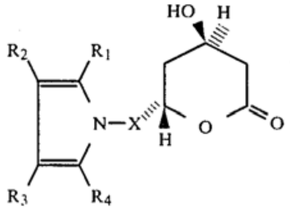
5. (3 min) What did A.S. Couper find philososphically objectionable about the contemporary radical theory.

"It tends to arrest scientific inquiry by adopting the notion that these quasi elements contain some unknown and ultimate power which it is impossible to explain."

6. (6 min) Use curved arrows to show the several steps for **ONE** (one only) of the following transformations: (**a**) addition of NH_3 to HN=C=O to give urea; **or** (**b**) conversion of CH_4 to CH_3Cl; **or** (**c**) addition of Cl_2 to $CH_2=CH_2$.

See animations of ***(a)*** Lecture 23, 10/26/05, frame 3 ; ***(b)*** Lecture 28, 10/28/05, frames 6 and 7 ; ***(c)*** Lecture 28, 10/28/05, frame 7.

7. (5 min) How did the following structure create patent problems for Pfizer?



While the structure shows the single biologically active stereoisomer (Lipitor), the preparation described gives a racemic mixture. There was thus a question whether the structure was meant to show a single enantiomer or a racemate, and whether the patent covers use of the single enantiomer as a drug. [The UK judge decided that it did, because "a person skilled in the art" as of the patent's date would have understood that a single enantiomer was the active ingredient of the drug.]

8. (2 min) Name compounds that could be used to illustrate the Law of Multiple Proportions. (**just names**, no discussion necessary)

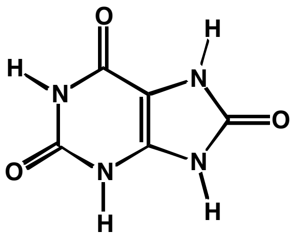
Many possibilities, but the examples cited in class were CO/CO_2 and $N_2O/NO/NO_2$.
[N.B. Formulas that are simple multiples of one another are **not** related to the law of multiple proportions.]

9. (5 min) What did this device contribute to chemistry? Mention BOTH EXPERIMENT and ORGANIC THEORY.

This part of one of the batteries used by Humphrey Davy to electrolyze sodium and potassium hydroxides to give the new elements sodium and potassium, respectively. (Water electrolysis also gave twice as large a volume of hydrogen as of oxygen gas, suggesting the formula H_2O.)

That the components of the two compounds were liberated at opposite poles of the electrolysis cell suggested that they may be held together in the compound by the coulombic attraction between + and – charges. This "dualistic" theory was applied to organic chemistry by invoking "radicals" which played the role of + or – elements in organic compounds.

10. (4.5 min) Use **orbitals** to explain why uric acid behaves as an acid, even though it has no COOH group.



There are low LUMOs (π^* of C=O) on both sides of the top left NH group. These mix with the unshared pair (high HOMO) of NH to make the compound unusually stable. When NH loses its proton, the resulting anion is REALLY stabilized because the nitrogen HOMO is much higher. Thus, resonance makes uric acid a strongish acid. [Without C=O amines are more basic than acidic]

11. (7.5 min) Berzelius, Fischer, Lavoisier, Pasteur, and Scheele (alphabetical) each used **tartaric acid** to advance organic chemistry. Describe their five contributions with tartaric acid briefly near the proper place on this timeline:

[As a group you did excellently on this question.]

1750

1775 (**Scheele**, ~1780) Isolates pure samples of a number of organic acids, including tartaric acid, as their heavy-metal salts. Pure samples were required for using analysis to determine the identity, and ultimately the structure, of organic compounds.

(**Lavoisier**, ~1785) Develops the theory that acids result from oxidation of "bases" or "radicals" and the there are "compound radicals" such as the radical of tartaric acid, which are composed of a set of elements. (I don't think he analyzed tartaric acid)

1800

1825

(**Berzelius**, 1830) Found that the lead salt of racemic acid (John's acid from the Vosges) had the same analysis as that of tartaric acid, which has different properties, and thus that they must be isomers, for which he coined the name. The existence of isomers showed that there must be more to the identity of a molecule than its elemental "composition."

1850 (**Pasteur**, 1848) Resolved the ***sodium ammonium salt*** of racemic acid to give the enantiomers of tartaric acid. This was the first resolution of a racemate. He suggested that the atoms must have a chiral arrangement (such as a helix or a tetrahedron), but this was before valence, so it was not possible to be more specific.

1875

(**Fischer**, 1890) Used Friedlander models of the isomers of tartaric acid to develop the Fischer Projection as a means of showing the orientation of substituents about an

1900 "asymmetric" carbon. This made it much easier to count stereoisomers for sugars and their relatives.

1925