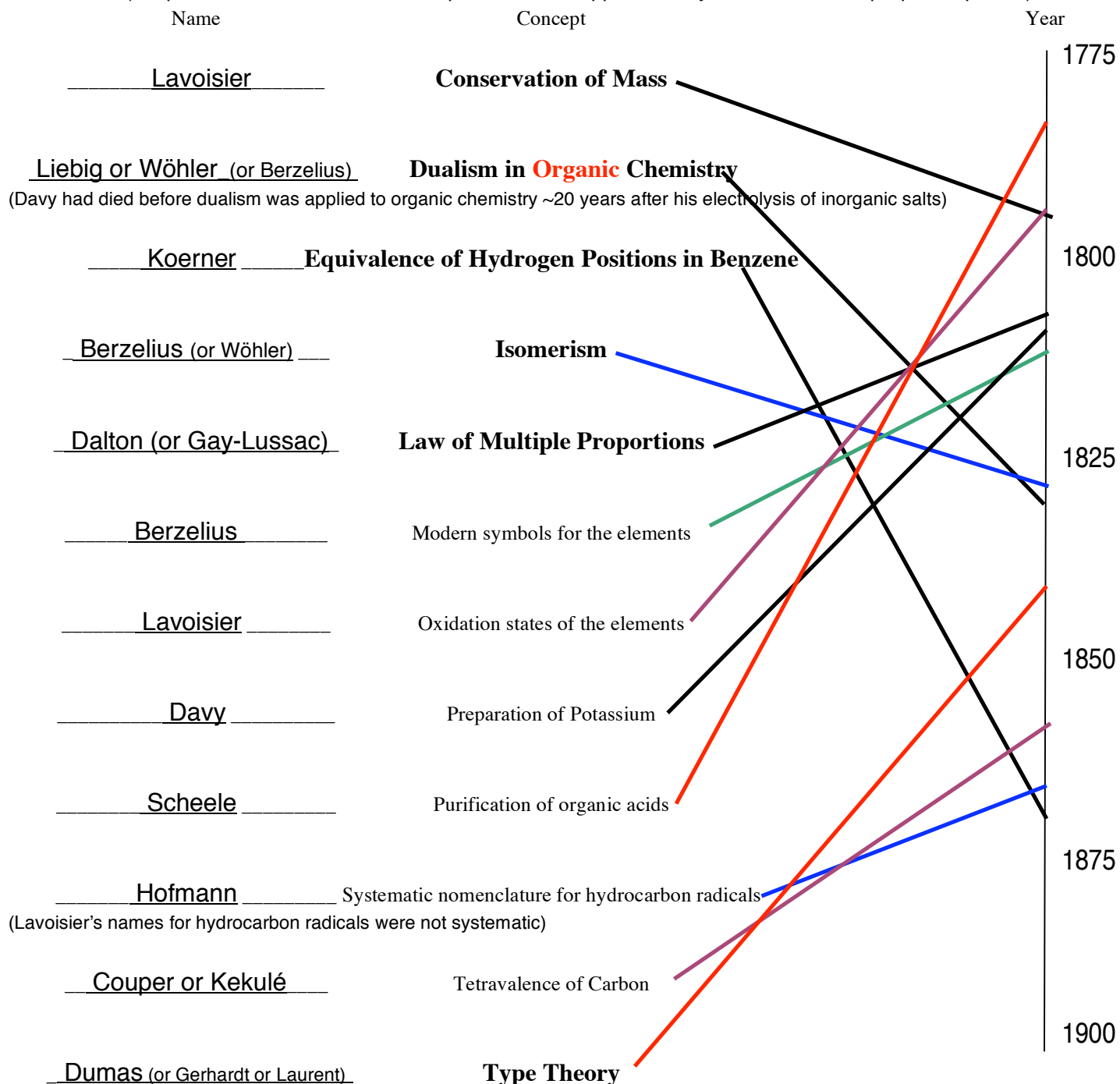


Chemistry 125 Third Examination Answers November 17, 2006

	Average	1/3 of scores >	2/3 of scores >
This exam	79.1	84	75
Sum of 3 exams	233.5	248	220

1. (9 minutes) **Name one** person associated with each of the following concepts or accomplishments and **draw an unambiguous line** from each to the timeline so as to arrange them in proper chronological order.

(1/2 point for each correct name, 1 point each for approximately correct date and proper sequence)



2. (9 min) Describe briefly a **key experimental result** that helped support **each of three** (3 only) of the concepts **in bold face** in the list above. Be as specific as you can (try to use real compounds, for example). Answer on back of this page.

A crucial feature of good answers to this kind of question is specification of **REAL** examples that prove a point, as opposed to theoretical generalizations.

Conservation of Mass: Everyone got that Lavoisier was key in developing this concept, but in regard to experimental results supporting it, his oil combustion experiment is not the best example, because he did not monitor the amount of oxygen consumed in forming products. As in almost all subsequent combustion schemes, he determined oxygen by difference. A much better example is the oxidation of charcoal in a heated tube by steam. In this case he monitored both the water and carbon consumed and the hydrogen and carbon dioxide produced. His results were not sufficiently precise to be perfectly convincing, but he had hitched his wagon to the proper horse.

Dualism in Organic Chemistry: The key experiments for carrying the theory of dualism, which had been accepted for 20 years in inorganic chemistry, into the realm of organic chemistry were the conversions of benzaldehyde (“oil of bitter almonds”) into a wide variety of compounds (*e.g.* with oxygen into benzoic acid, with chlorine into benzoyl chloride, with bromine into benzoyl bromide, and further conversion of benzoyl chloride into an amide, a sulfide, and an iodide). All of these products showed that the “benzoyl radical”, C_7H_5O had survived, as an element would be expected to do.

[Many individuals had failed to pick up on the word “organic” in the question and discussed Davy’s electrolysis, which indeed was a key experiment in the initial proposal of dualism in *inorganic* chemistry – such an answer was given substantial credit here, though it lost credit in Question 1. Apparently I gave the wrong impression in lecture that Davy discovered reaction of copper sulfate with sodium hydroxide to give the precipitate of copper hydroxide. This reaction, which fits well into the double decomposition theory of dualism, had no doubt been carried out loooong before the period of modern chemistry by alchemists or their predecessors.]

Equivalence of Hydrogen Positions in Benzene: People did very well on this question. Note that any one stage of Koerner’s proof (see lecture of 11/15/06) would have sufficed to answer the question, though a number of students discussed several stages, or the whole proof.

Isomerism: Key experiments for establishing isomerism were the identical C,H analyses (Berzelius) of tartaric and racemic acids (which have very different melting points, $170^{\circ}C$ and $206^{\circ}C$, respectively – note that these compounds do not boil without decomposition). Also Wöhler observed the difference between the observed properties (reaction with nitric acid, failure to evolve ammonia on treatment with base, failure to evolve cyanic acid on treatment with acid) of urea and the expected properties for the salt ammonium cyanate, which should have the same elemental analysis as Prout’s of urea. Earlier Gay-Lussac noted that corresponding salts of fulminate (Liebig) and cyanate (Wöhler) had identical analyses.

Law of Multiple Proportions: The weight ratios of C to O in the two oxides of carbon (like the weight ratios of N to O in the three oxides of nitrogen) are simple integral multiples of one another, as expected if they are composed of molecules containing small integral numbers of the elemental atoms.

Type Theory: Reaction of acetic acid with elemental chlorine in the presence of light results in the sequential substitution of three hydrogen atoms by chlorine atoms. Not only this substitution change the composition of the supposedly “elemental” acetyl radical, it also replaced a positive element (H) by a negative one (Cl) in contradiction of dualistic expectations.

3. (4 min) What is the Bürgi-Dunitz 110° angle, and how was it determined?

It is the angle at which the N of an amine approached the C of a carbonyl group to form a new N-C bond.

It was measured by comparing the relative positions of N, C, O, and the substituents on C in a large number of crystal structures determined by x-ray diffraction. For a wide range of N-C distances the N-C-O angle was about 110° .

4. (2 min) What did Couper consider to be the principal weakness of the Radical Theory?

It sidesteps the most challenging and relevant question – how it happens that elements assemble into the radicals which the theory treats as if they were elements.

5. (2 min) What did organic chemists at the time consider to be the most important piece of chemical apparatus invented in the 1800s?

Liebig's 5-bulb apparatus, the “kaliapparat”, which students flocked to his lab in Giessen to master, and which appears several places on SCL and in the logo of the American Chemical Society (from the 1870s). It is true that an analytical balance was required to use the kaliapparat and make other weighings, but it was only improved, not invented in the 19th century.

6. (2 min) What was the philosophical basis for Lieben's friendly criticism of Paternó's explanation for the possible existence of three isomers of dichloroethane?

Theorizing should not go beyond what experimental evidence can establish. Since there was obviously (obvious to the chemical establishment) no experimental way of discovering how atoms are arranged geometrically within molecules, it is “dangerous for science” to speculate about this subject. “Shooting off into space in search of atoms one risks losing the ground under one's feet.” [This was the point of view of “positivism”, a school of thought advocated by the French philosopher Auguste Comte, who founded sociology.]

7. Four important species in the formation of urea from ammonia and cyanic acid are illustrated in this scheme: $A \rightarrow B \rightarrow C + D$.

(Note that there are **TWO** isomeric resonance-stabilized **PRODUCTS**, one with a new N-H bond, the other with a new O-H bond.)

All necessary atoms are shown in this scheme, but some of the structures need more bonds or charges.

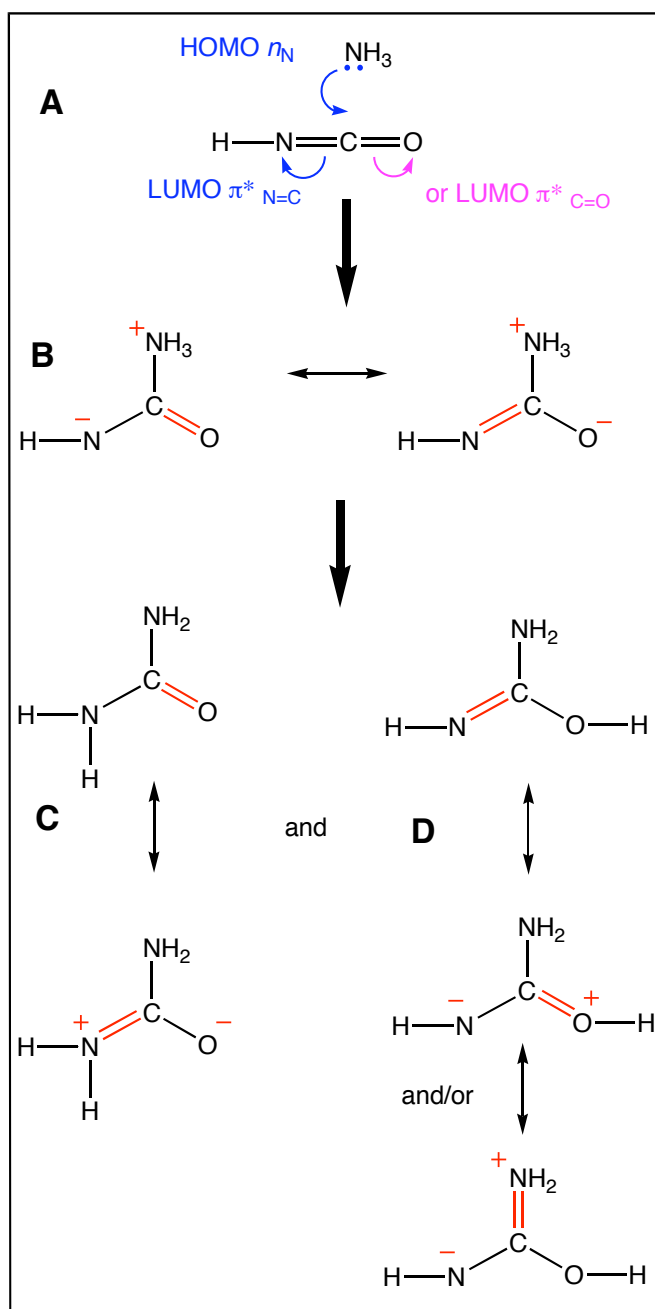
- A. (4.5 min) **ADD BONDS and CHARGES** as necessary to complete **all** partial structures in this scheme.
- B. (6 min) In **species A** identify and label plausible **HOMO** and **LUMO** and draw curved arrows to show formation of **ONE** of the resonance structures of species B. In the space below enumerate the **FACTORS** that makes these two molecular orbitals particularly reactive

HOMO

The unshared pair on N of NH_3 is unusually high in energy (compared to $\sigma_{\text{C-H}}$ or $\sigma_{\text{C-C}}$) because, although it is on an atom with a higher nuclear charge than carbon, it has not been stabilized by overlap with an atomic orbital of another atom to create a bonding orbital.

LUMO

The π^* orbital of $\text{N}=\text{C}$ (or $\text{C}=\text{O}$) is unusually low in energy because of the poor π overlap (raising it from the constituent AOs by much less than σ overlap would do) and because one of the constituent AOs is on an atom with high nuclear charge, leading to poor energy match and reduced AO mixing.



- C. (2 min) Identify plausible HOMO and LUMO in **ONE** of the resonance structures of **species B**.

In either case the charges should play a major role in determining HOMO and LUMO. Other factors could be unshared electron pairs in atomic orbitals and poor π overlap. The high HOMO should be the "anionic" unshared pair on the heteroatom (N or O); and the low LUMO, an N-H σ^* orbital of the ammonium group (or from a more sophisticated MO perspective, a combination of several such orbitals on the ammonium group, though such a sophisticated analysis is not very consonant with looking at a single resonance structure, where one is thinking of localized orbitals). One might speculate that the π^* orbital of the $\text{C}=\text{N}$ or $\text{C}=\text{O}$ group could be the LUMO, but if resonance were taken into account, this orbital would be raised by mixing with the anionic unshared pair on the adjacent heteroatom (O^- or N^- , respectively), so in a broader sense, it would not likely be the important LUMO.

- D.** (4.5 min) Consider the non-ionic resonance structures for C and D of the scheme on the previous page. Explain **IN TERMS OF ORBITAL ENERGIES** which of them should be more stabilized by “resonance”.

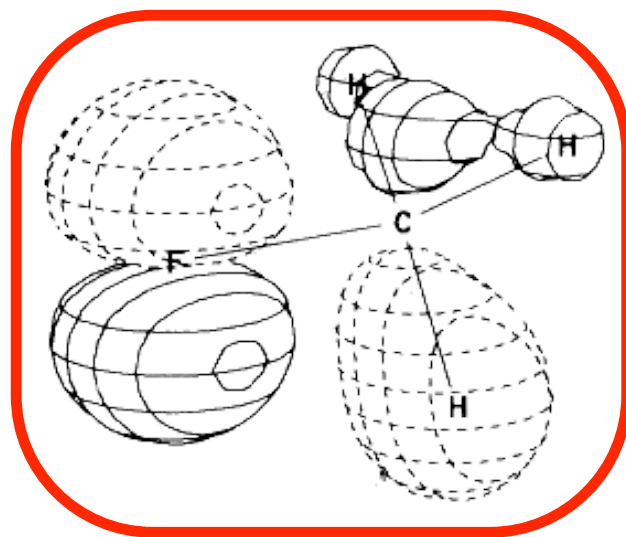
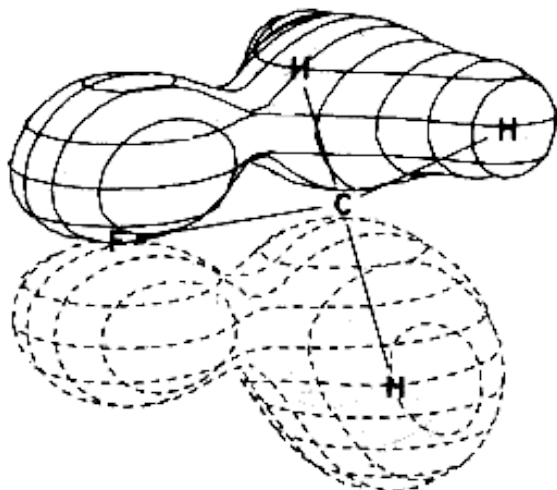
The π^* orbital of C=O is a lower localized LUMO than that of C=N, because the nuclear charge of O is higher than that of N. The unshared pair of N is a higher localized HOMO than that of O, for the same reason.

Thus the isomer with the C=O double bond and two N unshared pairs should benefit more from intramolecular mixing of localized HOMO(s) and LUMO than does the isomer with the C=N double bond and one overlapping unshared pair each from O and N.

Thus one would predict that urea would be more stabilized than its isomer.

[Incidentally, we will see later that C=O is an unusually stable double bond, even without resonance, which reinforces the view that the urea should be more stable isomer.]

- 8.** (4 min) **Circle** the HOMO of F-CH₃ and **explain** your choice (solid and dashed contours have opposite sign).



These are the favorable and unfavorable combinations of a 2p orbital on the F atom and the C-H sigma bond to the lowest H (with *very* small contributions from the other two H atoms). Since both of these component orbitals are occupied by a pair of electrons, both of their combinations are occupied. The unfavorable combination on the right has antibonding node (as well as the atomic orbital nodes on F and C), and is thus the higher occupied orbital of the pair. If one is the HOMO, it must be this one.