Chemistry 125 Third Examination

Name ____________________

November 18, 1998

Generally people did very well on the exam, the best ever on the history questions. The average score was 82.1 with 1/3 of the scores greater that 88 and 2/3 greater than 80.

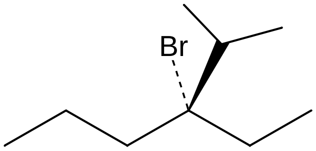
The sum of scores for three exams are also given on the exam paper. The average is 211/300 with 1/3 of the scores greater than 227 and 2/3 greater than 205.

Of course the final examination will count as much in the course grade as these three hour exams put together, but as a rough calibration letter grades are assigned with the following score boundaries:
A 225 A- 220 B+ 210 B 190 B- 170 C+ 150 C

1. (1 min) Give the **average bond energy** for a C-C single bond: ____83____kcal/mole.

Appendix III gives 83 as the average bond energy (ABE) for C-C. Remember that the ABEs are the values that are added for all the bonds in a molecule to predict the heat of atomization. Note that this is close to the experimental bond dissociation for C-C bonds in Appendix II (though the latter are generally 5 kcal/mole or so higher). A distressing number of answers were ludicrously small (e.g. 1 kcal/mole) showing that we haven't placed proper emphasis on these values yet. They are very important, especially for free-radical reactions. If bond energies were so small radical reactions would be fantastically easy.

2. (5 min) Give the **complete, systematic name** for the following isomer of $C_9H_{19}Br$.



(R)-3-bromo-3-ethyl-2-methylhexane (Remember to choose the chain that has the most substituents and to arrange the substituents alphabetically)

3 . (3 min) If you could not look up any values, what **three measurements** would you make to determine the **heat of formation** for a hydrocarbon? **How** would you use the three values to get ΔH_f?

You would measure the heats of combustion of the compound and for elemental carbon and hydrogen in their standard states (graphite and H_2 gas). The heat liberated by combustion of the hydrocarbon minus the heat liberated by combustion of the corresponding amount of the elements is the heat of formation of the compound.

4 . (3 min) **Name** the **Six** sources of strain energy calculated by molecular mechanics in *Chem3DPro*.

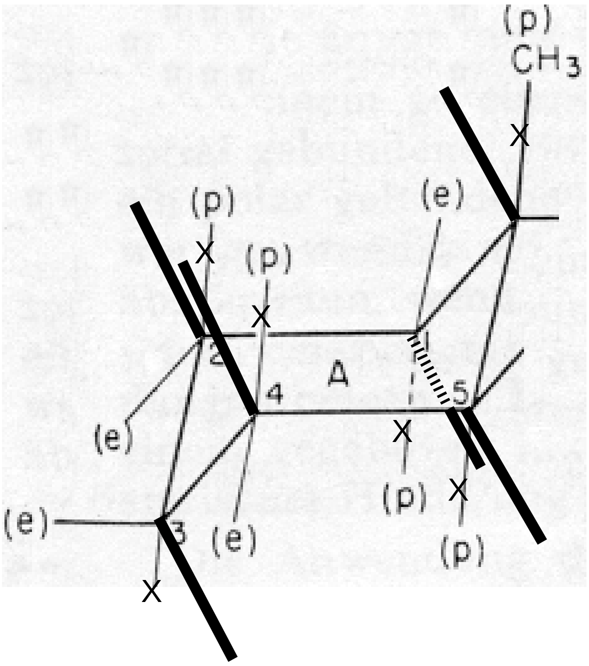
Bond Stretching
Bond Bending
Stretch-bend interaction
Torsion
1,4-van der Waals interaction
non-1,4-van der Waals interaction

5 . (3 min) **Explain** how two sources of strain energy compete to determine the conformation of cyclopentane.

Planar cyclopentane has negligible bond bending strain, because the angles of a regular pentagon are essentially identical to the tetrahedran angle, but in planar cyclopentane the torsional angles are fully eclipsed. By folding the pentagon like an envelope the torsional strain is reduced at a modest cost for making the C-C-C angles more acute.

6 . (5 min) Here is a portion of a drawing of a steroid molecule taken from the 1950 paper that earned Barton his Nobel Prize for introducing organic conformational analysis.

For purposes of this question **pretend that the drawing shows a chair form of methylcyclohexane**.



a) Barton labeled the bonds *polar* (p) and *equatorial* (e). **What do we call them now?**

Polar = Axial

Equatorial = Equatorial

b) Fix this figure by **putting a small 'x'** through every bond whose direction is wrong by more than about 15 degrees and **redrawing it**. (Don't redraw the labels, just the erroneous bonds.)

The axial bonds should be parallel to the 3-fold symmetry axis of the chair arrangement of carbon atoms. In this drawing the axis angles to the left substantially.

c) **Complete names** of the constitutional and configurational relationships between the **"p" hydrogens on carbons 2 and 4** of this structure:

Constitutionally homo topic. Configurationally enantio topic.

d) **Circle** the class(es) of reagents that might react faster with one of these two "p" hydrogens than the other.

Achiral Reagents [✓ **Resolved Chiral Reagents**] No Conceivable Reagent

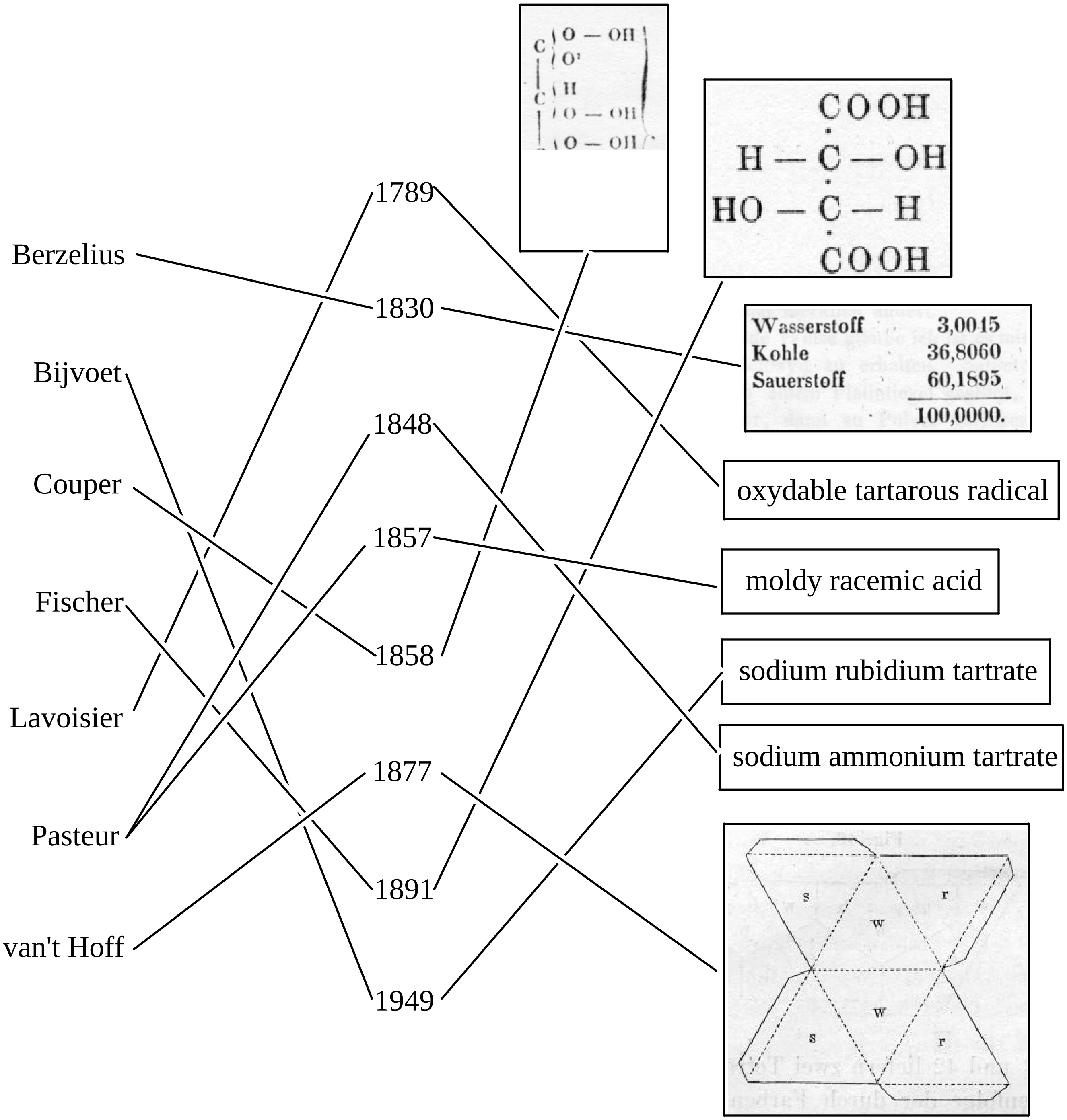
7 . (5 min) **Explain** how the energy difference between the conformational isomers of *n*-butane can be used to estimate the energy difference between the methylcyclohexane chair in Question 5 and the isomer formed by flipping the ring to interchange p and e bonds. Estimate the value of this energy difference in **kcal/mole**.

An axial methyl group is involved in two *gauche* interactions with ring carbons, while an equatorial methyl group is involved in two *anti* interactions. Since the difference between *gauche* and *anti* butane is 0.9 kcal/mole, one would predict an axial-equatorial difference of 2 x 0.9 = 1.8 kcal/mole

There is surely no more venerable set of compounds in the annals of structural organic chemistry than

Tartaric Acid and its Isomers.

8 . (7 minutes) Here are an alphabetical list of **chemists**, a chronological list of **dates**, and a random list of **names or formulas** for tartaric acid and related compounds.



Wasserstoff	3,0015
Kohle	36,8060
Sauerstoff	60,1895
	100,0000.

Draw STRAIGHT lines connecting each **date** with the proper **chemist** and **formula or name**.

(The lines for 1789 are drawn as an example. Draw carefully so there can be no ambiguity.)

HINT: One chemist needs two dates, 1848 and 1857. The latter date was not mentioned in lecture.

9. (12 min) Choose **Four (4 only)** examples from the previous page. For each of the four **explain briefly** (~ two sentences) how the work in which the compound or figure appeared made an important contribution to the **development of organic structural theory**.

Most people did very well on questions 8 and 9. Congratulations. For those who had difficulty note that what is important about this material is not memorizing dates and names but rather understanding how specific macroscopic experiments served as the basis for elucidating the atomic level structure of organic molecules.

Berzelius (1830) proposed the term "isomer" to describe the relationship between compounds that had the same composition (ratio of elements and molecular weight) but different properties. The original example was racemic vs. tartaric acid. This showed that there was more to a compound than its composition.

Pasteur (1840) separated racemic acid (as enantiomeric crystals of its sodium ammonium salt, a conglomerate) into familiar (+) tartaric acid and its unfamiliar enantiomer (-) tartaric acid. This was the first example of artifical resolution a racemate, and it showed that isomerism involving mirror-images was meaningful. Since bonding was not inferred for another 10 years, it was impossible to be more specific about the nature of the isomerism.

Pasteur (1857) found that a sample of racemic acid on which penicillium glaucum was growing contained more (-) than (+) tartaric acid, because the mold had metabolized the familiar (+) form. He thus discovered the method of separating enantiomers by reacting one of them with a chiral catlyst (enzyme).

Couper (1858) proposed the self-linking and tetravalence of carbon (that is the idea of bonds and structures), and drew formulas with dots (or lines) to denote the bonds. These formulas were readily developed into constitutional structures as we write them today.

van't Hoff (1877) explained some 40 known examples of isomerism on the basis of tetrahedral arrangement of the four bonds from a carbon atom. These included both examples of enantiomers (and diastereomers based on what we now call stereogenic centers) and examples of cis-trans isomerism. He predicted enantiomerism in allenes with the C=C=C structure some 60 years before they were observed experimentally.

Fischer (1891) proposed the Fischer projection as a clear, simple notation for showing the disposition of bonds about tetrahedral carbon atoms. His convention involved vertical bonds that receded into the page and horizontal bonds that projected toward the viewer from the stereogenic center in question, with no effort to indicate realistic relative positions of the atoms or molecular conformation.

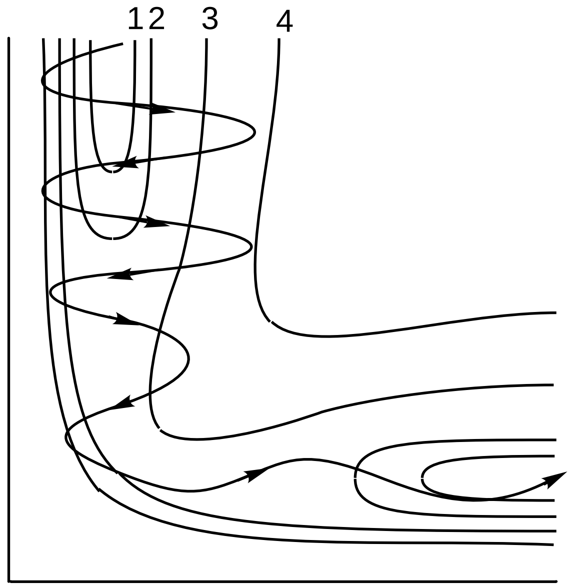
Bijvoet (1949) used the x-ray diffraction technique of analyzing "anomalous dispersion" to determine the absolute configuration of the bonds about stereogenic centers in sodium rubidium tartrate. In so doing he not only demonstrated that Fischer had been correct in guessing the configuration of D-glyceraldehyde, but he also provided a basis and motivation for absolute designation of configuration in the CIP or R/S scheme of nomenclature.

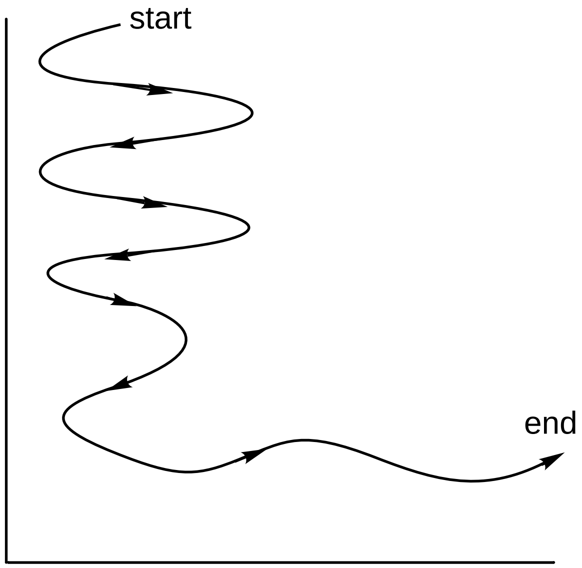
10. (2 min) In 1951 a chemist named Buchanan noted that, “standard text books [are] about equally divided in naming dextro-rotatory tartaric acid D(+) or L(+).”

Explain the source of this confusion in nomenclature.

The + sign refers to the direction in which the sample rotates polarized light and is synonymous with saying "dextro-rotatory". However the D or L refers to which isomer of glyceraldehyde one can make the compound from. These latter names assume that the sequence of reactions used in the conversion is obvious. Evidently it was not at all obvious, since some textbooks referred to one path, and other textbooks referred to another. [This confusion was cleared up when it became possible to use R/S nomenclature to name the absolute configuration of the compound. Using the nomenclature correctly required knowing the absolute configuration, which was deterimined in 1950 by Bijvoet.]

11. (4 min) The diagram on the left shows a hypothetical trajectory superimposed on a potential energy surface (PES). The lowest-energy contour is labeled 1; the highest is labeled 4. For clarity the trajectory is shown on the right without the PES.





a) **What chemical system** might this PES describe? a **linear triatomic** system in which a diatomic molecule is stable. e.g. H-H-H

b) **Label the axes** of the PES. Horizontal: 1-2 distance. Vertical: 2-3 distance

c) In words **describe what the atoms are doing** during this trajectory.

At the beginning molecule 1-2 is vibrating as atom 3 approaches atom 2. After passing over the transition state where all three atoms are close to one another, the trajectory shows much less vibration of the product 2-3 molecule as atom 1 flies away. The decrease in vibrational energy must be compensated by increased translational energy, i.e. atom 1 flies away faster than atom 3 approached.