

Chemistry 124 Third Examination Answers November 14, 2008

Statistics	mean	1/3 >	2/3 >
this exam	76.7	86	71
sum of 3 exams	229.9	247	219

1. Over the past three and a half years the American Chemical Society has honored 181 different compounds as "Molecule of the Week." This week (November 10, 2008) it belatedly honored L-(+)-Tartaric acid (shown in the figures to the right).

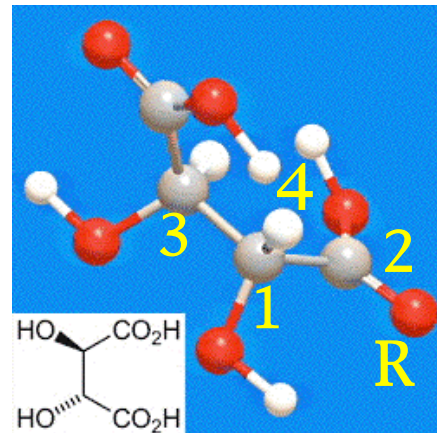
A) (1.5 min) Give common names for **three other** forms (or configurational isomers) of tartaric acid with sharp melting points.

racemic acid [*John's Acid from the Vosges* according to Berzelius]

meso-tartaric acid [originally pyrotartaric acid]

l-tartaric acid [first isolated by Pasteur]

NOTE: *the ACS has chosen to show d-tartaric acid in a very unlikely "eclipsed" conformation. We'll return to this point within a few lectures.*



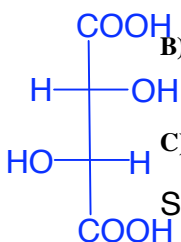
The other stereogenic carbon is also R.

B) (2 min) **Write CIP priority** numbers (1 is high) on the substituents of **one** of the stereogenic carbons in the ball-and-stick formula and **label** it as R or S.

C) (1.5 min) **Explain** whether L-(+)-Tartaric acid should be denoted *d*-, or *l*-, or whether the designation is uncertain?

Since *d*- means the same as (+), and *l*- means the same as (-), it should be *d*-tartaric acid.

D) (2 min) In the left margin **draw the Fischer Projection** of L-(+)-Tartaric acid.



2. (5 min) Briefly describe **two different ways** to separate 50:50 mixtures of enantiomers. Try to be specific. The methods must **NOT** involve the type of conglomerate used by Pasteur in his 1848 preparation of "unnatural" tartaric acid.

The key to separating enantiomers that do not crystallize as conglomerates (mixtures of enantiomerically pure solids) is to separate diastereomers formed by (temporary) interaction with a chiral, resolved substance.

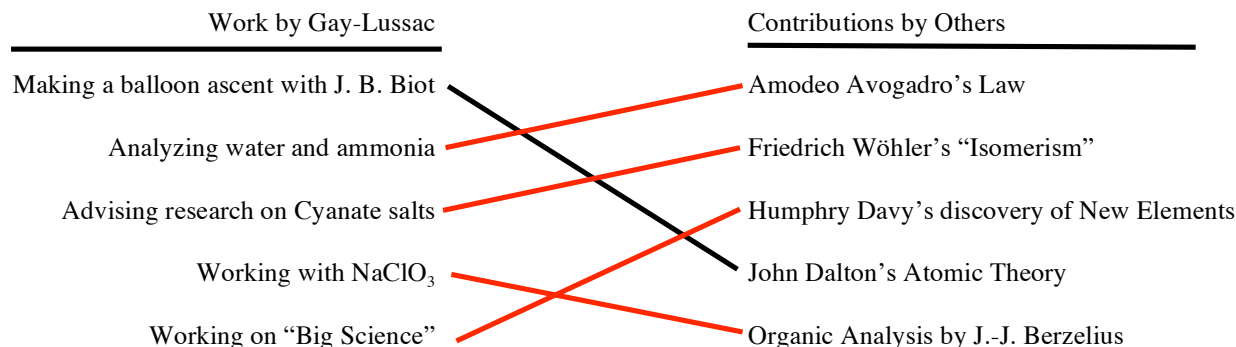
One method is chromatography using a natural solid (such as starch) as the stationary phase. This was used by Eisai scientists in a resolution during the synthesis of the drug candidate E-7389.

A second method is to prepare a salt from a racemic sample of acid and a single enantiomer of a natural alkaloid, such as brucine, separate the diastereomeric salts on the basis of their solubility, and recover the resolved acids from their salts by treating with mineral acid. This was used by Kohler, Walker, and Tishler in resolving an allene derivative to confirm van't Hoff's hypothesis that it should be chiral.

[A different approach to obtaining a single enantiomer, which does not involve separation of a racemate, is to synthesize just the one by starting with resolved starting materials or catalysts.]

3. Joseph Louis Gay-Lussac was involved in a number of important chemical developments at the beginning of the 19th Century that are more often associated with others.

A) (2 min) Draw clear lines to match each of Gay-Lussac's activities in the left column with one of the important contributors in the right column. One line already drawn to help you get started.



B) (5 min) Choose **two of the lines** drawn in part A and write a few explanatory sentences about the connection between Gay-Lussac's contribution and the related contribution by someone else.

During his record-setting balloon ascent with Biot, Gay-Lussac collected samples of the atmosphere to see whether the elemental composition varied with altitude. It was the failure of gases to stratify according to their density that had led Dalton to develop his atomic theory (on the basis of an erroneous theory about lack of heterorepulsion).

Gay-Lussac electrolyzed water and ammonia to their elemental gases and found that the volumes of the gases were simple integral multiples of one another (2:1 for water, 3:1 for ammonia). This led him to "Avogadro's hypothesis" that gases under identical temperature and pressure have equal molecular-number densities.

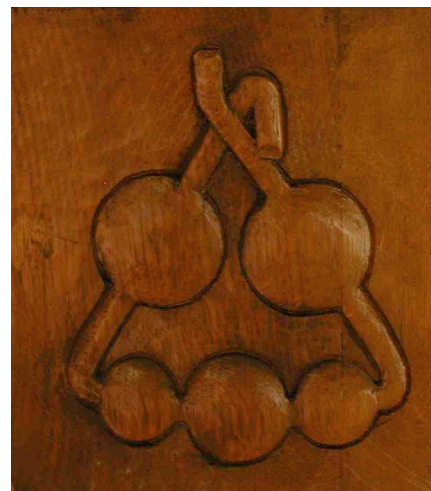
When Wöhler was working on cyanate salts in Gay-Lussac's Paris Laboratory, Gay-Lussac noticed that his elemental analyses for various salts were identical to those Liebig was reporting for the corresponding fulminate salts. In his urea paper Wöhler noted that the cyanates and fulminates were an example of what Berzelius would call "isomerism".

Gay-Lussac proposed the use of sodium chlorate (I had absent-mindedly written NaClO₄, which might have exploded!) as an oxidizing agent for analytical combustion of organic materials that would have charred upon burning in air. Berzelius adopted this oxidizer for elemental analysis.

It was Gay-Lussac to whom Napoleon turned to salvage French national pride after Davy in London had discovered exciting new elements (such as sodium and potassium) by electrolysis. It was in his lab that Napoleon discovered that electricity, in the form of the "Grande Batterie" was less likely to bend to his will than the nations of Europe.

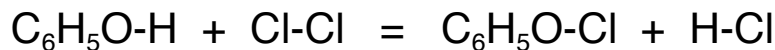
4. (3 min) Explain very briefly why the device shown on this woodcarving in the SCL Library was revolutionary for 19th Century organic chemistry.

Liebig's kaliapparat (or 5-bulb apparatus), by its clever self-stirring design, allowed a single student to carry out three elemental analyses by combustion of organic compounds in a single afternoon. Previously it had taken Berzelius, the world's leading chemist more than a day to analyze a single compound, because it took so long to absorb all the CO₂ with alkali.



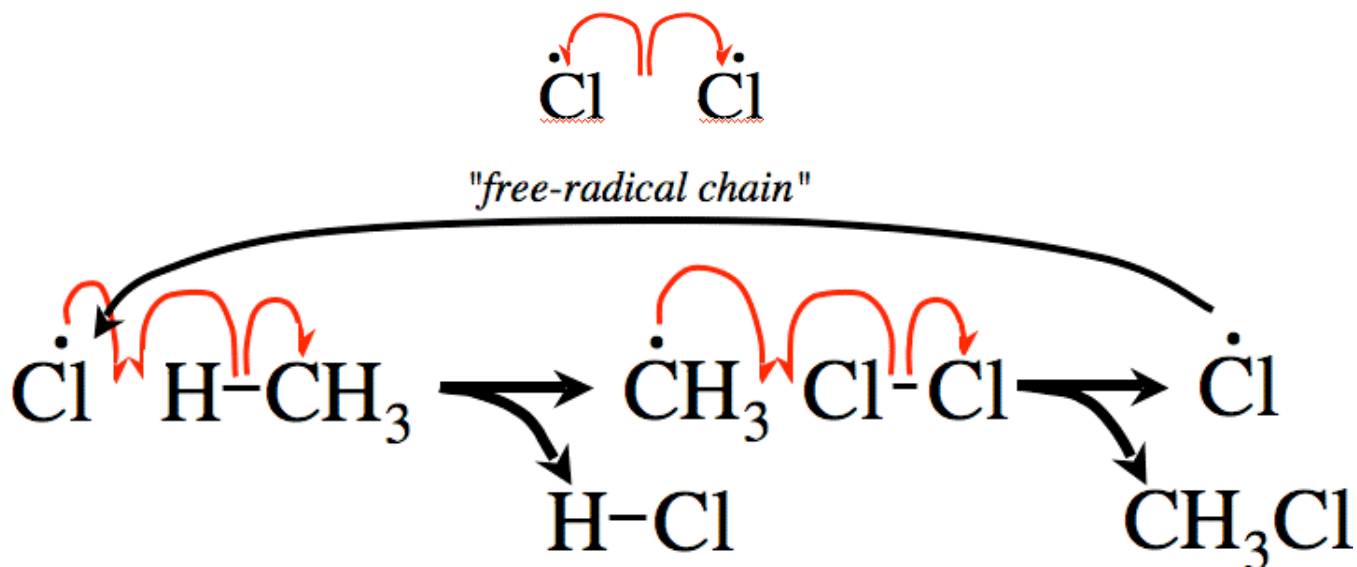
5. The dualistic radical theory of Wöhler, Liebig, and Berzelius was founded in part on the reaction between benzaldehyde (C₆H₅C-H) and elemental chlorine (Cl-Cl).

- A) (3 min) Write a **balanced equation** showing the composition of starting materials and products for this reaction, and **explain** how it might cast doubt on the theory of dualism.



If the benzoyl radical and hydrogen both bond to "negative" Cl, they must both be "positive", thus they should not hold together in benzaldehyde.

- B) (6 min) Draw a series of steps with **curved arrows** to show how the transformation actually *did* involve free radicals.



Free-Radical **Substitution** of $\text{Cl}\cdot$ for $\text{H}\cdot$ (SOMO)

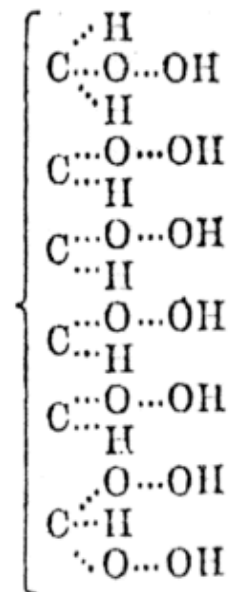
6. (8 min) Suppose a friend of yours who took organic chemistry somewhere else ridiculed this structural formula for glucose. What would you say to *explain* that his *criticism is naïve* and that in fact this formula is not only in its own terms *correct* but represents one of the *most important advances* ever in organic chemistry?

This correct constitution of glucose hydrate was published in the first paper to propose that there are such things as bonds and atomic valence. It is from Couper's paper on the tetravalence and self-linking of carbon from 1858. Before valence, structure had no real meaning.

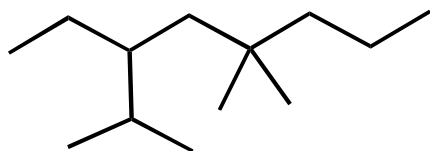
Although the bracket is a remnant from the type theory, Couper's clear, stated meaning is that the carbons are bonded to one another in a chain. The dots, which look funny to your friend, are how he drew bonds in this English version of the paper, but the French version had solid lines.

The doubling of oxygen atoms was because of the contemporary misunderstanding about the atomic weight of oxygen. Couper in this very paper had already corrected a similar misunderstanding about carbon, and said that he would carry on to correct other atoms later (thought mental illness intervened).

The absence of a carbonyl group at the bottom is simply due to the fact that he has drawn the hydrate, a perfectly reasonable form for glucose in aqueous solution.

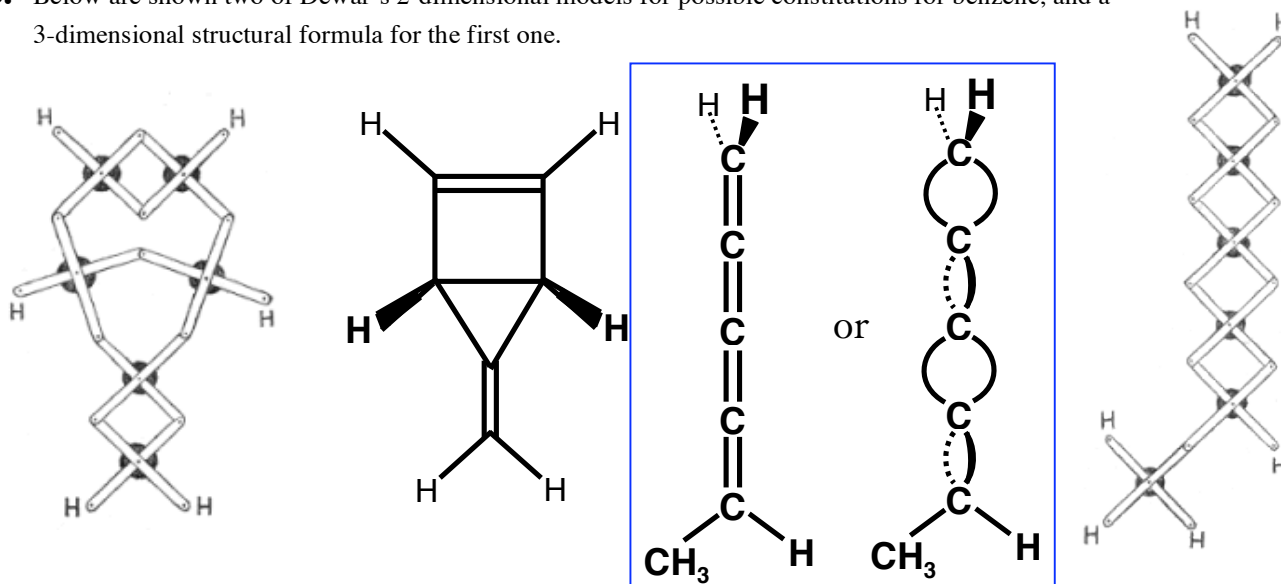


7. (4 min) Draw "3-isopropyl-5,5-dimethyloctane" and give its proper systematic (IUPAC) name.



3-ethyl-2,5,5-trimethyloctane

8. Below are shown two of Dewar's 2-dimensional models for possible constitutions for benzene, and a 3-dimensional structural formula for the first one.



No need to show CH₃ orientation, since that involves conformation (rotation) not configuration.

- A) (2 min) In the open space above draw an analogous 3-dimensional structural formula for the second Dewar model. Use wedges and/or dashed bonds as necessary to show the configuration unambiguously. (Do not worry about conformation.)
- B) (5 min) Explain how counting stereoisomers of monosubstituted versions of these molecules might allow discriminating between the 3-dimensional isomers in Question A.

A monosubstituted version of the bicyclic isomer on the left has three constitutional isomers, each of which is chiral and gives rise to a pair of enantiomers, because none of the hydrogens lies on the molecule's plane of mirror symmetry

A monosubstituted version of the tetraene isomer on the right also has three constitutional isomers, but only one of them is chiral and gives rise to a pair of enantiomers, because the hydrogen and the methyl group on the bottom lie on the molecule's plane of mirror symmetry.