Chemistry 125 Third Examination Answers **November 12, 2004**

1. Water

A. (0.5 minutes) **WHO** invented the names “hydrogen” and “oxygen”? Lavoisier

B. (0.5 min) **WHO** invented their symbols “H” and “O”? Berzelius

C. (2 min) What does the word “oxygen” mean?

“Oxy” means sharp ; “gen” means to create. Thus oxygen creates sharpness, specifically sharpness of taste or acidity. In Lavoisier’s theory a base or radical was converted to an acid by reacting with oxygen.

D. (2 min) Why did Dalton think water was **HO**?

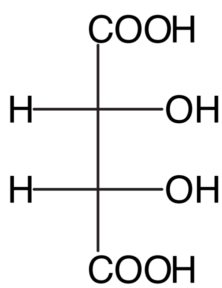
For greatest simplicity Dalton supposed that if only two elements formed only one compound it must contain one atom of each.

E. (2 min) Why did Gay-Lussac think water was $\mathbf{H_2O}$?

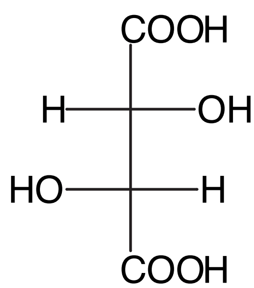
Gay-Lussac found that electrolysis of water yields almost exactly 2 VOLUMES of hydrogen gas for 1 VOLUME of oxygen gas (also a volume of hydrogen gas is completely burned by half of volume of oxygen gas). He assumed that gas volumes were proportional to the number of atoms.

2. (6 minutes) The four forms of the diacid HOOCCH(OH)CH(OH)COOH have the following properties. **Under each set of properties draw Fischer projection(s)** to show the configuration of the corresponding molecules. If you are uncertain, explain your uncertainty briefly.

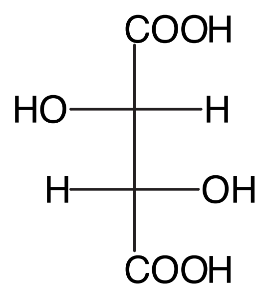
m.p.	140°C	170°C	170°C	206°C
$[\alpha]^{D}_{20}$	0	+13	-13	0



[meso]



[*d*-(+)]



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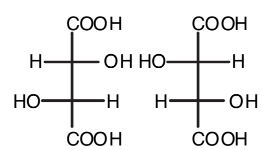


50:50 Mixture

[racemic]

Uncertainty: We have not yet discussed which of the enantiomeric tartaric acids (*d* and *l*) has which “absolute” structure. [This was not discovered until 1949, as we will discuss shortly.]

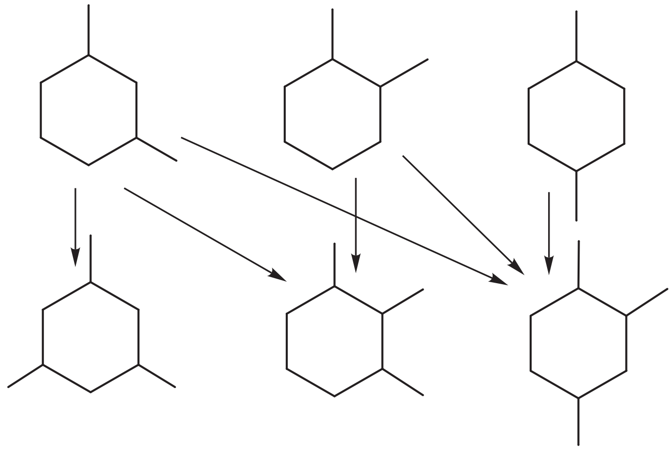
[We did mention in class that racemic acid has a higher melting point than meso-tartaric acid, but this result could not have been foreseen, not can it be understood in simple terms.]

3. (2 min) Explain briefly how elemental mercury played an important part in the **experimental** work of Lavoisier.

Liquid mercury helped Lavoisier handle gases. (1) He could collect gases (especially those that would react with or dissolve in water) by bubbling them into an inverted jar filled with liquid mercury. (2) He could measure the amount of gas before or after a reaction by adjusting the mercury to the same height inside and outside an inverted jar to set the pressure to atmospheric. (3) Although we did not discuss it explicitly, Lavoisier also used mercury to “fix” atmospheric oxygen (as HgO) and to generate pure oxygen gas (by heating HgO with a “burning glass”, used to focus sunlight - analogous to Scheele’s recommendation for heating Ag_2O to generate oxygen).

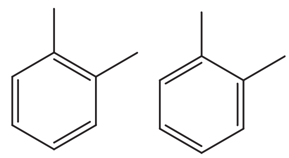
4. In 1866 August Kekulé suggested that his hexagonal structure for benzene was consistent with the existence of three isomers for disubstituted benzenes, but it was his former coworkers who tested this hypothesis with rigorous logic.

A. (3 min) Wilhelm Koerner showed how to demonstrate **which of the three isomers** in the first line below **was which** on the basis of chemical transformations. Complete the diagram to **illustrate this proof**. **(No words necessary)**

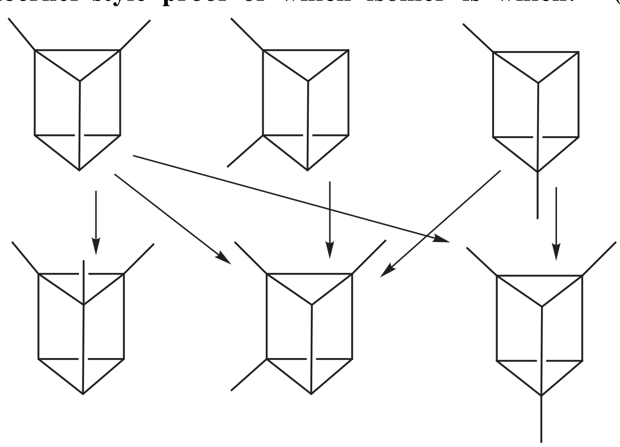


B . (3 minutes) Albert Ladenburg, a contemporary of Koerner in Kekulé's laboratory, preferred the prism structure, shown below, for benzene. **What was Ladenburg's main objection to Kekulé's hexagon structure?**

His main objection was that there should be two isomers for adjacent substituents, depending on whether the C-C bond between them was single or double.



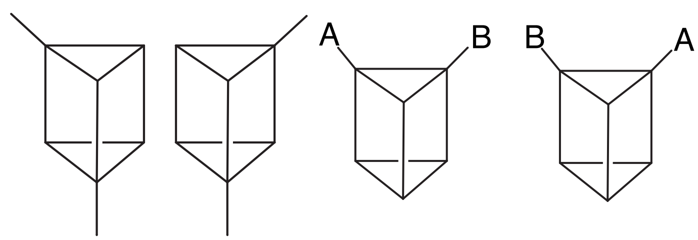
C . (5 minutes) Complete the diagrams below to **show Ladenburg's disubstituted isomers of prismane AND** to suggest a **Koerner-style proof of which isomer is which**. **(No words necessary)**



D . (4 minutes) In 1876 J. H. van't Hoff, a third s tudent of Kekulé, criticised Ladenburg's prism structure. Explain briefly **how this criticism related to other work** that van't Hoff was involved in at this time.

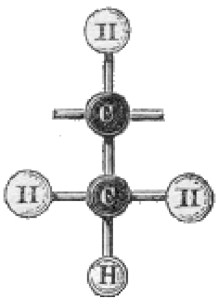
Van't Hoff pointed out that Ladenburg's prism predicts two enantiomeric versions of the structure where substituents are arranged diagonally across a square face, as well when different substituents occupy corners that share a triangular edge.

This was precisely at the time when van't Hoff was working on how consideration of the arrangement of atoms in space (and enantiomerism specifically) could explain previously mysterious cases of isomerism.



5. (5 min) **Choose ONE** of the following figures, and tell how its creator meant it to explain **experimental observations**

Kekulé meant this structure of "acetonic alcohol" to represent a second structural isomer of the alcohol where two CH_3 groups, an OH group and an H atom are connected to a common carbon. In this figure vertical tangency implies bonding, except for the topmost hydrogen circle, which forms a bond by touching the short oxygen" sausage" on its right. Longer sausages are tetravalent carbon atoms.
[We now know that there is but one isomer of isopropyl, or 2-methylethyl, alcohol, which is exactly what the "inferior" Crum-Brown notation suggested.]



This is Hofmann's croquet-ball model of the "olefiant gas", which we call ethene, or ethylene. He knew that this gas was reactive with Cl_2 to give the addition (not substitution) product $C_2H_4Cl_2$ (the "Dutch liquid"). He associated this reactivity with the presence of dangling "unfinished" or "non-saturated" bonds.

6. (3 min) In the opinion of Couper **what two properties of the carbon atom** "explain all that is characteristic of organic chemistry."

1) That the carbon atom is what we would call "tetravalent", forming bonds with 4 H, 4 Cl, 2 O, 2 S, *etc.*
[Couper actually said "equal numbers", because he was using incorrect atomic weights for O and S.]

2) That carbon atoms can bond with one another [surprising for believers in dualism]

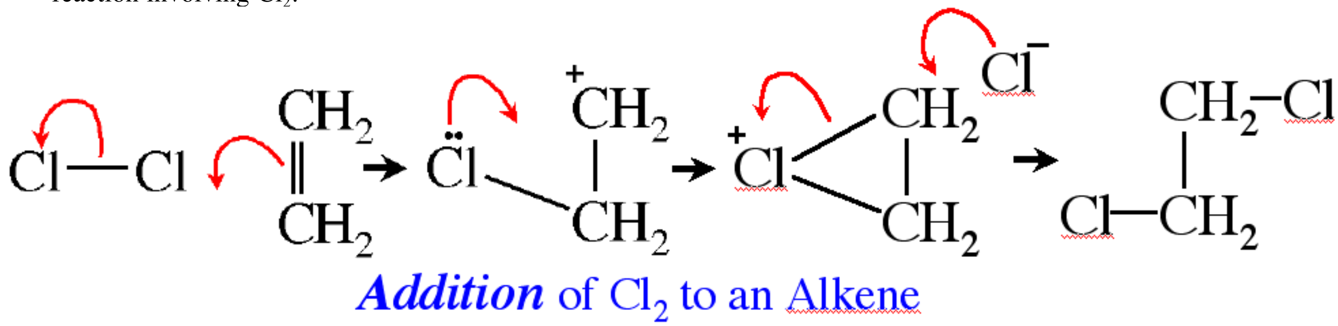
7. (4 min) **Explain why** we have **two** names, butyl bromide and bromobutane, to describe the same compound and why one name has a **space**, but not the other.

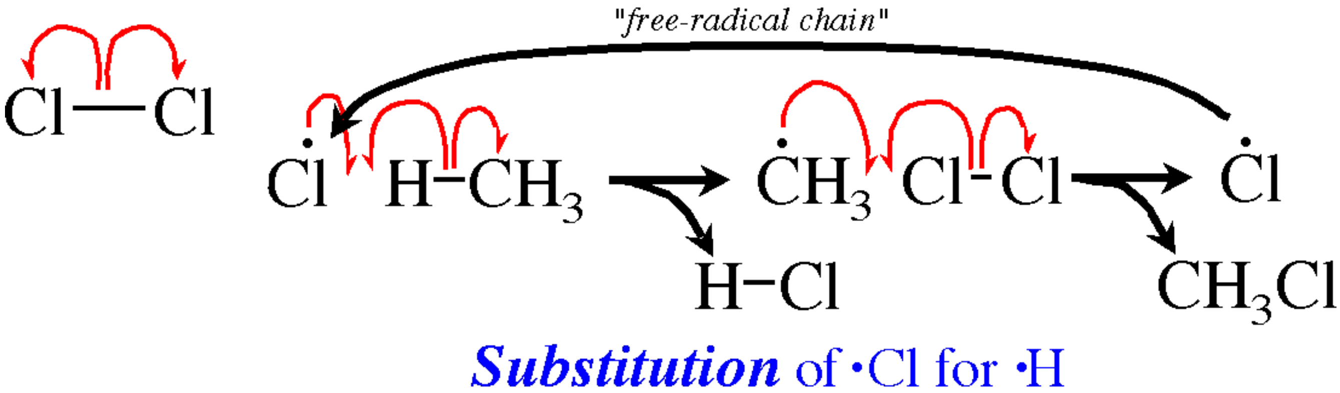
The two names derive from pre-1850 dualistic (radical) theory and unitary (type or substitution) theory.

Radical theory viewed such a compound as formed of two radicals held together by electrostatic attraction; hence the name is in two pieces and the bromine is called "bromide", as in a salt.

Substitution theory viewed such a compound as a derivative of butane in which an hydrogen atom has been replaced by a bromine atom without changing the fundamental nature of the overall compound; hence one word to denote the compound as a whole.

8. (8 min) Use **curved arrows** to show the mechanism of **EITHER an addition OR a substitution** reaction involving Cl_2.





X. EXTRA CREDIT (ONE POINT ONLY – DON'T WASTE TIME UNLESS YOU HAVE PLENTY TO SPARE)

Describe what you consider to be the most egregious example of lack of imagination by an important 19th Century organic chemist.

Examples abound, such as:

Lavoisier claiming , "we have ground to hope, even in our own times, to see [chemistry] approach near to the highest state of perfec-tion of which it is susceptible."

Dalton refusing to consider the possibility that water might be H_2O.

Dumas claiming that inorganic chemistry was completely understood "except for a few cracks here and there"

Dumas asserting that organic chemistry was now completely understood if we could just identify the radicals.

Dumas supposing that heaven would be everyone working on the same problem (his).

Berzelius claiming that an atom as electronegative as chlorine could never enter into an organic radical.

Liebig's refusal to think that anything good might come from the French chemists, "There you will not learn chemistry."

Lieben counselling Paternó to forget thinking about arrangement of atoms in space and failing to consider the implications of tetrahedral carbon.

Kolbe ridiculing van't Hoff for thinking about arrangement of atoms in space.

Ladenburg ridiculing van't Hoff for thinking about arrangement of atoms in space.