Chemistry 125 First Semester Final ExaminationAnswers

December 17, 2002

Average Score 205/300 1/3 > 220 2/3 > 190

1 . (5 min) **What amount** of hybridization occurs in the atomic orbitals that form the bond in a hydrogen molecule?

The AOs are mostly 1s but hybridized with 2.7% 2p (and 0.6% 2s)

Why does the hydrogen AO hybridize? To give better overlap between the two H orbitals

Why is hybridization more important in C-C bonds?

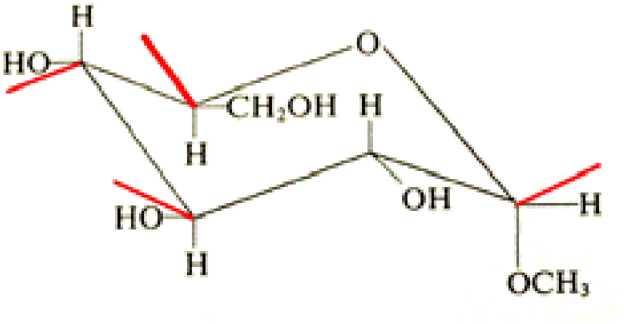
Because the AOs being mixed (2p and 2s in C *vs* 2p with1s in H) have the same principal quantum number. Thus less increase in the energy of the component atomic orbitals is created by hybridization.

What C hybridization gives the **best overlap** at normal C-C bonding distances? sp(1)

2 . (3 min) Yale organic chemistry students 35 years ago studied from a text that showed this figure of the chair conformation of a sugar derivative.

On the figure **redraw** any bonds that need to be adjusted by 15° or more to give a more realistic view of the positions of the substituents on the ring.

Three points were assigned for the really grossly incorrect bond to the CH_2OH group at the back of the molecule; 1 each to the three other equatorial bonds that are off by about 20°.



3 . a) (4 min) Reactions with favorable equilibrium constants (K > 1) usually occur with a release of heat. **Explain** why this is so with reference to the **Boltzmann** factor (don't derive the factor, just use it).

The Boltzmann factor for K is exp(-ΔG/RT), or exp(-ΔH/RT) × exp(ΔS/R).

The first term, involving H, typically dominates.

Thus for K to be greater than 1, ΔH will normally be negative, so the exponent will be positive.

This means that the products contain less energy than the products, the difference being released as heat.

b) (4 min) However, there are first-aid cold packs with two chambers, one containing water, the other ammonium nitrate. When the pack is squeezed, and contents of the two chambers mixed, **a dissolution proceeds that absorbs heat**. **WITHOUT** considering details of whatever change in bonding might occur, **explain using thermodynamic concepts** how it can be favorable for ammonium nitrate to dissolve, even though it absorbs heat.

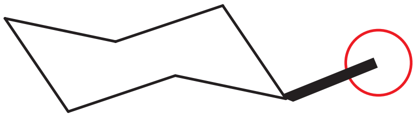
Since heat is being absorbed, the positive ΔH is unfavorable for the dissolution. This means that to be favorable and spontaneous the overall free energy change must be dominated by the ΔS term.

Obviously when an ammonium nitrate crystal dissolves into water, there are many more possible sets of locations for its component ions than when they must all be adjacent to one another in the solid, and the entropy must increase dramatically.

Thus dissolution can be favorable even though more heat energy is required to pull the ions apart that is released by the ions interacting favorably with the water molecules.

4. Using *Chem 3D* one can estimate strain energies for the **two** lowest energy chair conformations of **methylcyclohexane**, the **two** lowest energy chair conformations of ***cis*-1,3-dimethylcyclohexane**, and the lowest energy chair conformation of ***trans*-1,3-dimethylcyclohexane**.

a) (6 min) **Draw lines** indicating bonds to methyl groups on the following cyclohexane skeletons to show which of these five structures has the indicated strain energy (in kcal/mole).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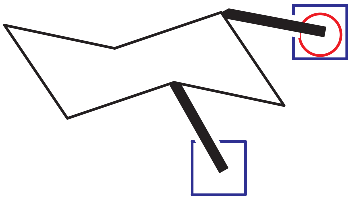
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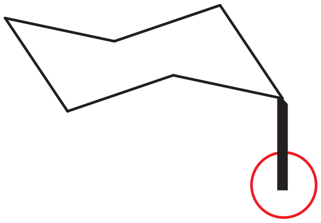
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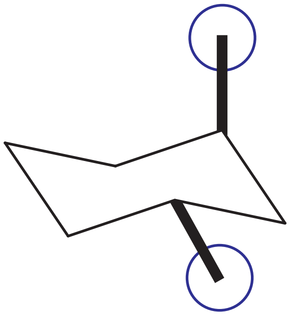
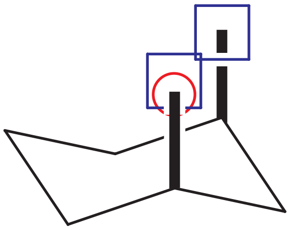

9.0


12.5

[Note that the difference in energy for structures that differ by one equatorial-axial change is 1.8 kcal/mole, as expected (twice the difference between *gauche* and *anti* butane). HOWEVER, the difference between the two structures in the bottom row, which involve single equatorial-axial change, is about twice this large, because the two axial methyl groups run into one another. This is called a “1,3-diaxial interaction”.]

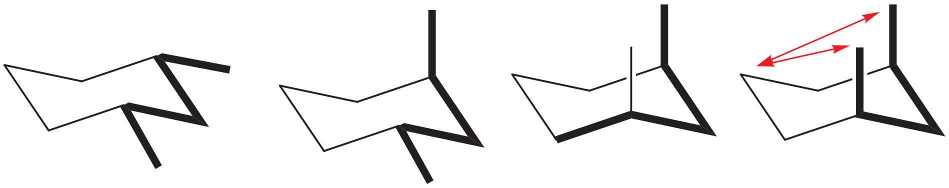
b) (3 min) In the scheme above draw **circles** around two methyl groups that are **conformationally diastereotopic**, and **squares** around two methyl groups that are **configurationally enantiotopic**.

(Only one pair of each is necessary – two circles and two squares)

Note that topicity relationships can be within or between molecules. In the figures above blue denotes relationships between two methyls within a single molecule, while red denotes relationships between methyls on different molecules. There is another intermolecular conformationally diastereopic pair involving the other methyls of the 7.2 and 12.5 conformations.

c) (6 min) **Explain** how some of the energies above relate to the difference in strain energy between the most and the least strained conformational isomers of n-pentane.

[Consider *gauche* and *anti* conformation about the two central C-C bonds of pentane]



Note the presence of the *anti-anti, anti-gauche*, and two different *gauche-gauche* pentanes within the structures in part a.

In particular note that the difference between the first and the last 1,3-dimethylcyclohexanes should be the same as that between *anti-anti* and the higher energy *gauche-gauche* pentane EXCEPT that the 1,3-dimethylcyclohexane transformation includes two *anti* to *gauche* butane changes (indicated by red arrows) that are absent in pentane. Thus one would predict a difference in the pentanes of 12.5 - 7.2 – 2 x 0.9 = 3.5 kcal/mole. The value calculated using molecular mechanics (*Chem 3D*) is 3.53 kcal/mole.

5 . (6 min) Indicate circumstances that might give rise to each of **TWO** of the following three reaction-order phenomena:
zeroth order **half** order **pseudo first** order

Zeroth order means that the rate is independent of the concentration of reactants. A common example is when a necessary catalyst (for example, an enzyme) is saturated, that is, operating at maximum velocity.

Half order occurs when the dominant form of the reactant is a dimer, but a monomer is the reacting species. Doubling the amount of reactant approximately doubles the concentration of dimer (since it is the dominant species), but the concentration of the small amount of reactive monomer, controlled by the relationship $[M]^2/[D] = K$, or $[M] = (K[D])^{1/2}$, increases by a factor of only $2^{1/2}$.

Pseudo first order means that the reaction rate appears to decrease exponentially, despite the fact that several species must get together in the rate determining transition state, so that the rate should be proportional to the concentration of each. This occurs when the concentrations of all but one species fail to change significantly during reaction, because they are catalysts or in gross excess (for example the solvent).

6 . Quantum mechanics deals in the kinetic and potential energies of a system. Although it is possible to solve the Schrödinger equation for any old form of the potential energy (*e.g.* harmonic oscillator or Morse potential), there is in fact just one fundamental force law involved in the quantum mechanics of electrons in atoms or molecules.

a) (2 min) **Name** the fundamental source of electron's potential energy and write a **formula** that expresses it.

Coulomb's Law. Energy $= q_a q_b / r$; or Force $= q_a q_b / r^2$

where the q values are charges of particles a and b, and r is the distance between them

b) (3 min) Given this formula, how did **Earnshaw's theorem** make it impossible for an atom to have a static "structure" in terms of classical physics.

Earnshaw's Theorem states that no energy minimum is possible for a set of separated bodies obeying inverse-square force laws. Thus the charged particles in atoms could have no stable stationary structure.

c) (2 min) Quantum mechanics made atomic structure possible by reformulating kinetic energy. Write the quantum-mechanical **formula for kinetic energy** (in one dimension) and express in words what the formula says.

$$KineticEnergy = \frac{-C}{m} \times \frac{\partial^2 \psi / \partial x^2}{\psi}$$

[where $C = h^2/8\pi^2$, h is Planck's constant and m is the particle's mass]

This says that the kinetic energy of a particle in one dimension is a negative constant times the "curvature" of its wave function divided by the value of the wave function and by the particle's mass.

[The word "curvature" is put in quotes, because it is used as a shorthand for the second derivative.]

7 . We have considered trivalent carbon (e.g. $\cdot CH_3$) as a reactive intermediate. Next semester we will briefly consider divalent $:CX_2$ intermediates as well. They are called carbenes.

a) (6 min) One can wonder whether the geometry of $:CH_2$ should be linear (∠HCH = 180°) or bent. Suppose the preferred angle is 100° (the value measured by spectroscopy for $:CCl_2$). Use this angle to **discuss** the **factors** determining the **hybridization** of the carbon atom in $:CH_2$ **and** the nature of its **HOMO** and **LUMO**. **Draw** these orbitals.

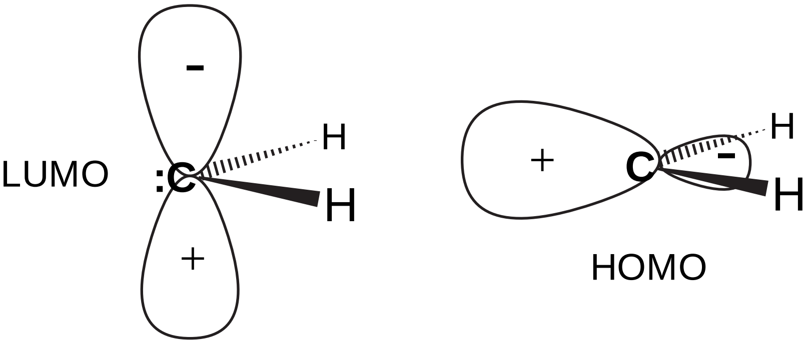
Having formed bonds to two H substituents, the carbon is left with two vacant valence-shell AOs and two electrons to put into them.

[Since the question specifies a HOMO and a LUMO, there must be one AO with no electrons and one with an unshared pair of electrons - not the alternative in which each of the AOs has one electron and functions as a SOMO, although this is indeed another option and sometimes occurs for divalent carbon species.]

(continued next page)

The LUMO will obviously be a 2*p* orbital of carbon, leaving the lower-energy 2*s* orbital character available for electron occupancy. [Actually this proved not to be as obvious as I had hoped, since many answers suggested $\sigma^*_{C\text{-}H}$ as the LUMO, which made the rest of Question 7 more difficult to answer reasonably.]

The HOMO will be some sort of sp^x hybrid reflecting a competition between maximizing *s*-character (to stabilize its two unshared electrons - the carbon has only ~ half a share in the pair of electrons in each bonding orbital) and maximizing the *s*-character in the two C-H bonding orbitals (to give the best possible overlap). The small 100° H–C–H bond angle shows that each bonding hybrid AO has <1/3 of *s*–character, leaving the unshared pair orbital a > 1/3 share.



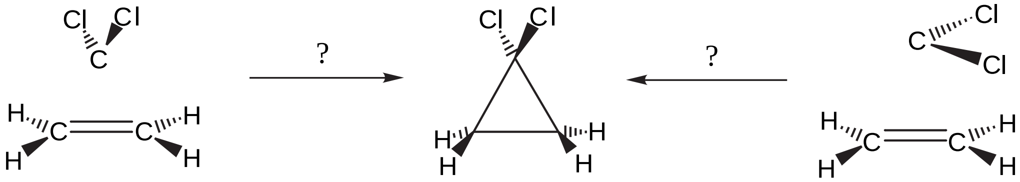
b) (2 min) **Explain** whether the **HOMO** of $:CH_2$ should be more or less reactive that that of NH_3, **and** whether the **LUMO** should be more or less reactive than that of BH_3.

The most significant differences involve the different nuclear charges.

The additional proton in the N nucleus makes its unshared-pair HOMO lower in energy, and less reactive, than the corresponding HOMO pair on C (despite the extra s-orbital character on carbon). To be reactive HOMOs should be high in energy.

The additional proton in the C nucleus makes its vacant *p* orbital lower in energy, and more reactive, than the vacant *p* orbital on BH_3.). To be reactive LUMOs should be low in energy.

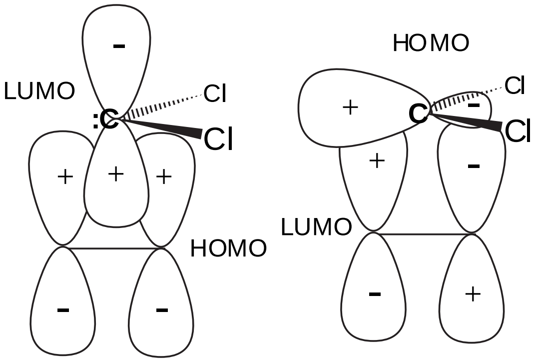
c) (6 min) A characteristic reaction of $:CCl_2$ is addition to an alkene to form a dichlorocyclopropane. **Discuss the orbital mixing** occurring at the transition state for this addition to decide whether it would be better for CCl_2 to approach ethene **"head-on"**, as shown at the left **or "sideways"**, as shown at the right.



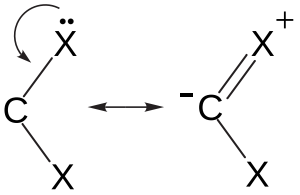
Initial "sideways" approach should be favored since it allows the divalent carbon LUMO to overlap with the π–HOMO of the alkene, and its HOMO to overlap with the π*–LUMO of the alkene.

"Head-on" approach would make the orbitals for both of these potentially stabilizing HOMO-LUMO interactions orthogonal.

[Next semester we'll see more such "pericyclic" reactions, where orbital signs are of paramount importance.]



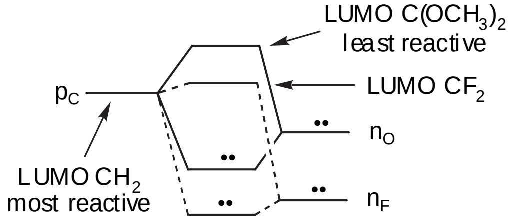
d) (6 min) Use plausible **resonance structures** and orbital-mixing **energy diagrams** to predict relative reactivities of the three CX_2 molecules where X is H, or F, or OCH_3.



Reasonable for X = OCH_3,

Possible for X = F
(poorer energy match)

Impossible for X = H
(no unshared pairs)



[Note that if you want to draw a plausible, non-trivial resonance structure, there must be a low vacant MO into which the electrons can shift. A distressing number of papers proposed electron shift toward the X group which has no low vacant orbitals. A trivial case where the vacant orbital is not necessary is the polar resonance structure of a normal valence bond, *e.g.* C^+ X^- as a resonance structure of C-X. Such polar resonance structures rarely explain a stabilization that is really worth explaining.]

8. (6 min) Describe the **experimental** (**NOT theoretical**) **basis** for **ONE** of the following claims. Be **specific.**

The favored path for attack of a HOMO nucleophile on a carbonyl group is not along a line perpendicular to the C=O bond.

Bürgi and Dunitz prepared a sort of movie of nitrogen attacking a carbonyl group. They found x-ray crystal structures of many different compounds that had both C=O groups and nitrogen atoms and plotted positions of the relevant atoms (N, C, O, and the two other atoms attached to C) on the same graph. For all N-C distances ranging from about 1.4 to 3 Å they found that the N-C-O angle was near 110°, not 90°.

[Furthermore as N approached the carbon, the C-O disance lengthened, and the other substituents on C bent back so that the 4 C bonds smoothly approached tetrahedral geometry.]

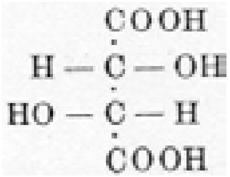
Cf. http://classes.yale.edu/chem125a/125/quantum/end/burgidunitz.htm

Molecular mechanics calculation of bromine-bromine repulsion in organic molecules should be taken with a grain of salt.

Using data from a very large number of x-ray crystal structure determinations a polar graph was prepared showing the positions of two bromine atoms and the carbon atom attached to one of them. It showed the distance of a Br atom from a reference Br atom and the angle it made with the Br-C bond of the reference Br. It was found that the average distance of close approach (which defines a “van der Waals radius”) varied with angle so that the Br van der Waals envelope is ellipsoidal rather than spherical. Approach is about 15% closer along the extension of the C–Br bond (~3.4Å) than at substantial angles off that axis (~4Å). Since molecular mechanics programs fail to take account of this angular variation of van der Waals radius, one should be suspicious of detailed interpretation of their results, especially when Br···Br (or I···I) contacts are involved.

Cf. http://classes.yale.edu/chem125a/125/Chem3D/BrvdW.html

9. No substance played a more central role in the development of organic chemistry generally, and stereochemistry in particular, than **tartaric acid** (2,3-dihydroxybutanedioic acid). Its monopotassium salt deposits on the inside of wine casks, and when recrystallized is called "cream of tartar." The salt was called tartarum already in the 13th Century.



a) (5 min) The structure of **L-(+)-tartaric acid** shown above is taken from the 1891 paper that first proposed this type of drawing for depicting stereochemistry. **Explain** what "**L**" and "**(+)**" mean in this name, **and** give the correct absolute (**CIP**) descriptor for the configuration shown by this structure.

"L" means that the molecule can be synthesized from levorotatory glyceraldehyde
[*i.e.* in this Fischer projection the OH is to the left and the H to the right on the next-to-bottom carbon.]

"+" means that a solution of the substance rotates the polarization plane of transmitted light clockwise as it passes toward the viewer.

The descriptor is (2R,3R). Both chiral centers are of R absolute configuration.
[priorities: O > C(OOO) > C(OCH) > H]

b) (10 min) Here are three years we mentioned in class in which tartaric acid played a role in the development of non-stereochemical organic theory: **1789, 1830, 1858**. Choose **TWO** of these three dates and explain, in a few sentences each, what the development was in which tartaric acid played a role.

1789: Lavoisier in his "Traité Élémentaire de Chimie" proposed that acids were formed by adding oxygen to a "radical" or "base". Many of these radicals were "simple", that is, composed of single elements, such as sulfur, charcoal, and phosphorus. Others, especially among organic substances, were "compound" radicals containing a number of elements. One of the compound radicals Lavoisier cited was the tartaric radical of "tartarous" acid [which he said had been "unknown until lately"].

1830: Berzelius performed careful elemental analysis on both tartaric acid ("Weinsäure") and racemic acid ("John's Acid from the Vosges"), and found that, although they had different melting points and other properties, they had exactly the same elemental composition. In the paper describing this discovery he proposed calling compounds that had the same analysis but different properties "isomeric", because they were composed of the same (iso) parts (mers). This showed that there was more to organic molecules than what atoms they contained – an idea that ultimately led to the concept of molecular structure.

1858: In his paper proposing the tetravalence and self–linking of carbon atoms, Couper drew the first correct constitutional formulas for a number of simple organic molecules (and for some molecules as complex as glucose). One of these formulas was for tartaric acid. [Of course his formulas look confusing today because he assumed that the atomic weight of oxygen was only 8 times that of hydrogen, so all of his oxygen atoms were doubled.]

c) (15 min) Here are four years we mentioned in class in which tartaric acid played a role in the development of organic **stereochemistry**: **1848, 1857, 1877, 1949**. Choose **THREE** of these four dates and explain, in a few sentences each, what the development was in which tartaric acid played a role. [We didn't mention 1857, which was the year of the second discovery by the individual who made the 1848 discovery.]

1848: Pasteur carefully studied the form of crystals of the sodium ammonium salt of racemic acid and noticed that while some of the crystals had the same form as crystals of sodium ammonium tartrate, others were the non-superimposable mirror image of this form. He separated these mirror image crystals, converted them to the acid, and found that it had the same properties as tartaric acid, except that it rotated polarized light in the opposite direction. This was the first intentional resolution of a racemate. [Pasteur noted that the atoms must be arranged in some sort of chiral structure, such as on a helix. He was "lucky" that this particular racemate salt crystallized as a conglomerate in which not only did the enantiomers segregate into different crystals, but also the crystals showed faces that made the mirror image relationship obvious to the careful observer.]

1857: In purifying an old bottle of racemic acid upon which a penicillium mold had grown, Pasteur found that the remaining acid was the enantiomer of normal tartaric acid, *i.e.* it was the same acid he had discovered in 1848. He concluded that the microorganism must have destroyed the "natural" enantiomer of tartaric acid, leaving behind the unnatural form. This was the first discovery of resolution of a racemate by biological reagents. [This was also the line of work that ultimately led Pasteur, who had begun as a physicist, into the study of microbiology.]

1877: In the German edition of his *"The Arrangement of Atoms in Space",* van t'Hoff explained the existence of three stereoisomeric versions of the tartaric acid molecule, one of which fails to rotate the plane of polarized light, as an example of the operation of two chiral centers. They may reinforce one another by being of the same (right or left) hand, or cancel one another to give an achiral "meso" compound.

1949: On the basis of unusually careful x-ray diffraction measurements on crystals of the rubidium sodium salt of tartaric acid, the Dutch crystallographer Bijvoet was able to determine which mirror image was which of the enantiomeric tartaric acids. From this time on it was possible to speak of absolute, rather than relative, configuration of chiral centers, and a new scheme was introduced (the "R/S" nomenclature of CIP) to denote absolution configuration. [Bijvoet's work was published in 1951.]

d) (6 min) Consider the two H atoms **bound to carbon** in L-(+)-tartaric acid, and the two H atoms **bound to carbon** in *meso*-tartaric acid. In the "topicity" column of the following table **enter the name of the configurational topicity** relationship between the indicated H atoms. Put an **"X"** in each box where the indicated reagent **could *in principle* discriminate** between them:

H-Pair	Topicity Name	Br Atom?	Dehydrogenase Enzyme?	No Possible Reagent?
two Hs of L-(+)	**HOMOTOPIC**			X
two Hs of *meso*	**ENANTIOTOPIC**		X	
H of L-(+) and H of *meso*	**DIASTEREOTOPIC**	X	X	

10. (8 min) Consider the energy of the lowest allowed level for an electron in a double-minimum potential (for example, H_2^+) as the distance between the minima (the protons) changes. Would you agree with the claim that significant bonding occurs only when tunneling becomes rapid? **Why**? [A proper answer must mention what determines the rate of tunneling.]

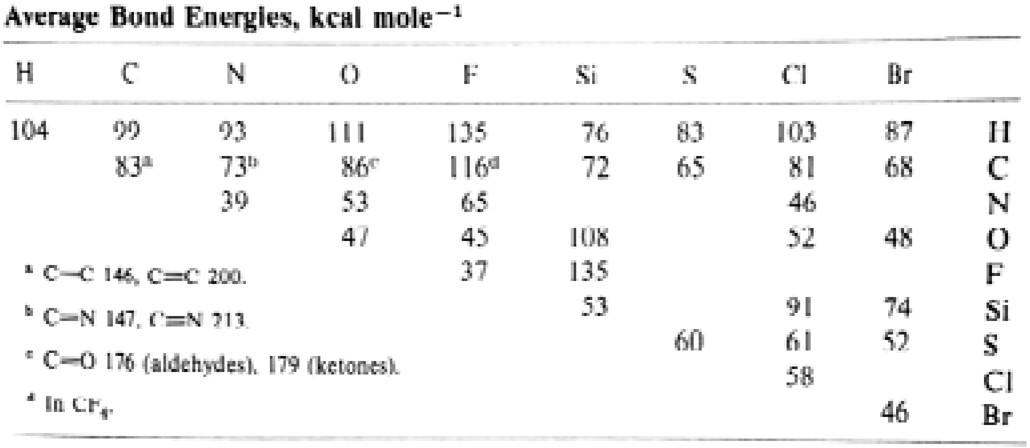
When two orbitals of the same energy overlap (as in the case of H_2^+) they mix to give a "sum" combination that is lower in energy than either of the initial orbitals and a "difference" combination that is higher. The amount by which the energy of the "sum" combination is lowered determines the strength of bonding when the orbitals are occupied by two electrons, both in the lower orbital. The difference between the "sum" and the "difference" orbital (the splitting) is roughly twice as large as the bonding stabilization. However, this same splitting is proportional to the rate at which electrons tunnel back and forth between the two overlapping atomic orbitals.

[The tunneling rate is about 10^{13}/sec times the energy separation in kcal/mole;
see http://classes.yale.edu/chem125a/125/quantum/tunnelbond/tunnelbond.html]

Once the atoms come close enough together for significant bonding to occur ("sum" energy lower than isolated AO energy), the tunneling rate must be very high ("sum"-"difference" splitting large). Even if bonding lowers an electron's energy by only 5 kcal/mole, its tunneling rate is about 10^{14}/sec.

[Note, incidentally, that for the coulombic potential wells of atoms, the barrier between the two wells is almost always higher than the energy of bonded electrons, so the only way for electrons to pass back and forth between the wells is by tunneling.

Note also that this factor of 10^{13}/sec is completely independent of the similar factor that appears in transition state rate theory. Tunneling does not require collecting enough energy to get over a barrier, it is a purely quantum-mechanical phenomenon.]



Average Bond Energies, kcal mole^{-1}

H	C	N	O	F	Si	S	Cl	Br	
104	99	93	111	135	76	83	103	87	H
	83[a]	73[b]	86[c]	116[d]	72	65	81	68	C
		39	53	65			46		N
			47	45	108		52	48	O
				37	135				F
					53		91	74	Si
						60	61	52	S
							58		Cl
								46	Br

[a] C=C 146, C≡C 200.

[b] C=N 147, C≡N 213.

[c] C=O 176 (aldehydes), 179 (ketones).

[d] In CF_4.

11. It was found in 1832 that the oil of bitter almonds (benzaldehyde) reacted with chlorine to replace H by Cl.

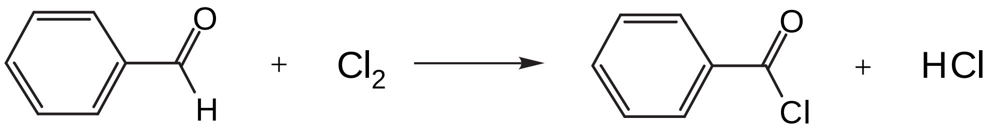
a) (4 min) **What theory** did this observation engender in 1832?

The “radical” or “dualistic” theory of Liebig and Wöhler

What subsequent line of research in the 1840s cast doubt on the correctness of this theory?

Reaction of elemental chlorine with acetic acid under the influence of light replaced H with Cl within the acetyl radical, which had been supposed to constitute the organic equivalent of an inviolable element. This led to the “type” or “unitary” or “substitution” theory of the French chemists. [It is ironic that *both* of these reactions (1832 and 1840s) actually involve free-radical reactive intermediates, SOMOs.]

b) (5 min) Use the data in the table above to **estimate the equilibrium constant** for this double decomposition:

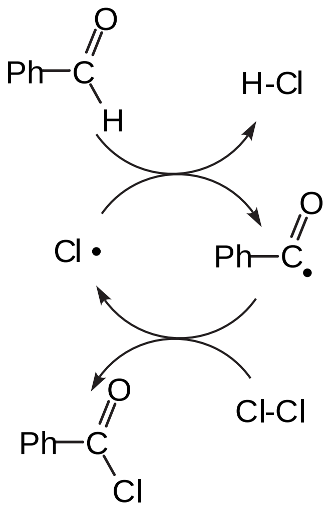


Bonds lost :	C-H (99 kcal/mole) and Cl-Cl (58 kcal/mole)	total 157 kcal/mole
Bonds gained:	C-Cl (81 kcal/mole) and H-Cl (103 kcal/mole)	total 184 kcal/mole
Net Gain in Stabilization		27 kcal/mole

$$K = 10^{-3/4\ \Delta H} \approx 10^{21}$$

[Obviously the sign of ΔH must be negative, since stronger bonds should be favored at equilibrium. Make sure to apply this common-sense test to your arithmetical treatment of equilibrium problems.]

c) (5 min) Use a **cyclic diagram** to show the radical-chain **propagation** steps that would be involved in this transformation. [You may abbreviate the benzene ring by “Ph”.]



d) (4 min) **Which** propagation step in 11c do you think should be slower? **Why**? Why might you worry about using the **numbers in the table** above for estimating its rate?

The first step is exothermic by 103 – 99 = 4 kcal/mole.

The second step is exothermic by 81 – 58 = 23 kcal/mole

Although one could not be certain *a priori*, it is quite likely that a simple one–stage reaction that is very exothermic should be much faster than an otherwise comparable reaction that is only slightly exothermic, so the first step probably has the smaller rate constant.

[The actual rate, as opposed to the rate constant, has to be identical for all steps in a cyclic mechanism. In this case equality in rates will be achieved by building up the concentration of Cl atoms at the expense of benzoyl radicals. This slows the “fast” step and accelerates the “slow” step until their rates become equal.]

The “average” values for C-H and C-Cl bond energies might not apply to bonds from a carbonyl group, because of the unusual C hybridization, the elecronegativity of O, and the possibility of resonance involving the C=O double bond.

[In fact the benzoyl-H bond is rather weak. Compare the acetyl-H bond, 86 kcal/mole in the Table of Bond Dissociation Energies, which would predict greater exothermicity and a faster first step.]

e) (2 min) Suggest plausible **initiation** and **termination** steps for this process

Initiation: Light-induced decomposition (“photolysis”) of Cl-Cl, or thermal decomposition (“thermolysis”) of an “initiator” with an unusually weak bond, such as RO-OR

Termination: Coupling of two radicals to form a bond - Cl with Cl, benzoyl with benzoyl, or Cl with benzoyl. [Since Cl radicals should be in higher concentration than benzoyl radicals (see part d) Cl with Cl may be the most likely termination.]

12. (8 min) Give the key reasoning behind **one** of the following arguments (complete details are not required):

Clerk-Maxwell’s derivation of the distribution of translational energy among atoms

By analyzing the mechanics of how rigid balls bounce off one another, Maxwell convinced himself that the velocities along three mutually perpendicular axes of any given atom in a randomly colliding set of atoms should be independent of one another. Furthermore the probability distribution of these three components of velocity should be identical. Thus the probability of any particular set of three velocities should be the PRODUCT of the distribution functions for the three component velocities. However, since this joint probability should be independent of direction, it must also be the probability of having the corresponding total velocity (which is the square root of the SUM of the three component velocities, each squared). There is only one function with the property that the product of three identical functions of the independent components is equal to a function of a sum of the squared components. This function which allows multiplication by addition is the exponential of the squared velocity. Thus the velocity distribution function must be proportional to the exponential of some constant times the velocity squared. [The constant must be negative to keep the probability finite for high velocity, and must include 1/T to give the proper average energy.]

Boltzmann’s derivation of the distribution of energy among molecular “degrees of freedom”

One assumes that a fixed amount of energy is distributed in bits among a number of “degrees of freedom” and that all distributions (which Boltzmann called complexions) are equally likely. Thus counting the number of complexions involving the permutations of remaining energy among the other degrees of freedom, for any particular number of energy “particles” in a particular degree of freedom, gives the relative probability of having the corresponding amount of energy in that degree of freedom. Statistical analysis shows that this probability decreases exponentially with the amount of energy in any particular degree of freedom. That is, the more energy is put in the one degree of freedom, the fewer permutations are available for the remaining energy. Boltzman used particulate energy only in order to be able to do statistics. He then took a limit for an infinite number of infinitesimal energy bits to simulate an energy continuum.

Planck’s explanation of why “black body radiation” passes through a maximum with decreasing wavelength.

Maxwell’s laws of electromagnetic radiation predicted that, in equilibrium with a set of oscillators containing equal amounts of excess energy, the density of radiation energy should increase with increasing frequency (decreasing wavelength). The observed decrease in density for very low wavelengths suggested that very high-frequency oscillators must be less populated and thus have less excess energy. Planck showed that this would occur if energy were particulate and the bits that could enter or leave oscillators were of a size proportional to the oscillation frequency. Applying Boltzmann’s method to such particulate energy explained the empirical form of the intensity distribution of “black body radiation” that had been determined by Lummer and Pringsheim at the PTR.

13. (8 min) The website (www.blacklightpower.com) of a startup company in Cranbury, NJ, claims invention of a promising new source of abundant, clean energy in the following words:

> *Blacklight Power cells generate energy through a chemical process (BlackLight Process), which the Company believes causes the electrons of hydrogen atoms to drop to lower orbits, thus releasing energy in excess of the energy required to start the process.*

The idea seems to be that they can start with H atoms in their lowest previously known energy state, and make them release energy by falling to a still lower energy state, previously unknown, presumably one where the electron is nearer to the nucleus on average.

From what you know of how quantum mechanics works, construct an argument that such a process may, or may not, be possible.

From the point of view of quantum mechanics, there can be no orbital with a lower energy that the well-known orbital with no nodes (the 1s orbital of the H-atom). Any orbital with higher density near the nucleus would fail to solve the Schrödinger Equation by have increased curvature near the nucleus. Not only would this destroy the balance between kinetic and potential energy required by Schrödinger's Equation, but the tight curvature toward the baseline would result in increased kinetic energy, resuting in a overall increase in total energy, rather than the hoped-for reduction. Also you cannot have fewer than zero nodes, which is what the 1s orbital has.

[If you are worried that there might be two different solutions with zero nodes, stop worrying. It turns out that the solutions of the Schrödinger equation for a given problem must be mutually orthogonal. It is impossible for two functions with no nodes to be orthogonal to one another, since they they never change signs.]