

Which Chapter/Sections are covered?

All of Chapters 2 and 3. All material covered on homeworks 3-6. Concentrate on the subject matter I emphasized in class and on the homeworks. Come in mentally prepared to answer at least 20 questions, maybe more. There will be no calculations on this exam unless you think that counting electrons, formal charge, and $S = N - A$ is a real calculation. Once again, you need to *understand* the theory and concepts – getting a homework question right does not necessarily mean you really understand the material.

Fundamentals

Know the differences in ionic and covalent (molecular) compounds. Best to reread Chapter C for much of this. Know your nomenclature – Chapter D and Appendix 3.

Ionic vs Covalent

Know the difference in these two types of bonding and compounds.

Ionic compounds: These are all a continuous lattice of alternating cations and anions. We refer to their identities as formula units and NOT as molecules. Check out page 56 about ionic compounds: they are held together by strong coulombic attractions which leads to all (99.9%) of them being solids at room temperature. Not just solid but brittle solids – they will shatter if you whack them hard enough. If you want to melt them you need to get well above 500°C and for some, well above 1000°C . If you do get them melted, the resulting liquid WILL conduct electricity due to all the positive and negative ions flowing around. Let's not say this: ionic bonds are the transfer of electrons. Yes, we've all heard that and I hate it. The fact is simply there are lots and lots of ions (cations and anions) already out there in nature. These ions can and do find one another and they STICK together. THAT my friend is an ionic bond. As far as I'm concerned, the concept of electron transfer is best reserved for oxidation/reduction reactions and electrochemistry. To say that NaCl is made by taking one electron away from sodium and giving it to chlorine is to speak of an oxidation/reduction reaction – the result of which (in this particular case) is an ionic compound. My point is that you do NOT need to transfer any electrons to get an ionic bond or compound – you need IONS – cations and anions – find them where you may.

Covalent compounds: These consist of discrete molecules. These generally are NOT a continuum of covalent bonds (OK, there are network solids which do this – but those are exceptions and are rare in the grand

scheme of things). 99.9% of all covalent compounds are molecules – we DO refer to their identities as molecular formulas. They can be solids, liquids, or gases at room temperature. It all depends on their intermolecular forces (Chapter 5 – we'll get there soon enough). Covalent bonds are identified by the sharing of electron pairs by two nuclei.

Lewis Electron Dot Structures

Electron dot structures for ionic compounds show the cation first, then a comma, then the anion. If there is more than one ion in the formula then you put that number in front of the ion. See number 4 on homework04 for an example of calcium fluoride.

Of course MOST of what you'll be doing is writing out structures for various polyatomic anions and molecules. We'll ask you questions about the structure – how many lone pairs in all? how many lone pairs on a specific atom? how many bonding pairs? how many total valence electrons in the structure? What does the formula $S = N - A$ do for you? Does it work on ALL structures? No, it ONLY works if all the atoms truly do obey the octet rule. The fact is that many don't obey the octet rule. The $S = N - A$ rule will work as long as you use the right number for N (needed electrons). Obeying the octet rule can undercut N in a big way. Sometimes you need 10, or 12, or even 14 electrons around a central atom.

One way to get the right structure: Get your skeletal structure drawn – remember that symmetry is good. “Glue” the atoms together with single bonds. Now use your remaining electrons to fill out the octets on all the atoms. If you come up short (ran out of electrons before you reached all the octets), you MUST start introducing multiple bonds into the structure – do this until you get the octets you need for all the atoms. If you actually get the octets taken care of (all atoms are satisfied with complete octets) AND you have some left over electrons put them on the central atom as lone pairs (see numbers 4, 7, and 16 on homework05 for examples of this). Be sure and check formal charge as your final check on your structure – the more atoms at zero (or close to it) the better.

Bond Order: You can quickly look at a structure and know the bond orders of each bond. Single bonds have bond orders of 1.0, double bonds have bond orders of 2.0, and so on. Can you get fractional bond orders? Yes, but in order to show a fractional bond order we must develop a way to show these things. Lewis dot structures (solo ones) by themselves do not allow for cutting up bonds like 1.5 or 1.25 bonds. That's why we have resonance structures.

Resonance

Know what resonance is. What are resonance structures and how do we depict them on the page? Please realize that in every single case of resonance, all the structures have the EXACT same skeletal structure (where the atoms are). What is different is WHERE the multiple bonds go. The double bond could go here, or here, or here, etc... The equivalent choices for the double (or triple) bonds effectively show that those electrons are in fact *delocalized* about the molecule. Resonance structures also allow us to show bond orders other than perfect integers. Consider nitrate ion, NO_3^- (see top of page 64 in your book). The double bond is delocalized over 3 different oxygens. The bonds to all the oxygens are actually all identical and have bond orders of 1.33 each. That is essentially an average of the three structures shown.

Formal Charge

Know how to “calculate” formal charge. I WILL ask at least one question on formal charge. What is the best formal charge to have for an atom in a formula? Zero! A formal charge of zero will give you the lowest energy state possible also – that’s why we like zero for formal charge. Sometimes we HAVE to go beyond zero though. +1 and -1 are OK when necessary – like for charged species and when you just can’t get all zeros to work out. +2, -2, and beyond are no-no’s though – try to avoid them in your formulas. For *p*-block elements (atoms) beyond phosphorus, there is the possibility of having an expanded octet (10 or 12 usually – could go higher even). The formal charge “rule” will often force you to expand your octet on the central atom to 10 or 12 electrons.

Electronegativity and Polarity

Memorize the trend in electronegativity and that fluorine is the top-dog at 4.0 and oxygen comes in second at 3.4. Note that all the non-metals are greater or equal to 2.0 while the metals fall below that. This is a relative measure of the PULL on electrons. Unequal pulling on electrons and where they are ultimately determine the polarity of molecules. If we only look at bonds we can quickly assign δ^+ and δ^- (read that as partial positive and partial negative) to the two ends by looking up the electronegativities. However, a polar bond does not mean that the entire molecule is polar. You must consider the overall geometry and symmetry. You must also look at lone pair electrons in the molecule. A polar molecule MUST have a non-zero net dipole moment. This means that you must add up all the individual polar bond dipoles and see if they all cancel out or do you get an overall dipole. All five of the basic electronic geometries we’ve covered are perfectly symmetric as

long as ALL the positions are equivalent. Any mismatch will result in a polar molecule. Lone pairs are a dead give away for polarity. The only match for a lone pair is another lone pair in the opposite direction – this IS possible on a few of our molecular shapes – look and see which ones. Page 96 in the book has only 3 structures with lone pairs in the non-polar column – please look and see why those 3 structures can’t possibly be polar and while your at it learn why every structure on the page is in the column it is in (polar or non-polar).

Bond Lengths and Strengths

Know the trends in bond strengths. How does a single bond relate in strength to a double bond? Triple bond? Bond lengths? Strengths are often shown in a table of bond dissociation energies (p. 75).

VSEPR, VB, and MO Theories

Know what each of these theories “brings to the table” as far as chemical bonding and shapes goes. You’ll need to know all the shapes that are covered in the book – yes even pentagonal bipyramidal (realize that to get this shape you must have 14 electrons in the outer shell of the central atom). Know the VB hybrids that are necessary to get each shape that we covered. VSEPR will help you arrive at the right shape but it says nothing about HOW you get there. VB theory steps in and helps us visualize how this gets done. By allowing atomic orbitals to hybridize, we can get all the necessary shapes and we can “see” orbitals on neighboring atoms overlapping to give bonding orbitals (σ and π bonds).

Sigma and Pi bonding: VB theory also brings us σ and π bonds. Know the key difference in these two types of bonds. What kind of overlap does each bond use? Which one is generally stronger? A double bond in VB theory is always a σ bond reinforced with a π bond. A triple bond is a σ bond reinforced with two π bonds. Unfortunately VB theory doesn’t always work out – especially for certain non-bonding electrons and radical species (O_2 is a good example).

MO Theory: In general we do not hybridize in MO theory. We use all the atomic orbitals (actually the ψ ’s) throughout the molecule and combine them (LCAO, p. 108) into molecular orbitals – hence the name, LCAO-MO. MO theory still uses the σ and π designations for bonding orbitals. MO also introduces antibonding orbitals σ^* and π^* . Antibonding orbitals are the result of destructive interference when combining the wavefunctions for the atomic orbitals (ψ_1 and ψ_2 are out of phase). Know the relative energies of bonding vs antibonding orbitals. Know the ordering of the molecular orbitals for all 2nd row homonuclear diatomic molecules (Figures 3.34 and 3.35).

Diamagnetism vs Paramagnetism

What's the difference in diamagnetic and paramagnetic?

See page 106, Box 3.2. Diamagnetic is where all electrons are paired within a molecule ($\uparrow\downarrow$).

Paramagnetic is when you have one or more unpaired electrons (\uparrow) in a molecule (radicals).

Other Stuff I didn't elaborate on (yet)

Yes, read your book. Know what a radical is and a biradical. Flip to page 679 in your book – tell me the hybridization for every atom in the structure for acetylsalicylic acid, for propyne (realize they don't show lone pairs on the oxygens). What is HOMO and LUMO (p. 115). Band theory of solids – know what they are saying on pages 116 and 117.

Standard Disclaimer

Any mistakes on this review sheet are NOT intentional. You should crosscheck all stated information. You should double check your book too (see errata).