

Which Chapter/Sections are covered?

All of Chapter 13 and Chapter 14 sections 1-6. Plus some general nomenclature stuff (polyatomic ions). Concentrate on the subject matter that was emphasized in class and on the homeworks. Come in mentally prepared to answer 25 to 35 question. Once again, you need to *understand* the theory and concepts – getting a homework question right does not necessarily mean you really understand the material. Ask yourself why you chose an answer. Try to explain the question to someone else.

Nomenclature

This is clearly stated in our textbook in section 2.9 of our book. There is also a listing of polyatomic ions on one of my help sheets from the website. You may or may not have to even be faced with knowing these - best to be prepared either way though. A question could read... how many available (A) electrons for nitrate? You have to know the correct formula for nitrate to answer this question. The answer is 24 if you must know.

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. They are held together by strong coulombic attractions which leads to nearly 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. 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.

Lattice Energies: The lattice energy for a compound is a measure of how much “glue” is holding it together. For ionic compounds (salts), the “glue” is the attractions between cations and anions. Know what this is and what factors increase/decrease the values. Lattice energies really follow nicely with Coulomb's Law which says that the potential energy (V) between two charges is proportional to the amount of the two charges (q_1 and q_2) divided by the distance between them (r):

$$V \propto \frac{q_1 q_2}{r}$$

Charge is the bigger factor here. Why? Charge can easily double (+2) or even triple (+3). The distance, r , will depend on the size of the ions. The trends you learned in chapter 12 will help you here, but very rarely do you double or triple a ionic radius. Check section 13.4b on ionic radius size... as you go down a group the size goes up by about 25-30% for each jump. Going from left to right is even more subtle: yes, F^- is smaller than O^{2-} , but only by 4 pm. Also, some books define lattice energies one direction (gaseous ions combining to make the salt) and others define it the other direction (salt expanded into gaseous ions). So they can be defined as positive or negative quantities. You need to know which is higher in energy and the direction will not matter. Expanded ions are in a much higher energy state than close-packed ions in a lattice. Know which way you are going and the sign is obvious.

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 (we'll get there soon enough after this exam). Covalent bonds are identified by the sharing of electron pairs by two nuclei.

Dipole Moments and Polarity

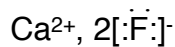
A dipole moment is the measured strength of a dipole. A quantity of charge (Q) is separated by a distance (R) and the dipole moment is realized:

$$\text{dipole moment} = \mu = Q \cdot R$$

This is all explained in section 13.3 of your book. If you need the conversion from C·m to debye units I'll give that. You DO need to know though that any polar molecule MUST have a net dipole moment. All non-polar molecules (and other chemical species) have zero net dipole moments. Symmetry is another factor you must consider when assigning whether a species is polar or not.

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. Here is an example of calcium fluoride (CaF₂):



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?

S = N - A

I gave you this helpful little formula in class.

S = shared electrons : total number of electrons that will be shared and therefore are the bonding electrons.
Divide “S” by 2 and you'll have the number of bonds (lines) in the structure.

N = needed electrons : needed is based on the octet rule which is 8 electrons for all atoms except hydrogen which is 2. Also, the 8 can (and should) be upped to 10, or 12 for those elements with expanded octets.

A = available electrons : actual number of valence electrons that each atom brings to the structure.
Remember to adjust your total up or down here if you have an anion (up) or a cation (down).

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 a great many don't necessarily obey the octet rule (I like to refer to them as everything except C, N, O, and F). 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:

1. Get your skeletal structure drawn – remember that symmetry is good.
2. “Glue” the atoms together with single bonds.
3. Now use your remaining electrons to fill out the octets on all the atoms.
4. 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.
5. 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.

6. Be sure and check formal charge (see discussion later on this review sheet) as your final check on your structure – the more atoms at zero (or close to it) the better. Remember that “sub-octet” atoms like B have only three valence electrons and generally make only three bonds. “expanded-octet” atoms like S may make six bonds. If you minimize the formal charges you will always find the “best” structure even for these octet rule “exceptions”

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. Also, looking even further into the chapter 14, bond order is very simple to “calculate” when using MO Theory. It is simply the number of bonding electrons minus the number of antibonding electrons quantity divided by two (section 14.2a).

Radicals: The book DOES talk about ODD electron species (like NO for example). You cannot obey the octet rule with an odd number of electrons. This also means there will be at least one unpaired electron in the structure, which is what a free radical is.

Resonance

Know what resonance is. What are resonance structures and how do we depict them on the page? See section 13.11 in our book. 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 (and potentially lone pairs). 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, NO₃⁻.

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. Delocalized bonding is handled best by MO Theory in that there are actual molecular orbitals that cover the entire delocalized region (see figure 14.51 in our book for the π-bonding system in nitrate).

Formal Charge

Know how to “calculate” formal charge. WE WILL ask at least one question on formal charge, maybe more.

First, know the “**kernel charge**” which is the same as the regular number of valence electrons. It's the number of the group on the American periodic table. The kernel charge is positive due to the nucleus being positive.

Next, you assign electrons to each atom in the formula:

- Lone pair electrons belong completely to the atom that they are on.
- Bonding electrons are perfectly split between the two atoms that make the bond.

formal charge = kernel charge - assigned electrons

The SUM of all the formal charges in a species must equal the overall charge of the species. For example, all the formal charges in acetic acid (CH_3COOH) must total to zero because it is a neutral molecule. The sum of the formal charges in sulfate (SO_4^{2-}) must equal -2.

In general, we'd like to see as many formal charges of zero as possible in a formula. A formal charge of zero is giving you the "best" covalent structure possible with electron sharing at its optimum setting so to speak. You can't always have all zeroes though. Sometimes we HAVE to go to positive or negative formal charges. Values of +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 less acceptable though – try to avoid them in your formulas if you truly want a covalent compound. 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. Remember, if asked to pick the *most likely* structure or the *best* structure - pick the one with the *least* amount of formal charges. Also remember that although that might be the MOST important structure, it might not be the ONLY structure necessary to illustrate the proper representation of the molecule. There CAN be resonance structures. The structure with the lowest formal charge per atom is the one that contributes the most to the structure, however, the other structures (with more charges) will simply contribute less to the overall structure.

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 (loss of symmetry) 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 (180°). This IS possible on a few of our molecular shapes – look and see which ones.

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? Take a peak at Table 13.7 in your book. Strengths are often shown in a table of average bond energies (Table 13.6 in your book). Know how to calculate the energy absorbed or released by a reaction by using bond dissociation energies. To break a bond you INCREASE (+) energy, to make a bond you LOWER (-) energy. The "formula" for this is on page in your book. A good example of this is in section 13.8a. Note that energy change (ΔE) is shown as enthalpy change (ΔH). Feel free to equate energy and enthalpy at this point. We will really get into enthalpy a lot more when we cover thermodynamics (Chapters 9 and 10). Also, I do NOT plan on putting this on exam 2 - it will be on exam 4.

VSEPR and VB 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 – linear to octahedral which matches up with 2 electron regions through 6 electron regions. Know the VB hybrids that are necessary to get each shape that we covered (Section 14.1 and summarized in Figure 14.24) 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 geometries and we can "see" orbitals on neighboring atoms overlapping to give bonding orbitals (σ and π bonds). Know your shapes, angles, angle tweaks, and hybridization. Be sure and check out my other help sheet on VSEPR and VB Theory - and read the book.

Angle "Tweaking"

Yes, of course you must know the standard bond angles for the five electronic geometries. You must also know how to "tweak" a bond angle based on the slight differences in electron region repulsions. We say that lone pair electrons are more repulsive than any bonding pair. This means that lone pairs need a bit more space and therefore "squish" the bond angles that are adjacent to it. This is also why lone pairs always go into the equatorial positions of a trigonal bipyramid electronic geometry and never go into the axial positions.

Sigma (σ) and Pi (π) Bonding

VB theory (LE or Localized Electron theory in your book) 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 MO theory we use the atomic orbitals (ψ wavefunctions) to generate new orbitals (wavefunctions) for the electrons in the complete molecule. For each atomic orbital we will get a new molecular orbital. 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 (Figure 14.41). Know HOW to fill this diagram properly with electrons. For heteronuclear diatomics know how to fill in a diagram if one is given to you. You should also realize that the MO diagram for heteronuclear molecules with atomic orbitals of similar energy (such as NO) are essentially the same as the homonuclear diatomics. In heteronuclear diatomics the most electronegative element will have the lower orbital energies. As a result the bonding MOs will more closely resemble the atomic orbitals from those elements. The anti-bonding will be more similar to the atom with the lower electronegativity. Lastly, there are times in which atomic orbitals (AO) on one atom don't overlap at all with the AOs on the other atom. This results in non-bonding orbitals. These orbitals are essentially identical to the AO on that element. They don't lower or raise the energy compared to the AO. Therefore they don't participate in the bonding (or bond order calculation).

Orbitals in Polyatomic Molecules

Know what the overall concept is. We often COMBINE VB theory and MO theory taking the best parts out of each. Don't fret the details but do know that atomic orbitals will combine in all sorts of ways to get you various levels of energies within a molecule. Check out how the π -system in benzene is really represented with MO's even though the 6-carbon ring is best pictured as 6 carbon atoms with sp^2 hybridization. Realize that the idea of bond "delocalization" is best understood from MOs.

Diamagnetism vs Paramagnetism

What's the difference in diamagnetic and paramagnetic? Diamagnetic is where all electrons are paired within a molecule ($\downarrow\downarrow$). Paramagnetic is when you have one or more unpaired electrons (\uparrow) in a molecule. MO Theory properly predicts (unlike the Lewis dot structure) the paramagnetic nature of oxygen, O_2 . I originally mentioned paramagnetism and diamagnetism when we were filling atomic orbitals in chapter 12. Now you can have a better idea about them and even have a question or two on the exam about them (read section 14.3a).

Class Matters

Attending class does matter. Anything I told you in class is fair game on an exam. Turns out that about 97% of what I tell you is in the book - so if you know the book and what it preaches, then you'll do fine. If I ever tell you in class about a good exam question, you should wake up and take note. I generally don't kid about this stuff. Those who are alert and pay attention can reap the rewards.

Standard Disclaimer

This review does not reflect the emphasis of the material on the exam. Some things require more words than others. For example the statement "Know your shapes, angles, angle tweaks, and hybridization" is brief but covers a huge amount of the material we covered in class. Use your notes and HW as a guide.

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