Note that I have not seen your midterm exam, and cannot guarantee that the topics I emphasize will be those that appear on it. The questions I pose are intentionally trickier than your run-of-the-mill homework problems to enhance your understanding, but they might not actually be that helpful. Be discerning. Pick out what will help you, and read the rest if you find it interesting.

**Balancing reactions.** This is rather straightforward. Make sure you have states of matter for all species, even if I omit them here. Once you have a balanced reaction, you can—and should—check it by counting the number of atoms of each element on both sides of the expression.

If you want to learn about a systematic process, here is a cute reaction to try to balance:

$$K_{4}Fe(CN)_{6} + KMnO_{4} + H_{2}SO_{4} \longrightarrow KHSO_{4} + Fe_{2}(SO_{4})_{3} + MnSO_{4} + HNO_{3} + CO_{2} + H_{2}O_{4} + HO_{3} + CO_{2} + H_{2}O_{4} + HO_{3} + CO_{2} + H_{2}O_{4} + H_{2}$$

Did you do it? I recommend you *not* try it before you read on, but it's up to you. I hope you realize that brute force here will be painful, so let's go about this in a smart way. Identify an element that only shows up in one species on both sides of the reaction. I see Fe. Because all the coefficients are determined up to a multiplicative constant, I'll just let the coefficient of  $Fe_2(SO_4)_3$  be 1. Then, on the left, the coefficient of  $K_4Fe(CN)_6$  must be 2, because it's the only other place where Fe appears. So we have

$$2 K_4 Fe(CN)_6 + \alpha KMnO_4 + \beta H_2 SO_4 \longrightarrow \gamma KHSO_4 + 1 Fe_2(SO_4)_3 + \delta MnSO_4 + \epsilon HNO_3 + \zeta CO_2 + \eta H_2O_3 + \delta MnSO_4 + \epsilon HNO_3 + \zeta CO_2 + \eta H_2O_3 + \delta MnSO_4 + \epsilon HNO_3 + \zeta CO_2 + \eta H_2O_3 + \delta MnSO_4 + \epsilon HNO_3 + \delta MnSO_4 + \delta$$

The Greek letters are just undetermined coefficients. We can keep repeating this step. C only appears in K<sub>4</sub>Fe(CN)<sub>6</sub> and in CO<sub>2</sub>, so balancing with respect to C means that  $\zeta = 12$ . And N only appears in K<sub>4</sub>Fe(CN)<sub>6</sub> and in HNO<sub>3</sub>, so  $\varepsilon = 12$  also. And I see that Mn only appears on both sides in KMnO<sub>4</sub> and in MnSO<sub>4</sub>, so  $\alpha = \delta$ . Then

$$2 K_4 Fe(CN)_6 + \alpha KMnO_4 + \beta H_2 SO_4 \longrightarrow \gamma KHSO_4 + 1 Fe_2(SO_4)_3 + \alpha MnSO_4 + 12 HNO_3 + 12 CO_2 + \eta H_2 O_3 + 12 HNO_3 + 12 HNO$$

I think that's all the simple stuff. Everything else becomes a system of equations: just balance each remaining element on both sides of the reaction...

$$8 + \alpha = \gamma, \tag{K}$$

$$2\beta = \gamma + 12 + 2\eta, \tag{H}$$

$$\beta = \gamma + 3 + \alpha, \tag{S}$$

$$4\alpha + 4\beta = 4\gamma + 12 + 4\alpha + 36 + 24 + \eta,$$
 (O)

Eww. I plucked this reaction off the Internet and didn't realize how gross it was. Anyway, you can solve this system of four equations in four unknowns by hand, but I'll just use WolframAlpha and get

$$\alpha = \frac{122}{5}, \quad \beta = \frac{299}{5}, \quad \gamma = \frac{162}{5}, \quad \eta = \frac{188}{5}.$$

Now we can cancel out fractions, if we're so inclined, and we'll find

 $10\,K_4Fe(CN)_6 + 122\,KMnO_4 + 299\,H_2SO_4 \longrightarrow 162\,KHSO_4 + 5\,Fe_2(SO_4)_3 + 122\,MnSO_4 + 60\,HNO_3 + 60\,CO_2 + 188\,H_2O_2 + 122\,MnSO_4 +$ 

Wow. It's so long it even goes past my margins. Aren't you glad you didn't try to balance it?

*Practice.* Here is a reasonably simple equation you might be asked to balance:

$$Br_2 + H_2O \longrightarrow HBrO + Br^- + H^+$$

It's simple enough that you could probably do it with brute force, but you could also try the method illustrated above. Note that sometimes there *isn't* an element that appears in just one place, in which case you would just choose a random species to have coefficient 1 and set up the system of undetermined coefficients right away.

Practice. Here's another interesting reaction:

$$XeF_4 + H_2O \longrightarrow Xe + XeO_3 + HF + O_2$$

If you tried it with brute force, you probably got an acceptable result. But it won't be the only answer-consider

$$\begin{array}{l} 6 \operatorname{XeF_4} + 12 \operatorname{H_2O} \longrightarrow 4 \operatorname{Xe} + 2 \operatorname{XeO_3} + 24 \operatorname{HF} + 3 \operatorname{O_2} \\ 4 \operatorname{XeF_4} + 8 \operatorname{H_2O} \longrightarrow 2 \operatorname{Xe} + 2 \operatorname{XeO_3} + 16 \operatorname{HF} + \operatorname{O_2} \end{array}$$

Different coefficients, but both work. You might have something else entirely. What's up with that? If you try balancing with the algebraic method, you'll find that you have more unknowns than equations. When you solve everything, you'll find that your coefficients will depend on some unknown, call it  $\xi$ . Split up the constant terms from the  $\xi$ -dependent terms, and your original equation will decouple into *two* separate, balanced equations, which explains why you weren't able to balance it uniquely: you can add up any linear combination of two balanced equation to get a new balanced equation. All such equations have the same chemical species in them, but they can certainly have different coefficients. Cool!

On a deeper level, you might have realized that the algebraic method that I propose simply reduces to solving a system of linear equations, exactly the purview of linear algebra. So, in a sense, all our chemical species just form a basis, and we have a coefficient matrix, and all we're doing is a simple matrix inversion to solve  $A\mathbf{x} = \mathbf{b}$ .

**Periodic trends and the Aufbau principle.** I assume you know the simple periodic trends and how to fill energy levels with electrons. Here are some common exceptions.

Example. Explain why the first ionization energy of oxygen is lower than that of nitrogen.

The rationale commonly taught for this curious exception is based on "half-shell stability", the notion that half-filled shells are quite stable (more so than half-plus-one-filled shells). But why? In quantum mechanics, you will learn that these electrons in the same energy state and with the same spin are *indistinguishable*. Indistinguishability lowers the system energy through the so-called *exchange interaction*, and the more indistinguishable electrons you have, the stronger this effect. Half-filled shells have the most such indistinguishable electrons. If you have more, then some orbitals start getting filled, and electrons in that orbital now suffer from electron-electron repulsion and become distinguishable from the rest.

*Example*. Explain why, in transition metals like Zn, the 4s energy level is filled before the 3d energy levels, but when Zn is ionized, electrons in the 4s energy level are removed *before* those in the 3d energy level. Shouldn't the electrons in the 3d energy level get removed first if they're filled last?

This just goes to show that lots of things in general chemistry are more complicated than they appear at first glance, and a lot of the simple explanations you learn are, well, deceptively simple. The crux of the issue is that filled 4s orbitals are lower in energy than filled 3d orbitals, but empty 4s orbitals are higher in energy than empty 3d orbitals. *There is a crossover region where the energy of the 4s levels start to become greater than the 3d levels.* This is because the 4s orbitals are more diffuse, so are affected less by an increasing nuclear charge, and because 3d orbitals screen the nuclear charge from the 4s orbitals. The energies of the 4s and 3d orbitals are really quite finely balanced, which is why you end up with these weird exceptions and things like half-shell stability, even though the exchange interaction isn't as strong as it seems.

There are also other fun things like d-block and f-block contraction, as well as relativistic effects (ooh!), which, among other things, explain the interesting colors of elements like gold and mercury. But these are probably beyond the scope of this course, so I won't mention them here.

Lewis structures, valence bond theory, and molecular orbital theory. This is where things are getting quite confusing. I expect that you know how to draw out simple Lewis structures for molecules. Note that elements in the second period cannot *exceed* an octet—but they can certainly not have an octet and still be somewhat stable, as is the case with Be and B—whereas elements in the third period and up can. This is commonly explained by an expanded octet, where d orbitals supposedly also participate in bonding, but this is essentially another lie propagated in general chemistry (Magnusson, 1990). Modern bonding theories suggest that what actually happens in compounds like sulfur hexafluoride is that three-center four-electron bonds form, as is common in many boron compounds. But this is beyond the scope of this course, and, at least for now, we may wrap ourselves in the comfortable cocoon of *d*-orbital hypervalency. I just hope you will break free soon.

*Resonance*. You may be able to draw multiple Lewis structures for certain compounds that follow all the rules—every element has a full octet, all formal charges are minimized, and so on. These structures are known as *resonance struc*-

*tures*. Resonance structures are not real in the sense that *molecules do not simply flicker between different resonance structures*. Instead, molecules are essentially weighted combinations of the resonance structures, and the weighting is related to how stable each resonance structure is. In certain cases, even resonance structures that don't follow all the rules and are less stable can be very important in determining the compound's structure. This is the case in formamide, as you will see (or have seen) in lab. Compounds with multiple resonance structures are usually more stable because of electron delocalization.

Drawing resonance structures. The skeletal structure of your compound will not change. Do not try to break single bonds, swap atoms, or do weird things with your molecules. What *can* change, in a specific way, are the lone pairs and  $\pi$  bonds. If an atom X has a lone pair, you can form a  $\pi$  bond between X and a neighboring atom. If you have a  $\pi$  bond between X and Y, then the  $\pi$  bond can become a lone pair on X or a lone pair on Y. These are essentially the only actions your free electrons can take. You may be able to get new structures by repeating these steps, which is fine, but don't violate your electrons and make them take impermissible actions. Make sure that your resonance structures are actually stable. No element in period two can exceed an octet.

*Practice.* Explain the polarity of azulene (Google its structure) by using resonance structures. It turns out that the unusual structure of azulene and the considerable electron delocalization within it makes it appear blue, hence the name. This is highly unusual for a wholly organic molecule!

Lewis structures, combined with VSEPR, work surprisingly well for a lot of elementary chemical compounds, considering how basic the theory is. You will use them throughout general chemistry and organic chemistry, which deals mainly with carbon-containing compounds. Things get weird when you have metals, and for those compounds Lewis structures aren't all that great. You should also note some specific, common exceptions, like molecular oxygen ( $O_2$ ).  $O_2$  is paramagnetic, but it doesn't look it from just the Lewis structure alone. For that, you need MO theory.

*Valence bond theory.* Valence bond theory is compatible with Lewis structures, and can be viewed as a means of formalizing these structures by adding quantum mechanics (orbitals) to them. In the valence bond picture, the orbitals are localized about bonds and lone pairs—each such bond or lone pair has an associated orbital. This theory works best for period two elements, where the octet rule remains largely satisfied and is not exceeded. For hypervalent compounds like sulfur hexafluoride, valence bond theory has to start bringing in d orbitals to explain the expanded octet in sulfur, which I've already stated is incorrect.

A significant part of valence bond theory is *hybridization*, which involves mixing together s and p orbitals. If you mix together an s and a p orbital, you get two sp orbitals. If you mix together an s and two p orbitals, you get three sp<sup>2</sup> orbitals. If you mix together an s and three p orbitals, you get four sp<sup>3</sup> orbitals. How many p orbitals you choose to mix together depends on how many neighbors—lone pairs and other atoms—the atom you're hybridizing has. If there are two neighbors, then you only need sp orbitals; if there are four neighbors, then you need sp3 orbitals. The remaining p orbitals stay as p orbitals. *You can also hybridize unoccupied orbitals!* Carbon has one 2s orbital and three 2p orbitals. Only one 2s orbital and one 2p orbital are occupied, but this distinction does not matter for hybridization. Note that hybridization is a mathematical construct only—electrons are not promoted, and orbitals do not physically hybridize—if one that is kept around because it is so useful.

*Practice.* Draw out the bonding orbitals in allene,  $H_2CCCH_2$  (structure as described). Is allene planar? If your answer is *yes*, you have done this exercise incorrectly. A key insight is that, in sp<sup>2</sup> orbitals, the remaining p orbital will be orthogonal to (perpendicular to the plane defined by) the sp<sup>2</sup> orbitals. Why should this be the case? Let's imagine that we're hybridizing an s orbital with a  $p_x$  and a  $p_y$  orbital. Well, none of these orbitals point in the *z*-direction, so neither can their hybrids.

*Practice.* Explain, using Lewis structures and resonance, why formamide (the last molecule you consider in lab) is planar (!). Provide further justification by drawing out the relevant bonding orbitals in formamide.

*Molecular orbital theory.* This is the complicated one. Molecular orbital theory deals with orbitals spread out over the entire molecule, the key difference between molecular orbitals and valence bond orbitals. Molecular orbital theory is more accurate than valence bond theory, but is much harder to use. MO diagrams are quite complicated even for simple homonuclear diatomic molecules, which you'll find on the next page. I stole these diagrams from http://ch301.cm.utexas.edu/pdfs/mo-diagrams-diatomics.pdf.

Keywords associated with MO theory: molecular orbitals, bonding and antibonding orbitals, overlap integral, HOMO,



LUMO, nonbonding MOs, paramagnetism, diamagnetism,  $\sigma_{1s}$ ,  $\pi_{2p}^*$ , *etc.* Lots of greek characters with subscripts <sub>u</sub> and <sub>g</sub> and star \* superscripts.

Keywords associated with valence bond theory: promotion, hybridization,  $\sigma$  bonds,  $\pi$  bonds (no subscripts or superscripts!), sp, sp<sup>2</sup>, sp<sup>3</sup>.

Keywords associated with Lewis structures: resonance, VSEPR, formal charge, full octet, simplicity.

*Molecular orbital diagrams.* For the purposes of this paragraph, please refer to the MO diagrams for homonuclear diatomic molecules provided in the previous page. On the left and right sides are the orbitals of the constituent parts of your molecules. For diatomic molecules this is easy, and these orbitals are just the simple atomic orbitals that you are all familiar with. In the middle is the actual MO diagram. *Molecular orbitals are formed by combining atomic orbitals together.* You will always get back the same number of molecular orbitals as the number of atomic orbitals you combine. Generally these orbitals come in easy-to-identify bonding-antibonding pairs, like the  $\sigma_{1s}$  and  $\sigma_{1s}^*$  MOs at the bottom of the page. Things are more complicated for more complicated molecules. You'll also note that there are actually two different MO diagrams for the period two elements, because the  $\sigma_{2p}$  and  $\pi_{2p}$  orbital energy levels actually swap places. This is because of sp-mixing, which lowers the energy of the  $\sigma_{2p}$  orbital at the expense of increasing the energy of the  $\sigma_{2p}$  orbital. This is good for molecules in the first few groups of period two, because the  $\sigma_{2s}$  MO is filled, whereas the  $\sigma_{2p}$  MO is not. Constructing an MO diagram is hard!



MO diagrams for homonuclear diatomic molecules across the period. Taken from Chemistry, OpenStax.

Conversely, actually using an MO diagram once it's constructed is quite easy. You simply count all the electrons you have in the molecule, and fill the MO diagram from the bottom up, following the same rules you learnt for filling electrons in atomic energy levels. This allows you to determine whether the molecule is paramagnetic or diamagnetic—whether or not it has unpaired electrons—and tells you about the bond order of the molecule—count the number of electrons in bonding orbitals, subtract those in antibonding orbitals, and divide by two (each pair of bonding electrons contributes one bond; nonbonding orbitals contribute nothing)—more accurately than will Lewis structures or valence bond theory. Other simple MO diagrams you might have to know include *hetero*nuclear diatomic molecules, where the left and right sides of the MO diagrams get tilted relative to each other and the orbitals get more localized on one atom as a result, and those for conjugated and cyclic compounds, which can be obtained by simple geometric considerations.