Chemistry 123 **Problem Set Solution** **Winter Term 2003**
Assignment #5 **Instructor: R. Rossi**

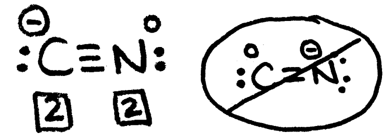
1. In solving these, it will be helpful to start out knowing the electronegativity and valence electron count of the atoms involved:

Atom	Electronegativity (Figure 8.3)	Valence Electrons	Electrons required to fill valence shell
C	2.5	4	8
N	3.0	5	8
O	3.5	6	8
H	2.1	1	2

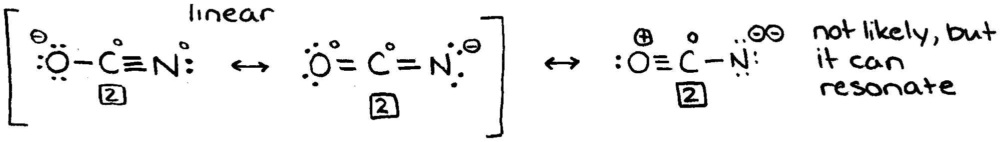
Formal Charges are circled

Steric Numbers are in boxes

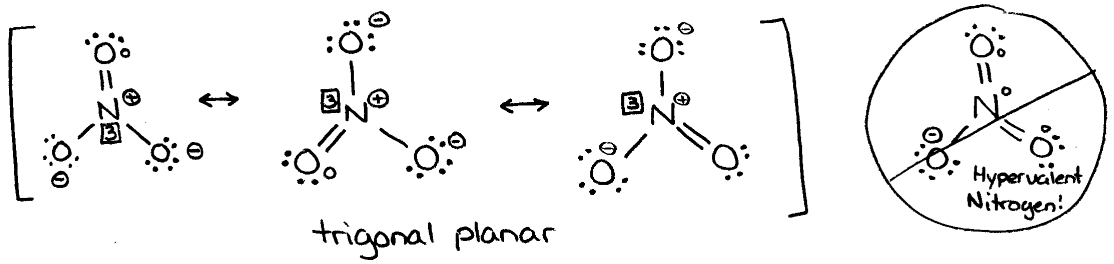
a. The best Lewis Dot representation of cyanide doesn't have an ideal formal charge distribution, because N is appreciably more electronegative than is C [Rule 6]. But the only possible fix violates the octet rule (crossed out structure at right) [Rule 4, which overrides Rule 6]. It's because of the loosely held negative charge on C that cyanide acts as a poison. It easily takes the place of oxygen in the ATP cycle but it won't let go like it's supposed to…it clogs up all of your hemoglobin and you die of oxygen starvation, basically. There's really nothing to say about the shape of cyanide, any two-atom ion is going to be linear, it just has to be. But it's important to understand that doesn't mean the atoms in a diatomic molecule don't have steric numbers! It's just that they could be four and six or three and five and it wouldn't make a whit of difference in the shape of a diatomic molecule. So we don't usually bother to determine steric numbers for anything but the "central" atom(s) in a polyatomic molecule (those with two or more other atoms bonded to them), of which cyanide has none.



b. The cyanate ion is linear. Its best Lewis representation is the one at left, below, because it has the negative formal charge on the most electronegative atom, oxygen. However, the structure in the middle isn't too bad, and it can resonate with the best one, so it probably has a role to play. The one at far right is pretty sketchy…it doesn't minimize formal charge. But because it can resonate with the good structures, you would not be wrong to draw it. There has to be a total of four bonding pairs of electrons, or you can't get full octets for everyone with the 16 valence electrons available in OCN^-.



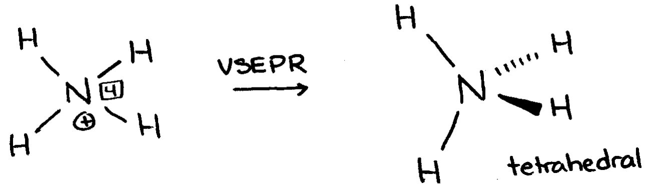
c. Nitrate ion really shouldn't have been much of challenge for you, we talked about it in class and it is also in your book!



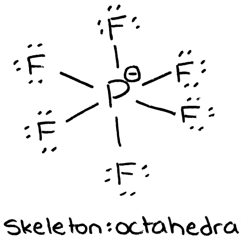
As explained in class, the linear $:\ddot{O}=\ddot{N}-\ddot{O}-\ddot{O}:^{\ominus}$ structure seems pretty nifty, but it can not delocalize the ion's negative charge the way the one above does, and an O–O bond is weaker than an N–O bond, so it also has less bonding.

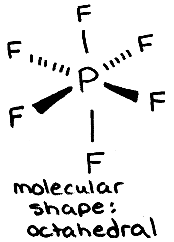
The crossed-out possibility doesn't work because nitrogen simply can't be hypervalent! But As or P could adopt such a structure were they in an analogous ion, because they are capable of hypervalency…they have d orbitals to work with!

d. The ammonium ion can't resonate, and it doesn't have a very optimal formal charge distribution. But because hydrogen can only hold two electrons in its valence shell, there's not much you can do about it. H can't form double bonds, and if you put a +1 formal charge on a hydrogen atom it can no longer be bonded to anything. So the positive formal charge ends up on the (more electronegative) nitrogen atom, and the ion has a tetrahedral shape, if VSEPR is to be believed:

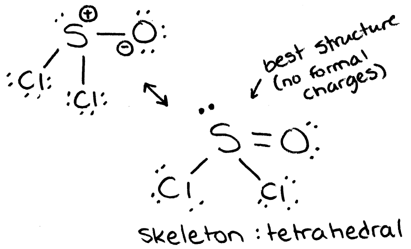


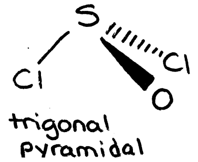
2. **All non-zero formal charges are indicated by circled + or – symbols**. Electronegativities are in Figure 8.3 of Zumdahl.
   a. There is only one viable structure for PF_6, because fluorine can only form single bonds. So the formal negative charge ends up on the phosphorus, even though fluorine is far more electronegative. With a steric number of 6 on the phosphorus, the electron clouds around it arrange themselves in an octahedron. Because each of those clouds is connected to a fluorine atom, the PF_6 molecule itself is also octahedral.





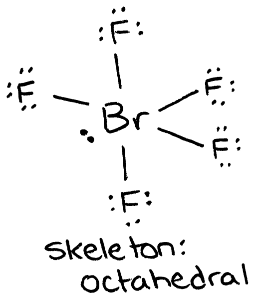
   b. The two best Lewis representations of $SOCl_2$ are able to resonate because they both have steric numbers of 4 around S:

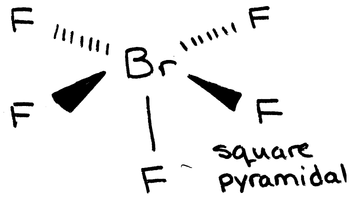




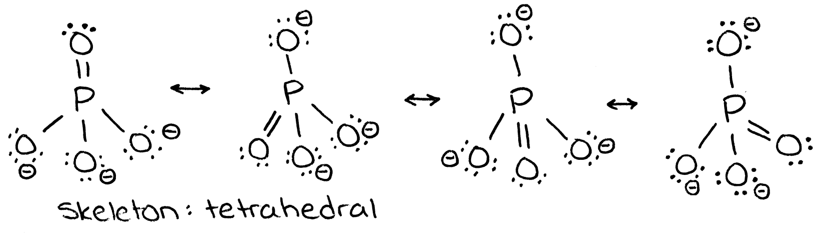
Note that the molecular shape of $SOCl_2$ is NOT tetrahedral, even though the electron pairs arrange themselves into a tetrahedron around the sulfur. The lone pair is invisible to our eyes (and to most sensing instruments we might employ) and thus the shape of the $SOCl_2$ molecule describes the locations of the atoms: it is a trigonal pyramid.

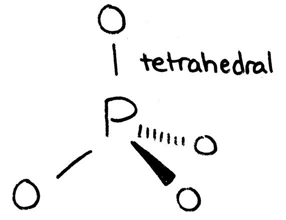
   c. BrF_5 doesn't leave us with many options, again because of fluorine's fickle nature. The molecule is a square pyramid:



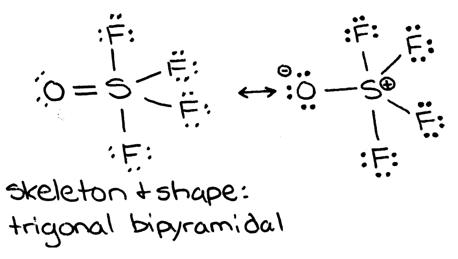


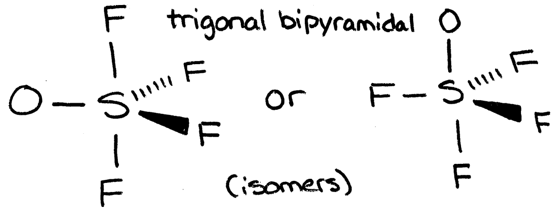
   d. You are going to want those negative formal charges on the oxygen atoms, not the phosphorus, folks!



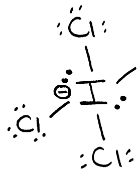


   e. VSEPR is capable of telling you that this molecule is a trigonal bipyramid, but it has nothing to say about whether the oxygen will prefer an axial or equatorial position. VSEPR deals with "electron pair" repulsion and can't differentiate between a bonding bonding pair (or two) connected to an oxygen and one connected to a fluorine. It can barely differentiate between a lone pair and a bonding pair, really. This molecule can have the O equatorial or axial:

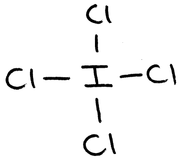




f. There's actually a good deal of potential ambiguity on this one. Cl is more electronegative than I, and only the central atom can have the formal negative charge…Cl and I both being capable of hypervalency, either could be in the center. So, do you go with Rule 2 and put I in the center, or does Rule 6 take over, leading you to put Cl in the center? Well, that's why I gave you the hint that the formal charge is on the iodine. That tells you the iodine is in the center:

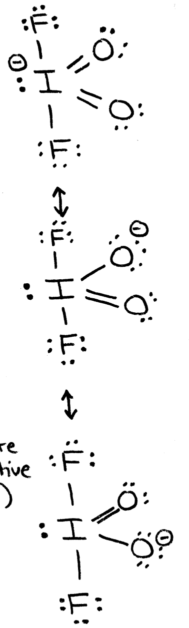


octahedral skeleton



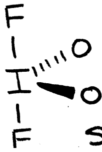
square planar

g. VSEPR can't tell you if the oxygen atoms prefer equatorial or axial locations on this one, either. It turns out the energetic difference is very small, and there are, in fact, a slew of stable isomers of the $IO_2F_2^-$ ion.



best structures (⊖ is on more electronegative element)

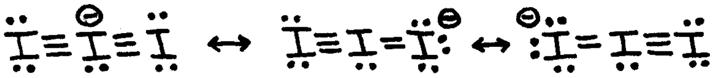
Skeleton: trigonal bipyramidal

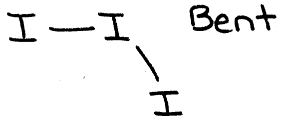


(several isomers, some with enantiomers)

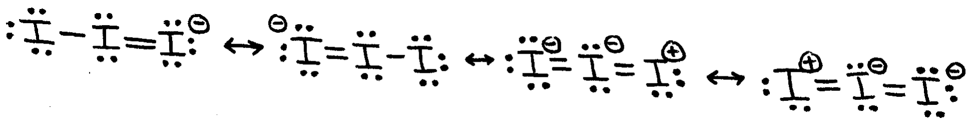
See saw

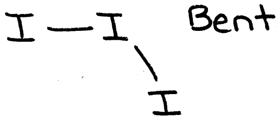
h. I_3 is a persistant pain in my arse, and I find I need to clarify my rules even further in order to better deal with it. However, the bit about hypervalency being "in the middle" in Rule 4 springs directly from this molecule. If you ignore that generalization, the best structure would seem to be this resonance set, because after all, it's got the bonding [Rule 7]:



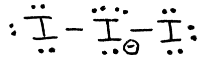


To the seasoned Lewis Structure drawer, this just plain tickles the Spidey Sense™, so you might opt instead for at least the first two of this (less-bonded) resonance set (which also manages to delocalize the negative charge):





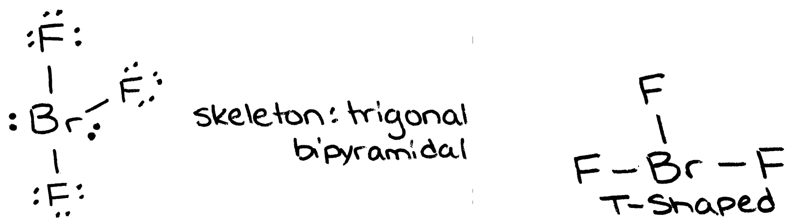
But even this set has hypervalent atoms at the edge of the molecule, and I hinted (not really strongly enough) in Rule 4 that this is a no-no. In fact, the strucutre below is what Zumdahl (p. 398) and several other textbooks agree is correct:



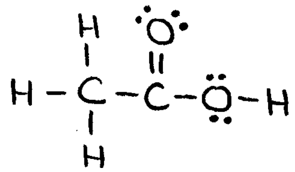
I-I-I Linear

Note that this Lewis strucutre leads to a *linear* molecule, because the lone pairs have only two neighbor atoms each in that configuration. In any other atomic configuration, you would have two lone pairs at 90° *and* at least two neighbors per lone pair. Both sets of hypervalent-ended resonant structures above, on the other hand, are truly bent, at least to the extent that we can trust VSEPR to make predictions about them.

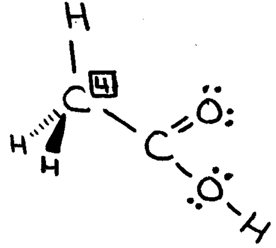
i. BrF_3 is T-shaped. But since you are all too young to know him personally, it is *Mr.* T to you. It might seem that the lone pairs could get the most space by adopting axial positions in the trigonal bipyramid, but that's not the right way to think about it. No, they don't care about neighbors more than about 90° away, so in the axial spots they would each notice three F atoms at 90°. In the equatorial positions they actually adopt, they have two neighbors at 120° that they couldn't care less about, and *two* F atoms at 90°, a much more pleasant scenario for them.



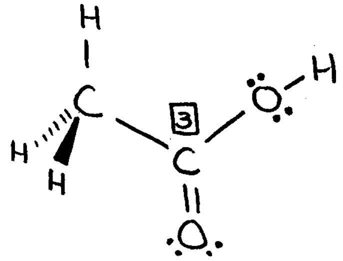
3. a. We'll start our analysis of acetic acid by drawing its Lewis structure. It is given to us in the format typically employed by organic chemists, in which the relative position of the atoms is indicated by proximity as much as possible within the constraints of an in-line formula: CH_3COOH. One might at first be tempted to assume the COOH group has its atoms arranged in exactly that order, but you'll find there is no reasonable Lewis structure you can make out of that. Instead, both oxygen atoms are attached to the carbon, and the H atom attaches to one of the oxygens. This leads to the structure



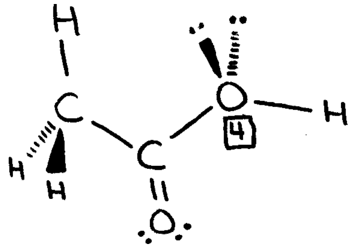
b. Deciphering the shape of a complex molecule with multiple geometric centers is simply a matter of considering one of them at a time. Starting with the CH_3 group at the left side of the Lewis structure above, we see that it has a steric number of four. As a result, the four steric centers arrange themselves into a tetrahedron:



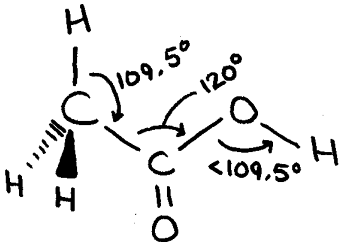
Now we conside the the second carbon, which has a steric number of three such that the three steric centers arrange themselves into a trigonal planar arrangement:



It's tempting to stop there, but the oxygen on the right is also a "central" atom, with two things bonded to it. Realizing that it has a steric number of four, we know that the C–O–H bond angle will be a bit less than 109.5°, the ideal angle for a tetrahedral arrangement of steric centers, and that the C–O–H connection certainly won't be linear!



We're now in a position to describe the shape of the molecule as a whole. To make it as easy to draw as possible, we put as many of the atoms into the plane of the page as possible. That leaves only two H's, on the terminal CH_3, that end up outside the plane of the page, so acetic acid is actually not too tough to draw out three-dimensionally:



(I've indicated the VSEPR-predicted bond angles in my drawing, but you didn't have to.)

c. It's tempting to trivialize the Lewis structure of the acetate ion, and not look for resonance! But it's there! While the proton (H) can't go bopping about from one oxygen atom to the other, the electrons involved in the bonds of the acetate ion are capable of "being in two places at once," that is, of having their wavefunctions have appreciable values between the carbon and *both* of the oxygen atoms. The Lewis structure for the acetate ion is the resonant pair