

## LEWIS STRUCTURES

A molecule achieves its structure by arranging its valence electrons into a particular combination of bonds and lone pairs which gives the molecule the lowest energy. The Lewis procedure is a method for how to dole out the valence electrons to bonds and to lone pairs. **Valence Shell Electron Pair Repulsion** uses the concept of number of electron pairs to ascribe an electronic geometry to the Lewis structures. Both procedures condense the rigorous (and difficult!) quantum mechanics to a set of simple rules.

To draw a Lewis structures make sure that you **always** determine the number of valence electrons (VAL below). If there are many electrons and you run into difficulty trying to use the rules on p. 526 of our text you may try using steps 2 - 6 below.

1. VAL (total number of valence electrons) = sum of the valence electrons of each element (sum of the group numbers, GN) - charge (if an ion).
2. STAB (stable noble gas configuration) = sum of the electrons in the noble gas configuration for each element (2 for H, 8 for C and beyond). Since an atom achieves its greatest stability and lowest energy when it has a filled shell, the noble gas configuration, we assume that an atom in a molecule or ion will also be most stable when it has its noble gas complement of electrons around it - the ubiquitous "octet" rule.
3. BOND (total number of bonding electrons) = STAB - VAL and BP (number of bond pairs) = BOND/2. Since electrons are shared between atoms that are bonded together the "octet" around each atom over counts the actual number of electrons involved. The amount of over counting is the number of bonding electrons.
4. LONE (total number of lone pair electrons) = VAL - BOND and LP (number of lone pairs) = LONE/2. Valence electrons are of two varieties: they are either bonding electrons (BOND) or nonbonding, lone electrons (LONE).
5. Draw the Lewis structure using your calculated BP and LP. Remember that nature likes symmetry, put the odd atom in the center. The central atom will generally be the less electronegative (more electropositive) element.
6. FC (formal charge on atom) = GN - LONE - BOND/2. The sum of the formal charges on all atoms is equal to the charge on the molecule or ion.

Exceptions to the octet rule:

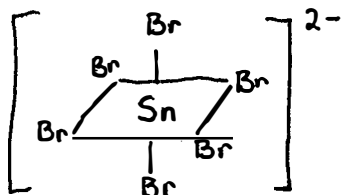
1. molecules or ions with an odd number of electrons
2. molecules with electron deficient atoms which are stable with less than eight electrons about them (such as B and Al with 6 or Be with 4)
3. some molecules or ions containing an element beyond the second period - these must be treated by a valence shell expansion

### Valence Shell Expansion (VSE)

Occasionally the octet rule is violated allowing more than eight electrons to surround an atom. The simplest case of this occurs when you are trying to attach more atoms to some central atom than you have bonds determined via calculation with octets. The other common situation arises when the Lewis structure drawn with octets exhibits charge separation (positive and negative FC in the same structure) and the VSE structure is more stable. In either case VSE is never done for first or second period elements.

1)  $\text{SnBr}_6^{2-}$        $\text{VAL} = 4 + 6(7) + 2 = 48$        $\text{STAB} = 7(8) = 56$   
                           $\text{BOND} = 56 - 48 = 8/2 = 4 \text{ BP}$        $\text{LONE} = 48 - 8 = 40/2 = 20 \text{ LP}$   
 6 Br  $\Rightarrow$  6 BP, 18 LP (expand twice to 12, gain 1 BP and lose 1 LP per each expansion)

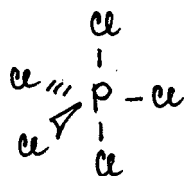
Sn STAB = 12  
 FC(Sn) =  $4 - 12/2 = -2$



VSEPR: octahedral

2)  $\text{PCl}_5$        $\text{VAL} = 5 + 5(7) = 40$        $\text{STAB} = 6(8) = 48$   
                           $\text{BOND} = 48 - 40 = 8/2 = 4 \text{ BP}$        $\text{LONE} = 40 - 8 = 32/2 = 16 \text{ LP}$   
 5 Cl  $\Rightarrow$  5 BP, 15 LP (one expansion)

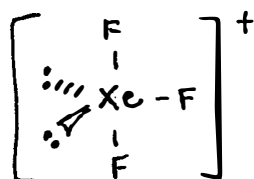
P STAB = 10



VSEPR: trigonal bipyramidal

3)  $\text{XeF}_3^+$        $\text{VAL} = 8 + 3(7) - 1 = 28$        $\text{STAB} = 4(8) = 32$   
                           $\text{BOND} = 32 - 28 = 4/2 = 2 \text{ BP}$        $\text{LONE} = 28 - 4 = 24/2 = 12 \text{ LP}$   
 3 F  $\Rightarrow$  3 BP, 11 LP (one expansion)

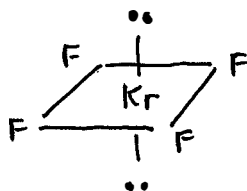
Xe STAB = 10



VSEPR: T-shaped

4)  $\text{KrF}_4$        $\text{VAL} = 8 + 4(7) = 36$        $\text{STAB} = 5(8) = 40$   
                           $\text{BOND} = 32 - 28 = 4/2 = 2 \text{ BP}$        $\text{LONE} = 28 - 4 = 24/2 = 12 \text{ LP}$   
 4 F  $\Rightarrow$  4 BP, 14 LP (two expansions)

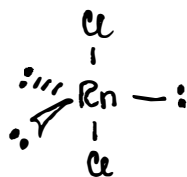
Kr STAB = 12



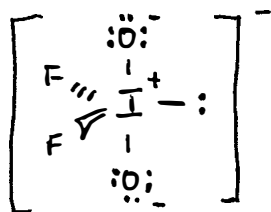
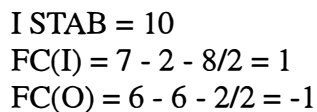
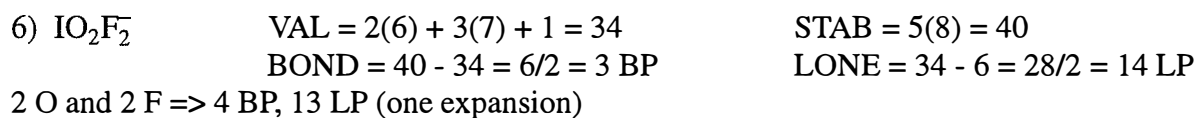
VSEPR: square planar

5)  $\text{RnCl}_2$        $\text{VAL} = 8 + 2(7) = 22$        $\text{STAB} = 3(8) = 24$   
                           $\text{BOND} = 24 - 22 = 2/2 = 1 \text{ BP}$        $\text{LONE} = 22 - 2 = 20/2 = 10 \text{ LP}$   
 2 Cl  $\Rightarrow$  2 BP, 9 LP (one expansion)

Rn STAB = 10



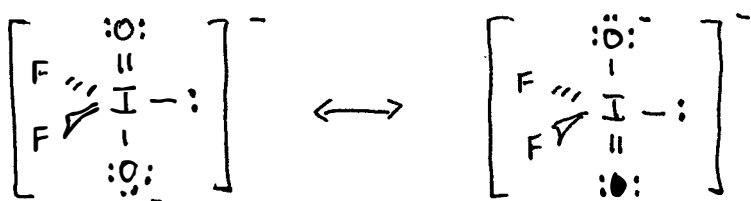
VSEPR: linear



VSEPR: seesaw

formal charge separation  $\Rightarrow$  5 BP, 12 LP (two expansions, extra bond between I and O)

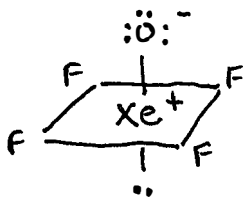
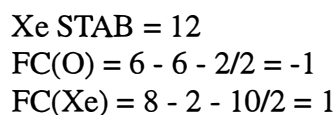
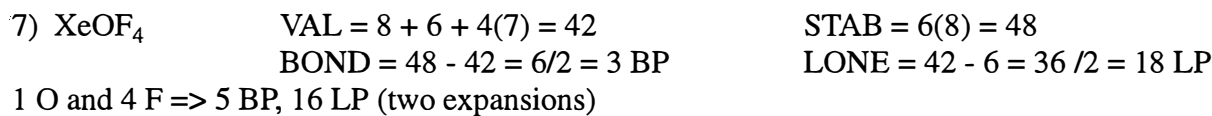
I STAB = 12



Now not only have we eliminated the formal charge (FC) separation in the structure when ten electrons were around I but we have also gained resonance. In looking for more **stable** Lewis structures expand to

- 1) reduce charge separation and
- 2) gain resonance structures

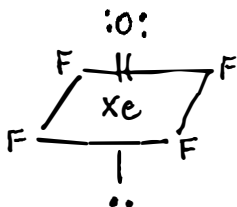
Keep in mind that the more resonance structures you can draw the more stable the structure is.



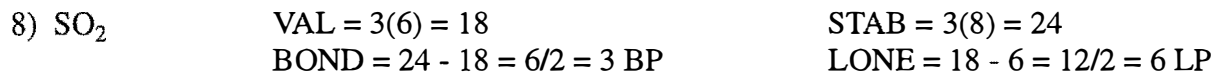
VSEPR: square pyramidal

formal charge separation  $\Rightarrow$  6 BP, 15 LP (three expansions)  
 (put extra bond between two atoms that have FC's and you reduce charge separation)

Xe STAB = 14



Now to examine some examples where it may not be obvious that a VSE need be done; sufficient bonds exist from just assuming the normal octets. Here the idea of a **stable** Lewis structure will predominate. If possible always try to reduce the formal charge separation. The only time this may be problematic is when a FC reduction also leads to a loss of resonance structures. Since it is difficult to unambiguously say which is more important, reducing charge separation or possessing resonance, when such an option arises we will take the route of simplest is best and not expand.



S STAB = 8

$$\text{FC}(\text{O}) = 6 - 6 - 2/2 = -1$$

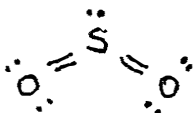
$$\text{FC}(\text{S}) = 6 - 2 - 6/2 = 1$$



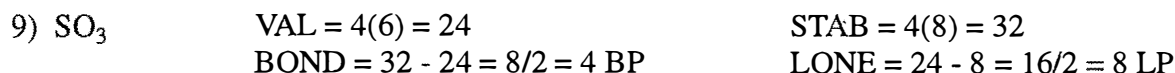
VSEPR: bent

two resonance structures good but FC separation => 4 BP, 5 LP (one expansion)

S STAB = 10



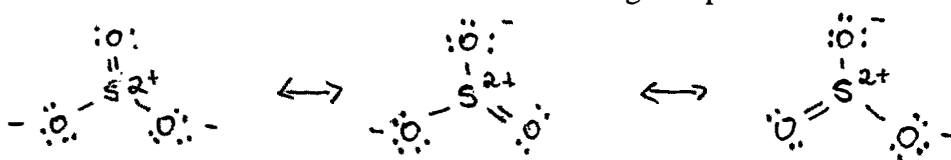
The loss of charge separation is good but the concurrent loss of resonance is not. We would conclude that nothing is gained overall by doing a VSE. Simplest, in this case, is best so stay with the octet. Experimentally it is observed that the SO bonds in  $\text{SO}_2$  are equivalent and intermediate between a single bond, S - O, and a double bond S = O, in length. Our decision best accords with experiment.



S STAB = 8

$$\text{FC}(\text{O}) = 6 - 6 - 2/2 = -1$$

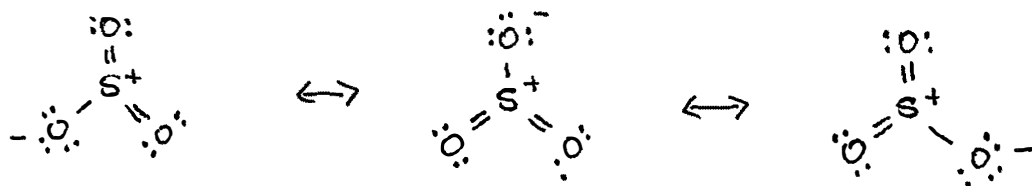
$$\text{FC}(\text{S}) = 6 - 8/2 = 2$$



VSEPR: trigonal planar

three resonance structures excellent but charge separation => 5 BP, 7 LP (one expansion)

S STAB = 10

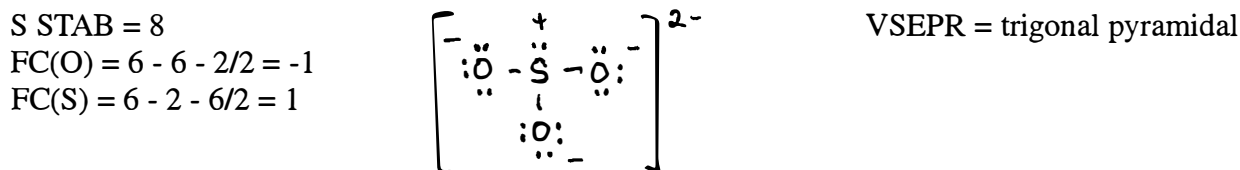


retained resonance but still charge separation => 6 BP, 6 LP (two expansions)

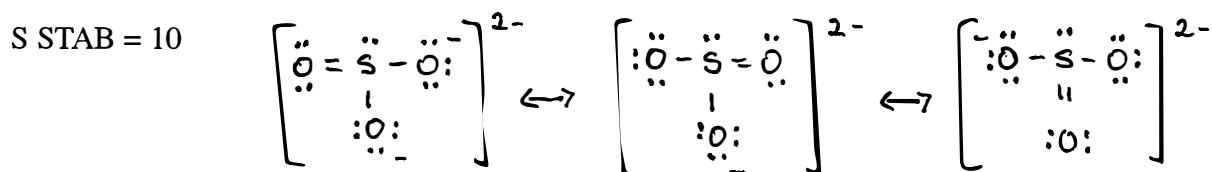
S STAB = 12

Now all resonance has been lost. As with SO<sub>2</sub>, nothing has been gained overall by this last expansion so stay with ten electrons about sulfur (STAB = 10). Experimental data on SO<sub>3</sub> shows that all three SO bonds are equivalent and intermediate between a double and single bond.

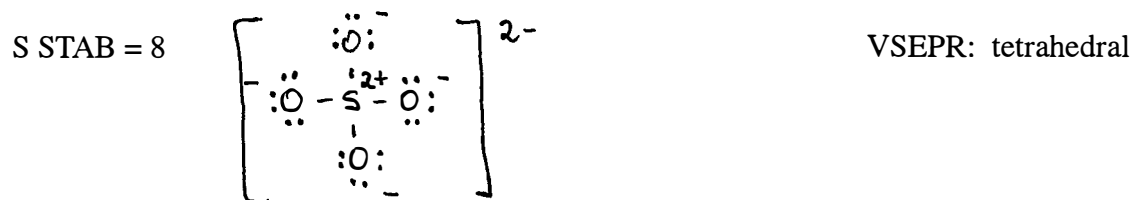
10) SO<sub>3</sub><sup>2-</sup>                      VAL = 4(6) + 2 = 26                      STAB = 4(8) = 32  
     BOND = 32 - 26 = 6/2 = 3 BP                      LONE = 26 - 6 = 20/2 = 10 LP



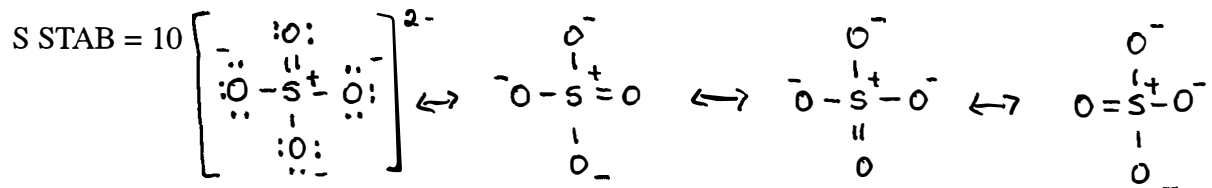
charge separation => 4 BP, 9 LP (one expansion)



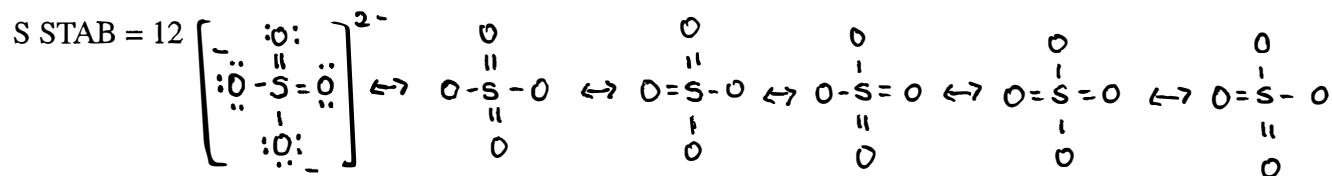
11) SO<sub>4</sub><sup>2-</sup>                      VAL = 5(6) + 2 = 32                      STAB = 5(8) = 40  
     BOND = 40 - 32 = 8/2 = 4 BP                      LONE = 32 - 8 = 24/2 = 12 LP



charge separation => 5 BP, 11 LP (one expansion)



charge separation => 6 BP, 10 LP (two expansions)



best - no charge separation and six resonance structures

## Valence Shell Electron Pair Repulsion Theory and Molecular Shape (Section 10.2)

Once you have drawn a structure that has the calculated number of bonds and lone pairs determine the electronic geometry (electron-group arrangement). The steric number (number of electron pairs) of an atom in a molecule is the total number of "things" that are bonded to it which is the sum of the number of bonded atoms and number of bonded lone pairs. The electronic geometry is named according to the number of electron pairs.

steric number (# electron pairs)	electron pair geometry molecular geometry (bond angle)	# lone pairs	example
2	linear (180°)	0	CO <sub>2</sub>
3	trigonal planar (120°)	0	SO <sub>3</sub>
	bent	1	SO <sub>2</sub>
4	tetrahedral (109.47°)	0	SO <sub>4</sub> <sup>2-</sup>
	trigonal pyramidal	1	SO <sub>3</sub> <sup>2-</sup>
	bent	2	H <sub>2</sub> O
5	trigonal bipyramidal (90°, 120°)	0	PCl <sub>5</sub>
	seesaw	1	IO <sub>2</sub> F <sub>2</sub> <sup>-</sup>
	T-shaped	2	XeF <sub>3</sub> <sup>+</sup>
	linear	3	RnCl <sub>2</sub>
6	octahedral (90°)	0	SnBr <sub>6</sub> <sup>2-</sup>
	square pyramidal	1	XeOF <sub>4</sub>
	square planar	2	KrF <sub>4</sub>

The electronic geometry gives the distribution of the valence electrons in space about the central atom. The molecular geometry (which one refers to as the "shape") is only given by the atoms. If there are no lone pairs then the electronic and molecular geometries are identical.