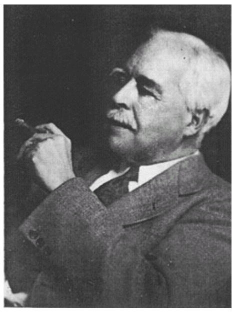
Chemical Bonding Basics

<u>Reading</u>: Ch 9, sections 5 - 9 <u>Homework</u>: Chapter 9: 49, 51, 53, 59, 63*, 69, 71*,73

* = 'important' homework question


G.N. Lewis

Recap and overview: We have already investigated the structure of the atom in terms of 'old style' *dot diagrams* and *Lewis symbols*.

Recall the *'battleship' analogy* with regard to # valence electrons an atom has (= element's column in p. table) *and* the number of shells of electrons an atom has (= element's row in p. table) an atom has**.**

<u>Review question</u>: Draw 'dot' diagrams and Lewis symbols for Li and F atoms

The Octet Rule (Full Valence Shell rule)

ATOMS WITH FULL OUTER (VALENCE) SHELLS ARE STABLE ⇒ Atoms will lose, gain or share electrons to have an inert gas (full valence shell) configuration.

THIS IS THE 'DRIVING' FORCE BEHIND ALL CHEMICAL PROCESSES.

1. Ionic bonding – the formation of LiF

Recall: Ionic bonds form between atoms (metal and non-metal, which then become ions) with a large difference in electronegativity.

Draw 'dot' diagrams illustrating the reaction between Li and F atoms to form LiF.

2. Covalent bonding – the formation of F_2 (g)

Recall: Covalent bonds form between atoms (two non-metals) with little or no difference in electronegativity.

Draw 'dot' diagrams illustrating the reaction between two F atoms to form F_2. Note: Lewis style diagrams of *covalently bound molecules* (e.g. F_2) are called *Lewis structure*s.

One time British soccer legend 'Gazza' with a gyro

Dr. Mills' favorite saying:

"Chemistry is a bit like Scottish soccer – it's basically a bunch of round things bumping into one another"

Gazza playing out his career with Glasgow Rangers

Simple Lewis Structures

Overview: Lewis structures are electron ‘maps’ of molecules, which are in turn constructed from the Lewis symbols of the molecule’s component atoms.

The number of bonds an atom forms in a molecule (VALENCEY)

≡

Number of UNPAIRED valence electrons it has as an atom

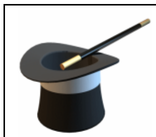
Task: Complete the following table

Atom	Number valence electrons	Lewis Symbol	Valencey (number of bonds formed)
C			
N			
O			
Cl			
H			

EZ Lewis Symbols – think of an *unpaired* valence electron as 'a hand that needs to be held' (I could not think of a more masculine analogy!). Then just have the atoms 'hold hands' (form bonds by converting unshared e^- to shared pairs of e^-) to make the required molecule's Lewis structure. **H_2O example**.

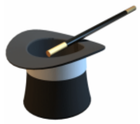
Task: Write formal Lewis symbols and 'EZ' Lewis symbols for the following atoms:

Atom	Formal Lewis Symbol*	'EZ' Lewis Symbol**	Valencey
C			
N			
O			
Cl			
H			



Remember: Just have the atoms, as represented by 'EZ' Lewis symbols, 'hold hands' to make the required molecule's Lewis structure

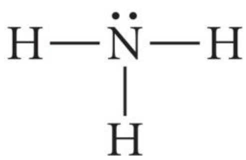
Task: Draw Lewis structures for the following molecules.



Remember: Each atom in a molecule must have as many bonds as its valencey (number of unpaired electrons). **Double or Triple bonds often arise from applying this rule**.

Note: The total number of valence electrons in a Lewis structure is simply the some of those 'owned' by each of the molecule's component atoms. Write this information next to each of the above Lewis structures.

Ammonia (NH_3)



Water (H_2O)

Methane (CH_4)

Phosphorus trichoride (PCl_3)

Oxygen gas (O_2)

Nitrogen Gas (N_2)

Hydrogen Fluoride (HF)

Dihydrogen monosulfide (H_2S)

Lewis Structures for More Complex Molecules - ‘The Rules’

Use the following rules to figure out the Lewis structure of ANY molecule (the above are simpler examples of the application of this ‘global’ set of rules)

<u>Worked Example – Carbon Dioxide (CO_2)</u>

1. Sum the valence electrons from all the atoms in the molecule or ion.

<u>For anions</u> (-ve), ADD one e^- per negative charge on the ion
<u>For cations</u> (+ve), SUBTRACT one e^- per positive charge on the ion

⇒ For CO_2:

2. Write the atoms on the page with the HIGHEST *valencey* atom in the center:

⇒ For CO_2:

3. Connect the outer atoms to the center atom with single lines(s) – these bonds (pair of shared electrons) are the minimum requirement for a molecule to exist.

4. Complete the valence shells of the ‘outside’ atoms to give them stable valence configurations.

5. Count up all the electrons in the structure and compare to the number required (from rule 1). Place any excess electrons on the center atom.

6. If the center atom does not have enough electrons for a complete valence shell, CONVERT 'OUTSIDE' LONE PAIR ELECTRONS TO DOUBLE BONDS. Remember that each outside atom's valencey must also be obeyed.

7. Double-check the valencey of all atoms and the total number of electrons in the structure.

<u>Task</u>: Follow the above rules to construct Lewis structures for the following molecules and ions:

1. CH_2O
2. CO_3^{2-}

Is there more than one way to write the Lewis structure of the carbonate (CO_3^{2-}) ion? Draw all possible versions.

These 'different versions' of the Lewis structure are called *resonance structures* (class demonstration). *Resonance structures stabilize otherwise 'impossible' molecules and molecular ions*

Breaking the Octet (Full Valencey Shell) Rule

The *expectation* that the valencey of each atom in a Lewis structure is the same as its respective Lewis symbol is often violated for more complex molecules or molecular ions (e.g. CO_3^{2-}). This is because Lewis structures are *empirical*, i.e. they don't completely model the *real* molecule in every detail.

Lewis structures can be 'modified' in order to account for these inconsistencies:

<u>Resonance forms</u>: Allow for the modeling of structures possessing atoms with apparent 'lower' or 'higher' valencies than expected.

<u>Octet expansion</u>: Allows for the modeling of center atoms with greatly *expanded* (numerically larger) valencies than expected. Such molecular models may also have a series of resonance forms

<u>Examples of structures modeled with ***resonance forms***</u>:

Follow the rules for drawing a regular Lewis structure - don't worry if the atom(s) expected valencies are *smaller* or *larger* than expected - if two of more resonance structures can be drawn the model 'works'. This is called *resonance stability* and leads to a stable, *delocalized* electronic structure in the 'real' molecule

<u>Examples</u>:

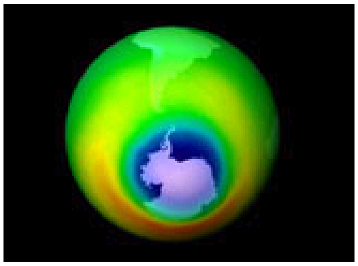
1. O_3
2. NO_2

[Over]

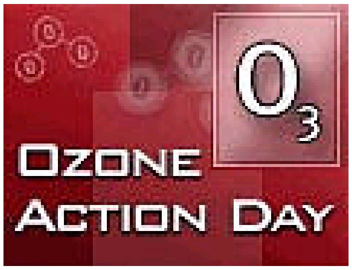
Work space

Environmental Concerns

LA smog (NO_2), mostly sourced from vehicle emissions. Note the brown color



The Ozone 'hole' over Antarctica



An Ozone action day sign warning of ***excess*** O_3

Discussion: How can there simultaneously be *too much* (ozone action days) and *too little* (Antarctica's ozone 'hole') ozone in the atmosphere.

Examples of structures modeled with using ***octet expansion***:

Two criteria must be met for a center atom to *expand its octet* (increase its valencey):

1. **The atom must be bonded to a highly electronegative atom, such as F, O or Cl (why)?**

2. **The atom must be in the 3rd row or lower of the periodic table (why?)**

⇒ Atoms that undergo octet expansion are limited to P, S, Cl, Br and I (as well as several other lower p block non-metals)

Expansion can only occur within *orbitals possessing the same principle quantum number* (i.e. within the same 'shell'). Recall: Have you seen something like this elsewhere already?

Orbital box diagrams can be used to explain the increased valencey of the 'lower p block' elements.

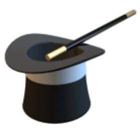
Example: Orbital 'box' diagrams for the valence shell of phosphorous

			3s	3p	3d
Unexpanded ('regular'):	P:	[Ne]	□	□□□	□□□□□
Expanded:	P:	[Ne]	□	□□□	□□□□□

Question: What is the valencey of phosphorus with a 'regular (unexpanded) and an expanded valence shell?

Task: Draw Lewis symbols for phosphorus with a ‘regular (unexpanded) and an expanded valence shell. Now draw ‘EZ’ Lewis structures for PCl_3 (unexpanded Octet) and PCl_5 (expanded octet)*

PCl_3 PCl_5



Electrons from the valence shell can be promoted to easily accessible (empty) 3d orbitals. This increases the number of unpaired valence electrons.

The total number of *unpaired* electrons in the expanded valence shell = the ‘new’ valencey of the atom. This can be expressed in the form of an ‘expanded’ Lewis symbol for the atom*.

*even though there are more than 8e in the expanded octet (after covalent bonds have been formed), the octet rule is still said to be obeyed as there are no remaining unpaired electrons in the valence shell of the center atom

Partial and complete octet expansion

Phosphorous (as shown above) can only promote ***one*** electron (from the 3s) to a 3d orbital in order to increase its valencey from 3 $\rightarrow$ 5

Third (and later) row elements in groups VI – VIII have more than one ‘box’ of paired electrons in the ground state, so can increase their valencies even further by promoting more (initially paired) electron(s) from the *s* and *p* orbitals to the *d* orbitals

Electrons are sequentially promoted from the *p*, then the *s*, orbitals to the d orbitals to increase valencey. See below example.

Example: Write Lewis structures for SO_2 (partially expanded octet) and SO_4^{2-} (fully expanded octet).

Trick: Draw box diagrams fist, and then construct an analogous ‘EZ’ or ‘rules’ Lewis structure.

Ground State: S: [Ne]

3s	3p			3d				

Partially expanded: S: [Ne]

3s	3p			3d				

Fully expanded: S: [Ne]

3s	3p			3d				

Additional Problems*: Draw Lewis structures for $\mathbf{XeF_2}$, $\mathbf{XeF_4}$ and $\mathbf{XeF_6}$

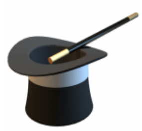
Formal Charge

Observation: We can now draw Lewis structures for molecular ions which, by definition (for anions), have ‘extra’ electrons. These ‘extra’ electrons give the ion its overall charge.

Fact: Where these ‘extra’ electrons are located in the Lewis structure is indicated by determining the *formal charge* of each atom in the structure.

The formal charge is the ‘charge’ on an atom in a Lewis structure, if it is assumed all the atoms in the structure have the same electronegativity (*yes, it’s another empirical model!*)

Formal charges allow us to determine the ‘best’ Lewis structure



As with drawing Lewis structures, follow a set series of empirical rules (shown below) to determine the final answer

Rules for assigning formal charge: Worked example - the cyanide ion

1. Construct a Lewis structure for the molecule or molecular ion.

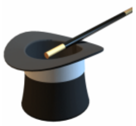
2. determine the formal charge on each atom in the Lewis structure

The formal charge on an atom in a Lewis structure equals:

 # valence electrons it has as an isolated atom

MINUS

# of valence electrons it *'owns'* in the Lewis structure



The sum of the formal charges for any molecule = zero

The sum of the formal charges for any molecular ion = *overall* ionic charge

For the cyanide ion:

Discussion: based on electronegativity trends, is the location of the electron in cyanide surprising? How does this compare with the hydroxide ion?

Example: Determine the formal charges on each atom in *one* resonance form of the CO_3^{2-} ion's Lewis structure.

“Lewis”

The following question was taken from your 3rd practice midterm:

Question 2a (20 points) Draw Lewis structure(s) for the PO_4^{3-} ion, *include all possible resonance forms* and include formal charge labels on one of your structures. Assume a completely expanded octet for phosphorus.