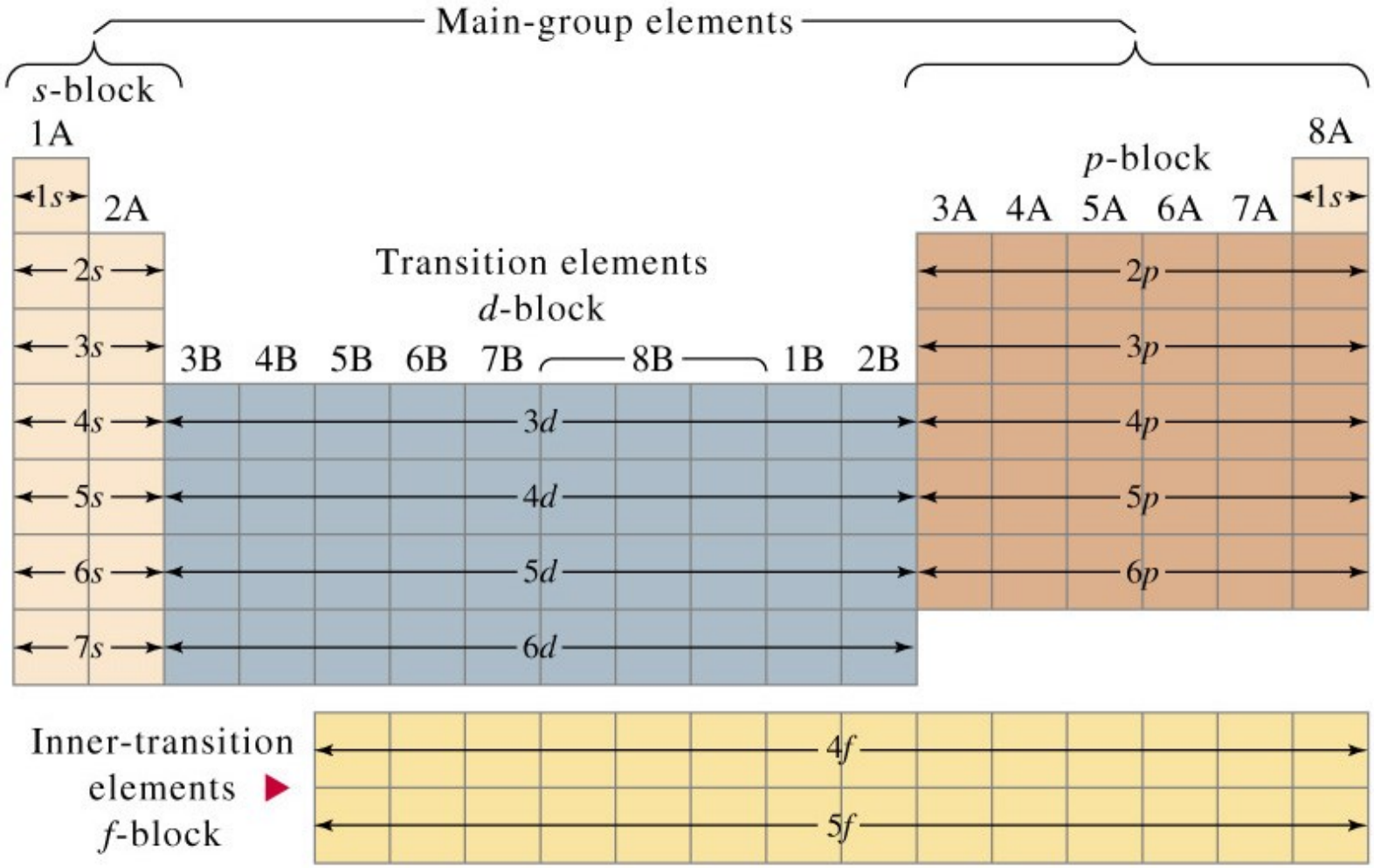
The Periodic Table

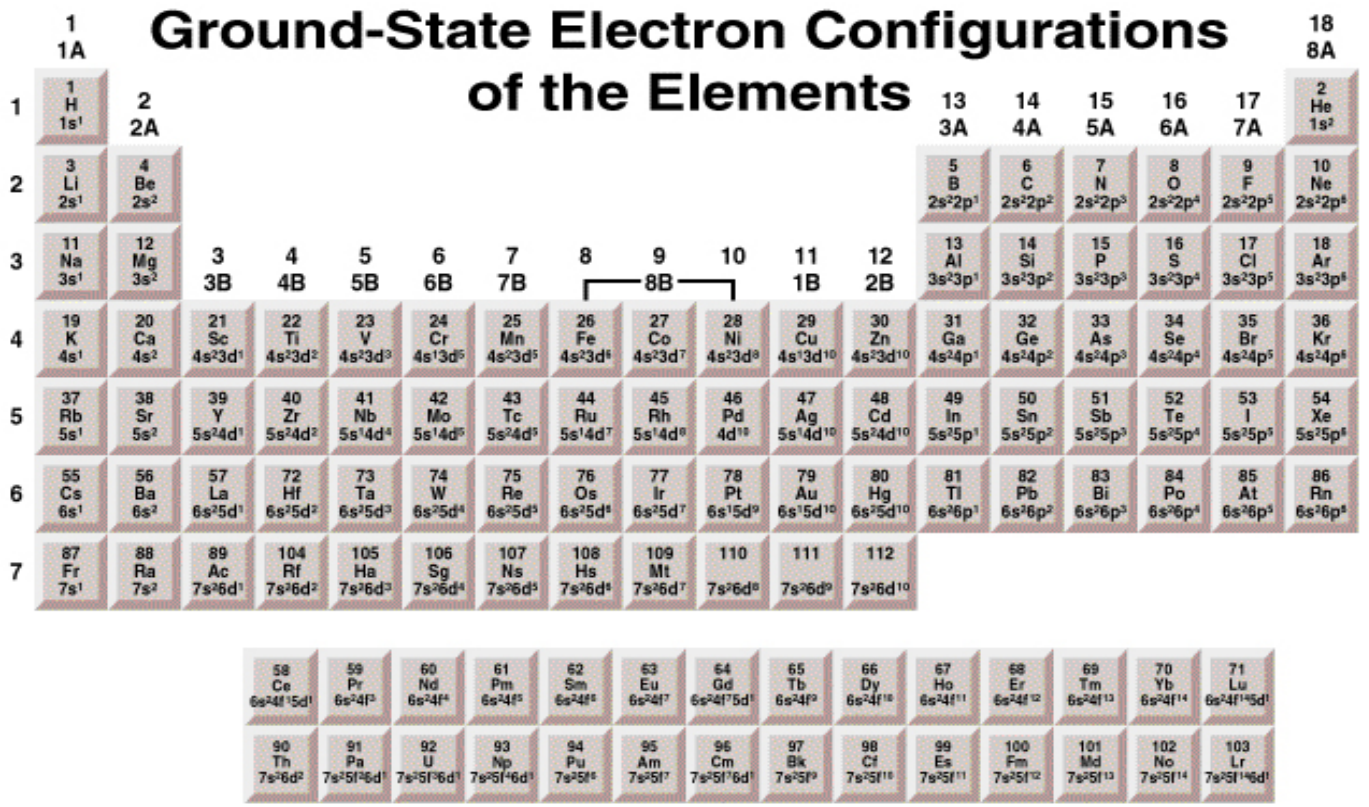
- for the following atoms/ions, provide the number of electrons that will have the desired quantum numbers
  - a) P: $n = +1$
  - B) Ar: $l = 1$, $m = 0$
  - C) Pt: $l = 0$, $m = +1$
  - D) As: $m = -1$
  - E) Br^-: $m = 0$, $s = -1/2$


Main-group elements
s-block
1A
8A
p-block
1s
2A
3A 4A 5A 6A 7A
1s
2s
2p
Transition elements
d-block
3s
3p
3B 4B 5B 6B 7B 8B 1B 2B
4s
3d
4p
5s
4d
5p
6s
5d
6p
7s
6d
Inner-transition elements
f-block
4f
5f

The Development of Periodic Table

- in the time of Mendeleïev, the electron had not yet been discovered
- Mendeleïev was convinced that the properties of the elements had a **periodicity** if they were organized in order of increasing atomic mass
    - he had such confidence in the periodicity of the properties that he proposed certain elements that remained to be discovered and left *holes* in his table in order to accommodate them
    - he accurately predicted the properties of those elements that were unknown
- one problem was the Ar (element 18) was heavier than Na (element 19)
    - after the discovery of the nucleus by Rutherford, it was found that the number of protons in the nucleus was the critical factor (and not the mass)

The Periodic Classification of Elements



- each column (group) in the periodic table shares the same electronic configuration for its valence electrons
- there are a few exceptions for the transition metals, the lanthanides, and the actinides

The Periodic Classification of Elements

- the valence electrons are peripheral electrons (in the shell with the highest value for the principal quantum number, *n*) of an atom

- the valence electrons are those that participate in the formation of chemical bonds

- the face that each member of a group shares the same number of valence electrons explains the similarities in reactivity

- N.B. the properties of the elements with the IA, IIA, and VIIA groups are very similar within the group
    - in the IIIA, IVA, VA, and VIA groups, the properties of the elements sometimes change when descending the group

Electron Configurations of Cations and Anions

- in an ionic compound, the cation of a representative element is produced by losing electrons in order for the cation to have the electron configuration of a noble gas

eg.; $Na: [Ne]3s^1$ becomes Na^+ : [Ne]

$Ca: [Ne]3s^2$ becomes Ca^{2+} : [Ne]

$Al: [Ne]3s^2 3p^1$ becomes Al^{3+} : [Ne]

- in an ionic compound, the anion of a representative element is produced by accepting electrons in order for the anion to have the electron configuration of a noble gas

eg.; $H: 1s^1$ becomes H^- : $1s^2$ or [He]

$F: [He]2s^2 2p^5$ becomes F^- : $[He]2s^2 2p^6$ or [Ne]

$O: [He]2s^2 2p^4$ becomes O^{2-} : $[He]2s^2 2p^6$ or [Ne]

$N: [He]2s^2 2p^3$ becomes N^{3-} : $[He]2s^2 2p^6$ or [Ne]

Electron Configurations of Cations and Anions

- these formed ions from their respective elements and the noble gases are **isoelectric** (having the same number of electrons, thus sharing the same electron configuration)

- for transition metals, we often find more than one type of cation and these cations are often not isoelectric with a noble gas
    - ex.; neither Fe^{2+} nor Fe^{3+} is isoelectric with a noble gas, but both are found in nature

- even if the *n*s orbital is filled before the (*n*–1)d orbital (Klechkowski rule), the *n*s electrons are removed first when a transition metal forms a cation
    - the *n*s and (*n*–1)d orbitals are very close in energy, and the electron-electron and electron-nucleus interactions change when changing from an atom to a cation, therefore the energetic order between *n*s and (*n*–1)d change
    - ex.; Mn^{2+} has the configuration $[Ar]3d^5$ and Zn^{2+} has the configuration $[Ar]3d^{10}$

To do Assignment 4 and Final Exam…
Units of Concentration

- the percent mass:

$$\frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$$

- the molarity (M, mol/L):

$$\frac{\text{moles of solute}}{\text{liters of solution (in L)}}$$

- the molality (m, mol/kg):

$$\frac{\text{moles of solute}}{\text{masse of solvant (in kg)}}$$

To do Assignment 4 and Final Exam…
Units of Concentration

- example: Calculate the molarity, mole fraction, and percent mass of a 1.74 m solution of saccharose ($C_{12}H_{22}O_{11}$, MM = 342.30 g/mol), where the density is 1.12 g/mL.

To do Assignment 4 and Final Exam…
Units of Concentration

- example: Calculate the molarity, the molality, and the mole fraction of an aqueous solution of NaCl (MM = 58.44 g/mol) at 44.6%. The density of the solution is 1.17 g/mL.

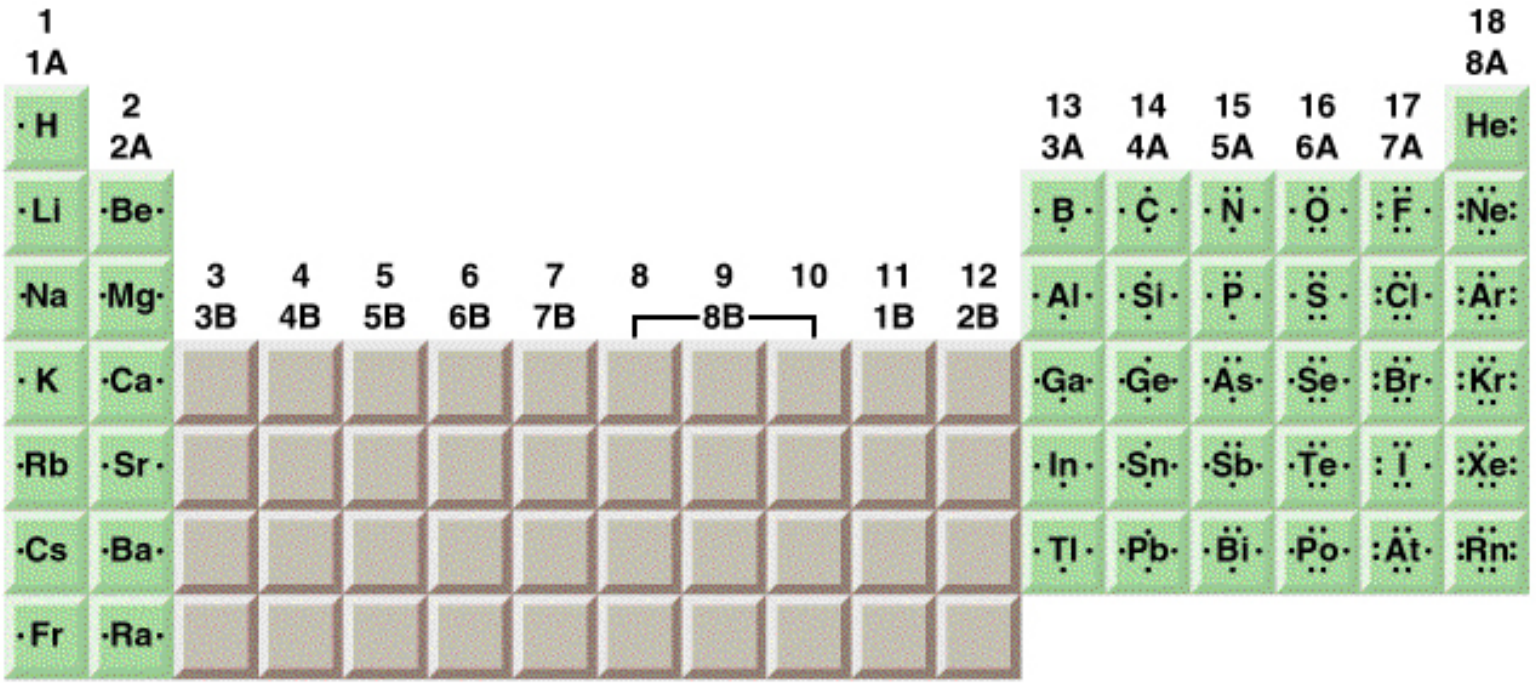
Tuesday, November 25th 2014

Chemical Bonds I: the covalent bond

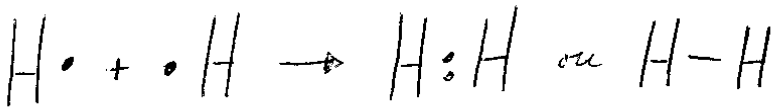
Lewis Dot Symbols

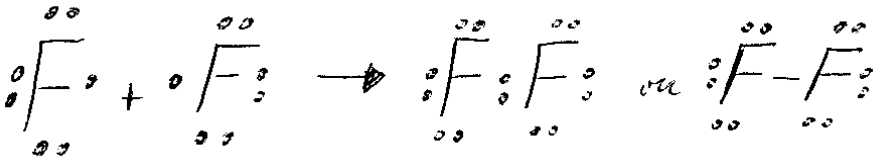
- atoms react together to form molecules in order to arrive at the most stable electronic configuration
- valence electrons are of interest to chemists the most since it is the valence electrons that are shared between two atoms in a covalent bond
- a Lewis dot symbol is the representation of an element by its atomic symbol surrounded by points that represent valence electrons
- since members of a group have the same number of valence electrons, they share the same Lewis dot symbol (with the exception of He, a noble gas)
- Lewis dot symbols work terribly for transition metals, lanthanides, and actinides

Lewis Dot Symbols



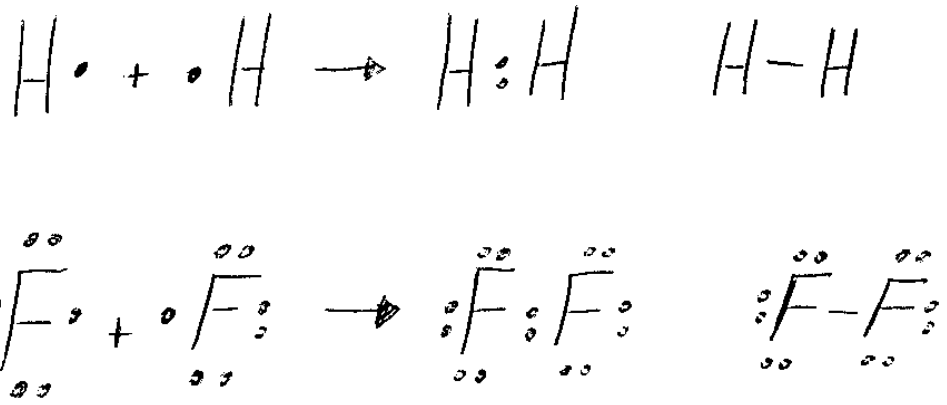
The Covalent Bond





- a covalent bond is a bond wherein two electrons are shared between two atoms
- in a covalent bond, each electron of the shared electron pair (or **bonding pair**) is attracted by the nuclei of both atoms
  - these interactions help hold the two atoms together
- only valence electrons participate in covalent bonds

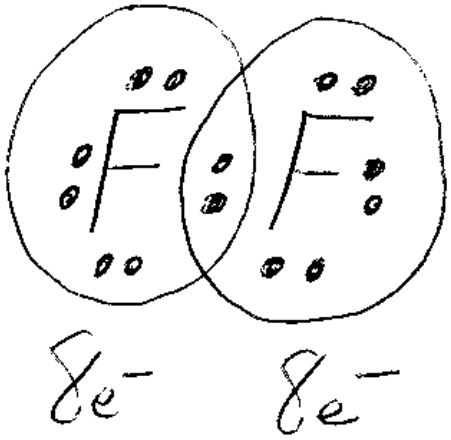
The Lewis Structure

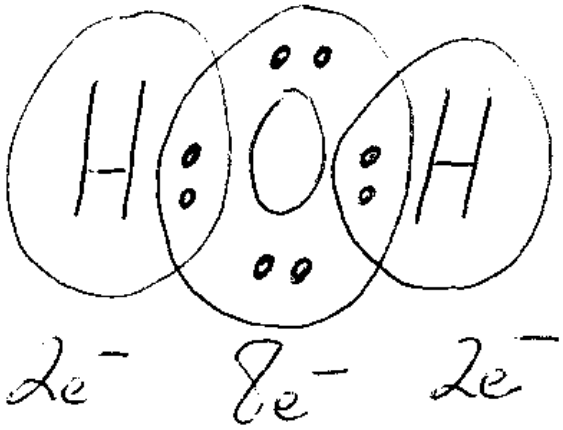


- the electrons that do not participate in the formation of covalent bonds are called **lone pairs**

- a Lewis structure is the representation of the covalent bonds using Lewis dot symbols where
  - the **bonding pairs** are illustrated by a straight line or by pairs of dots between two atoms
  - the lone pairs (non-bonding electron pairs) are each represented by pairs of dots associated with each atom

The Octet Rule

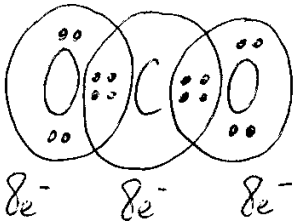


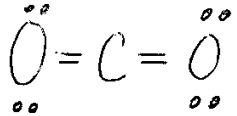


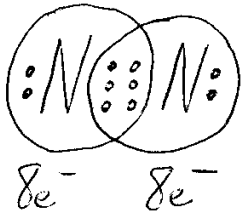
- Lewis proposed that all atoms, with the exception of hydrogen, have a tendency to form bonds until they are surrounded by eight valence electrons
  - this is the **octet rule**
  - hydrogen must possess two electrons

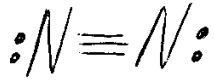
- after the second period (Li to F), we will see exceptions to the octet rule due to the availability of d orbitals in the same shell as valence s and p orbitals

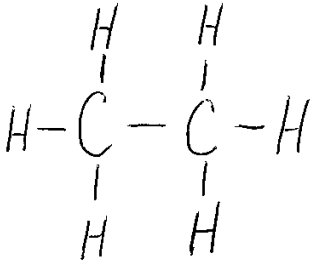
Multiple Bonds

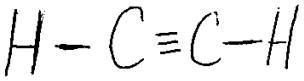


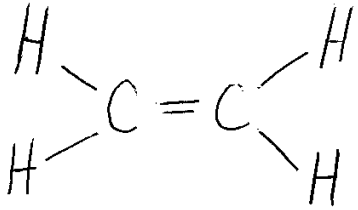






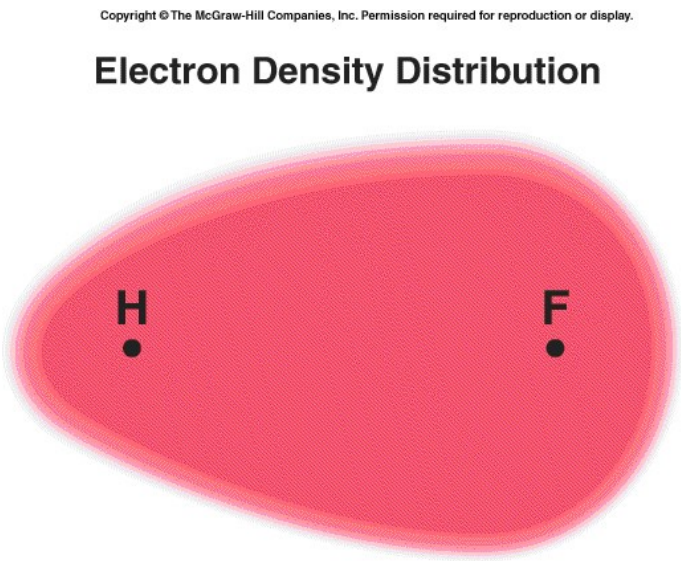






- if two atoms share one pair of electrons, they will form a single bond
- if two atoms share two pairs of electrons, they will form a double bond
- if two atoms share three pairs of electrons, they will form a triple bond
- for a given pair of atoms, triple bonds are shorter and more stable than double bonds, which, in turn, are shorter and more stable than single bond

A Covalent Polar Bond

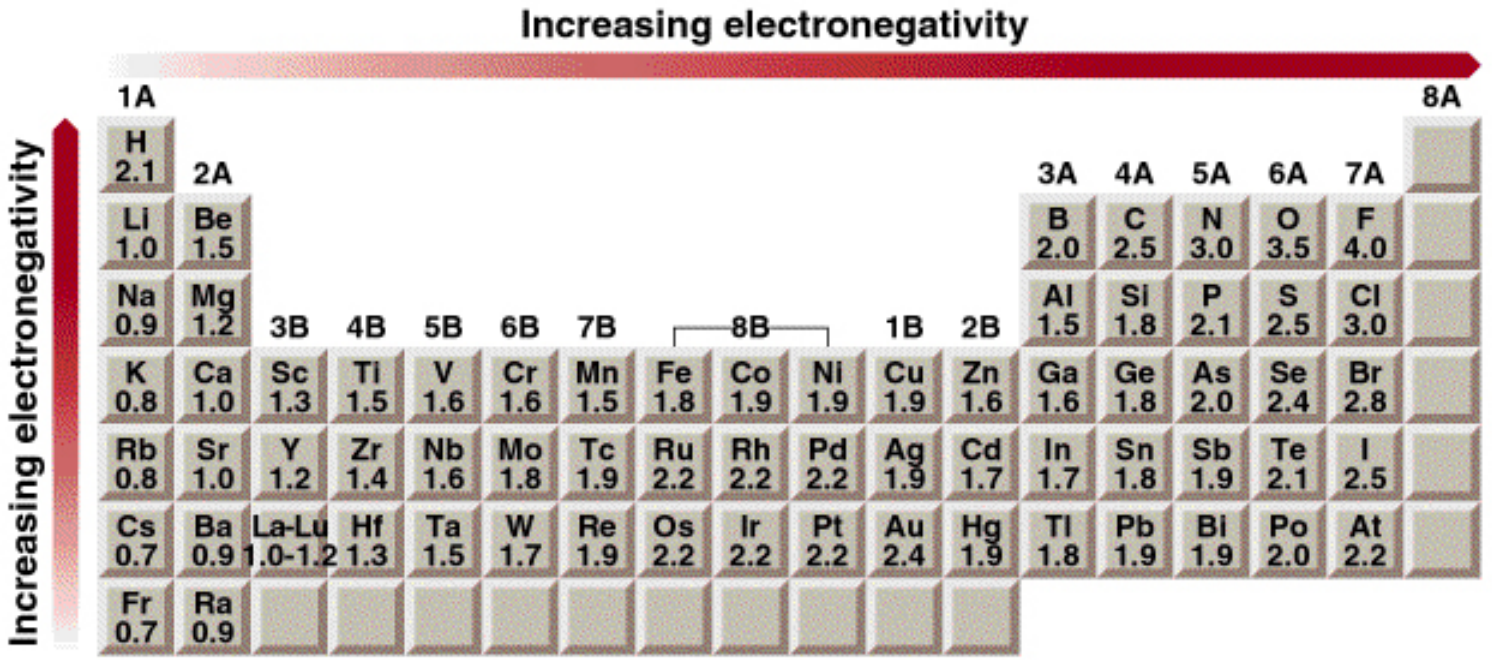


- in a **homonuclear diatomic** pair (such as H_2 and F_2), the sharing of electrons is perfect
- in the **heteronuclear diatomic** case (such as HF), the sharing of electrons is not done equally, i.e., the electrons spend more time closer to one atom than the other
  - the bond is said to be **covalent polar** (or simply polar)
- in an ionic bond, the transfer of electrons is almost complete
- in a polar bond, there is always an important amount of shared electron density

Electronegativity

- **electronegativity** is the tendency for one atom to attract to itself the electrons in a chemical bond
- electronegativity is a relative value, and thus has no units
- the more an element is electronegative, the more the element has a tendency to attract electrons
- Pauling established a method to calculate the electronegativity for most of the elements

Electronegativity



Covalent Polar Bonds and Ionic Bonds

- the bond between a metal and a non-metal tends to be ionic
- the bond between non-metallic elements tends to be covalent polar
- general rules:
    - if the difference in electronegativity is equal or higher than 2.0, the bond is essentially ionic
    - if the difference in electronegativity is smaller than 2.0, the bond is more covalent polar
    - if the bond is between two atoms of the same element, the bond is **covalent pure**

Electronegativity and the Oxidation State

- the oxidation state indicates the charge number of an atom in a molecule if the electrons were completely transferred to the most electronegative atom participating in the bond

- eg.; in water, the O atom is more electronegative than the H atom, therefore, the O atom will gain an electron from each H atom: the O now has a charge of −2 and each H atom has a charge of +1
- eg.; in hydrogen peroxide, each O atom has an oxidation state of −1 since each O atom gains one electron from one H atom but both electrons are perfectly shared between both O atoms

- in a compound containing fluorine (F), the F is always −1 because it is the most electronegative atom (and it is never bonded to itself except in F_2)

Rules for Writing Lewis Structures

- step 1: establish the skeletal structure of the compound using the chemical symbols and by placing each bonded atom side-by-side
    - when in doubt, in general, the least electronegative atom occupies the central position
- step 2: count the number of valence electrons
    - in the case of an anion, add the number of negative charges to the total
    - in the case of a cation, subtract the number of positive charges from the total

Rules for Writing Lewis Structures

- step 3: draw a single covalent bond between the central atom and each of the surrounding atoms
    - as much as possible, complete the octet of the atoms bonded to the central atom (except for hydrogen, which asks for two electrons)
    - place the remainder of the electrons on the central atom
    - the number of electrons remaining at the end of this step must match that determined in step 2
- step 4: if the octet rule is not respected by an atom, try to form double bonds between it and the neighboring atoms by using the lone pairs of the former

Lewis Structures

- example: Draw the Lewis structure of the carbonate ion (CO_3^{2-}).

Lewis Structures

- example: Draw the Lewis structure of the nitrite ion (NO_2^-).

Formal Charges and Lewis Structures

- for an isolated atom, the number of electrons associated to it corresponds to the number of valence electrons it has

- in a molecule, an atom possesses the two electrons in each of its lone pairs, but for bonding pairs shared between two atoms, the atom possesses only half of the electrons from the bonding pairs

- the formal charge of an atom in a molecule is the difference between the number of valence electrons contained in an isolated atom and the number of electrons associated to this same atom in the Lewis structure

Formal Charges and Lewis Structures

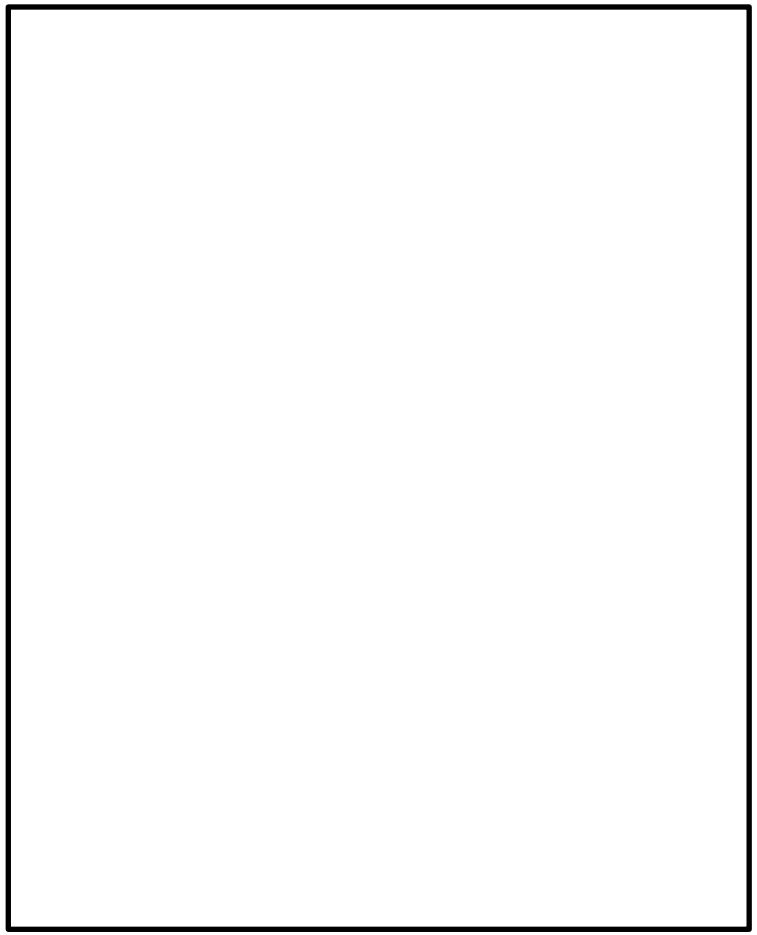
- formal charge = total number of valence electrons of the isolated atom
  - total number of lone pair electrons
  - 1/2 (total number of bond pair electrons)

- in the case of a neutral molecule, the sum of the formal charges must be zero

- in the case of an ion, the sum of the formal charges must equal the charge of the ion

- N.B. The formal charges do not represent the real distribution of charges in a molecule
  - eg.; for H_2O, there are no charges but we know that the electronegativity of the O atom is larger than that of the H atom, therefore the O atom will have a partial negative charge and the H atoms will each have a partial positive charge

Formal Charges and Lewis Structures



- example: Determine the formal charges of the carbonate ion.
- answer:
  - for the C atom:

$$\text{formal charge} = (4) - (0) - \frac{1}{2}(8) = 0$$

  - for the O atom is C=O

$$\text{formal charge} = (6) - (4) - \frac{1}{2}(4) = 0$$

  - for the O atoms in C–O

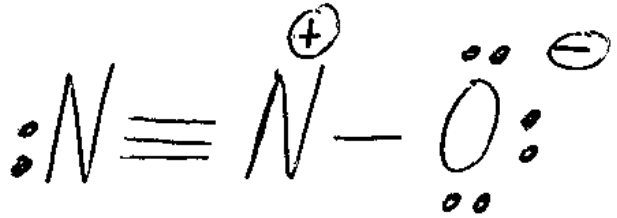
$$\text{formal charge} = (6) - (6) - \frac{1}{2}(2) = -1$$

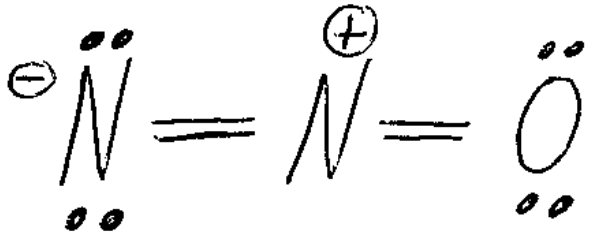
  - N.B. the sum of the formal charges (–2) is the charge of the ion

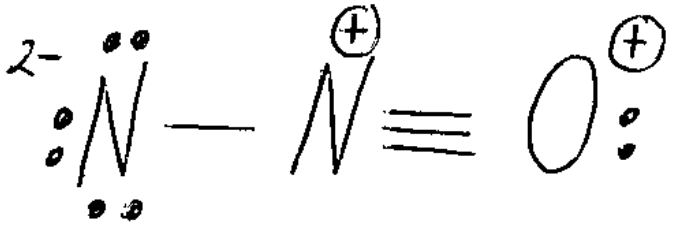
Formal Charges and Lewis Structures

- if we have many Lewis structures that obey the octet rule, we can use formal charges to determine the best structure
    - in the case of neutral molecules, a Lewis structure without any formal charges is preferable over another containing formal charges
    - a Lewis structure with elevated formal charges (±2, ±3, etc.) is less plausible than another where the charges are smaller
    - if the Lewis structures have a similar distribution in formal charges, the most plausible structure is that where the negative formal charges are placed on the most electronegative atoms

Formal Charges and Lewis Structures



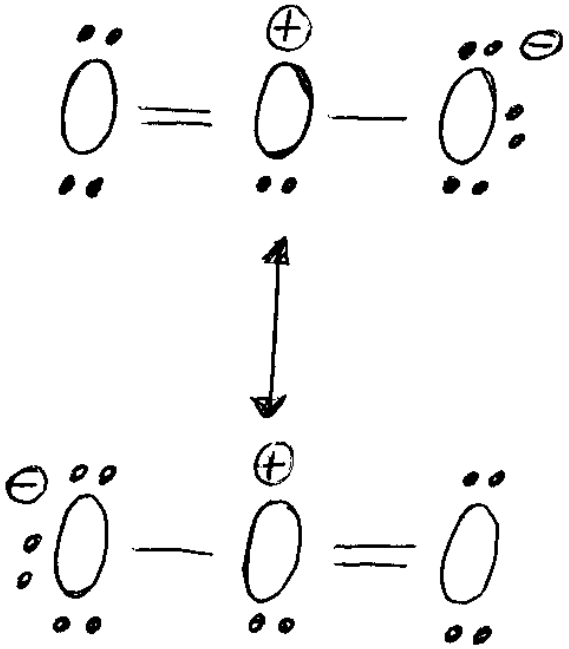




- example: Which of the Lewis structures for N_2O is the most plausible?

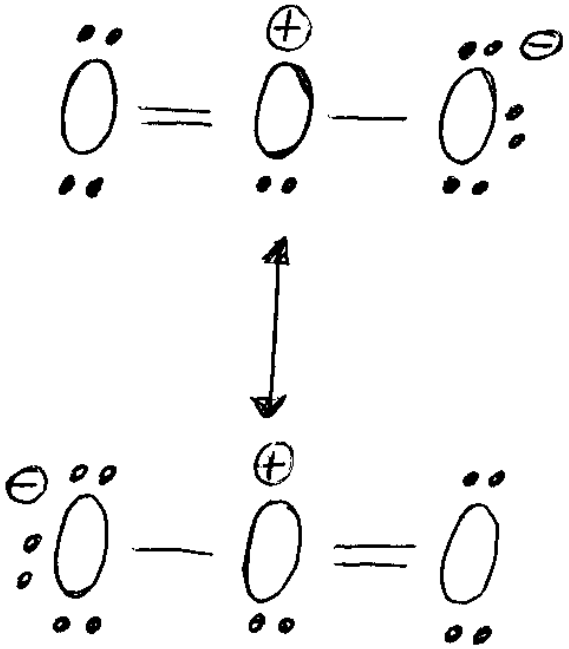
- answer: The third structure is the worst since the terminal N atom has a charge of –2. The first structure is better than the second structure because the O atom is more electronegative than N and the first structure has a formal negative charge on the O atom whereas the second structure places a formal negative charge on the N atom.

The Concept of Resonance



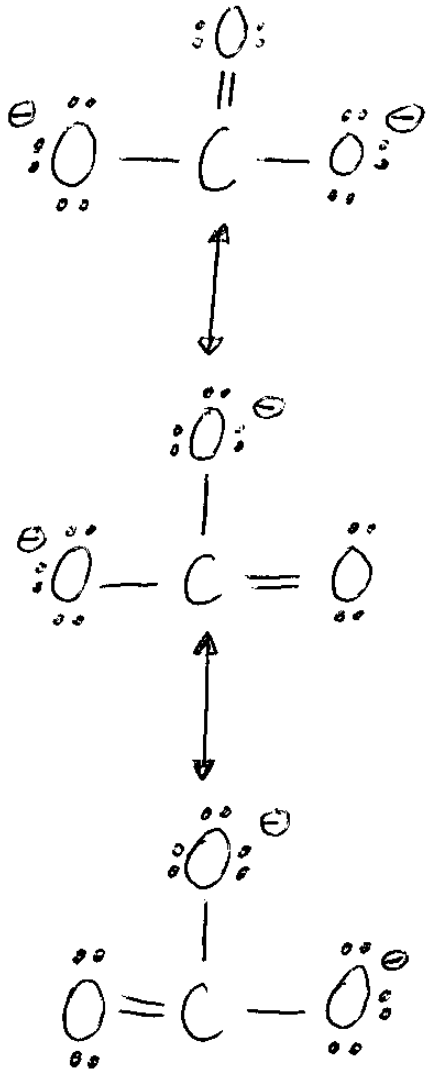
- if we look at the ozone molecule, O_3, for example, there a two different Lewis structures that are equivalent
- each Lewis structure predicts that ozone has one O=O double bond and one O–O single bond
    - however, we observe experimentally that both O–O bonds in ozone are identical (same length, same strength)
- in reality, ozone is a combination of both of these two Lewis structures

The Concept of Resonance



- **resonance** is the use of two or more Lewis structures to represent a given molecule
- each of these Lewis structures is called a resonance structure
- the symbol ↔ indicates that the drawn structures are resonance structures
- experimentally, we find that the bonds in ozone are stronger than the O–O single bond in H_2O_2 but they are longer and weaker than the O=O double bond in O_2

The Concept of Resonance

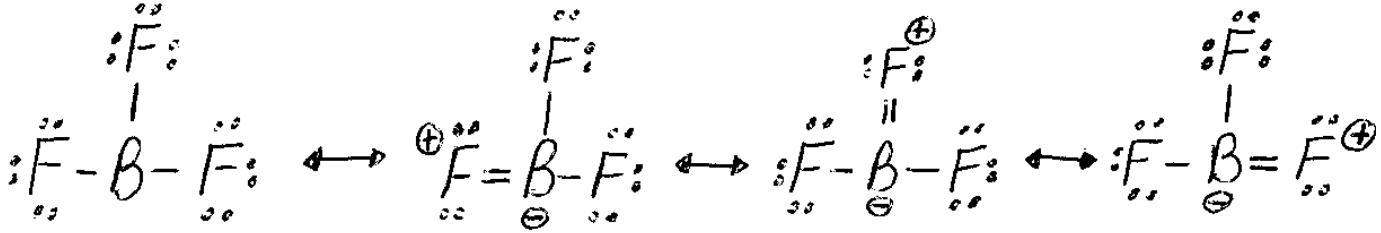


- we cannot believe that a molecule like the carbonate ion interchanges rapidly from one resonance structure to another
- *none* of the resonance structures represent adequately the real molecule
- we use the concept of resonance to explain why all three C–O bonds in the carbonate ion are identical
- N.B. if we change the positions of the atoms between two Lewis structures, we do not have a resonance structure (we have two distinct molecules)

Exceptions to the Octet Rule: Electron-Deficient Atoms

- in certain compounds, it is impossible to entirely fill the octet of an atom

- eg.; in the gas phase, BeH_2 forms distinct H–Be–H molecules where only 4 electrons surround the Be and it is impossible to fill its octet
- eg.; BF_3 is a relatively stable molecule

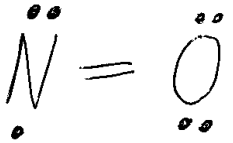


  - even if the three last resonance structures fill the octet of B, experiments show that the first resonance structure dominates

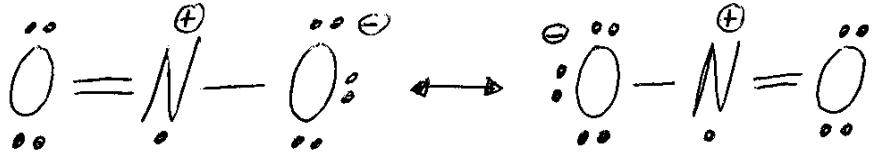
Exceptions to the Octet Rule: Molecules with an Odd Number of Electrons

- some molecules have an odd number of electrons
- these molecules are free radicals and are typically very reactive
- with an odd number of electrons, it is impossible to obey the octet rule
- examples of such molecules are

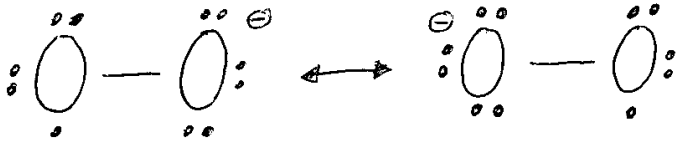
  - nitrogen monoxide:



  - nitrogen dioxide:



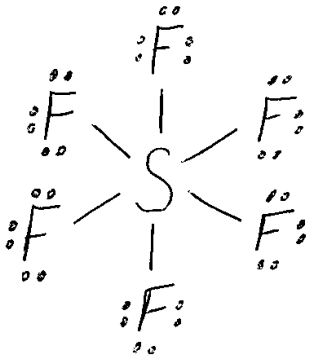
  - superoxide anion:



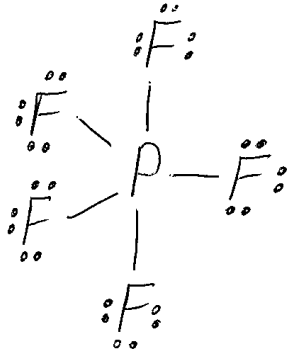
Exceptions to the Octet Rule: Expanded Octet

- if the central atom is of the third row (or even lower in the periodic table), the d orbitals of the central atom can participate in the covalent bonds
- these d orbitals allow for the central atom to accommodate more than eight electrons, an expanded octet
- N.B. even if an atom can have an expanded octet, it can always choose to obey the octet rule
- some examples:

sulfur hexafluoride



phosphorus pentafluoride



Suggested Problems

- 8.73–8.90