Basic Skills for Chemistry
CHEM-1020
Chapter 6 Lecture Notes
Kroschwitz, 3rd edition

Chemical Bonding

Chemical Bonds
What evidence exists that bonds or forces exist between atoms (and molecules)?

1) The existence of molecules
   Millions of compounds (substances) form combinations of the 100 (or fewer) elements.
   Therefore, atoms must somehow bond together (Dalton's hooks) to form molecules.
   (*Intramolecular* Forces)

2) Existence of liquids and solids.
   If there were no forces between molecules, all substances would exist as gases.
   (*Intermolecular* Forces)

Types of Intramolecular Bonds
Two extreme types of intramolecular bonds, **Ionic Bonds** and **Pure Covalent Bonds.**
Many real bonds lie between the two extremes.

Ionic Bonds

The ionic bond is simply the electrostatic attraction between oppositely charged particles.
One or more anions and one or more cations.
Examples: NaCl $CaCl_2$ MgO

Many atoms readily gain or lose electrons to form anions and cations.
Why are some ions more stable than the atoms they are derived from?

Electron Configuration Facts:
- Electron *positions* in the *electron cloud* cannot be specified.
- Electron *orbital* energies are very well known
- Electron energies have discrete "quantized" values, not a continuum of values.
- Electrons exist in certain "allowed" orbitals, not just anywhere around a nucleus.
- Electron energies depend on the principal energy level (**n = 1,2,3**,…)occupied by the electron.
- Energies also depend on the energies of individual orbitals (sublevels).
- Orbital types are specified by letters **s, p, d, f.**
- Any *one* orbital can hold a maximum of 2 electrons.
- An s orbitals can contain up to 2 electrons
- A set of three p orbitals can contain up to 6 electrons
- A set of five d orbitals can contain up to 10 electrons
- A set of seven f orbitals can contain up to 14 electrons.

The number of electrons in an atom or ion is determined using Z and the ionic charge.
The electron filling order for any atom is given: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4p, 5p, …
Distinguish between *valence* electrons and *core* electrons.
Determine the number of available electrons and add until they are all used up.
Examples: H, F, F^-, Na, Na^+, O, O^{2-}
The complete filling of the n = 1 level confers great stability to the atom.
The complete filling of the n = 2 level confers great stability to the atom.
The complete filling of any set of p orbitals confers stability to an atom.
Relation to the ***Octet Rule*.**
By sharing, gaining or losing electrons, an atom tends to achieve 8 electrons in its outermost shell.

Partial Explanation of how Ions Form

a) Group 18 (or VIIIA) atoms, the Noble Gases, do not form ions.
The atoms *already* obey the octet rule.
Noble gas atoms are more stable than any ions they might form.
The np^6 noble gas electron configuration confers stability that prevents ion formation.
Octet rule

b) All metal atoms exist in the elemental state as uncharged atoms.
Metal atoms hold electrons weakly allowing bulk metals to conduct electricity readily.
In compounds, metal atoms lose valence electrons to form the corresponding *cations*
Examples of cations that obey the Octet Rule: H^+ Na^+ K^+ Mg^{2+} Ca^{2+} Al^{3+}
(Cations that do not obey octet rule Fe^{2+}, Fe^{3+}, Zn^{2+}, etc.

c) Many, but not all, nonmetal atoms gain electrons to form anions.
Examples of monatomic anions obeying the octet rule: H^- F^- Cl^- O^{2-} S^{2-} N^{3-}
(Why does N^{3-} rarely form? Why is P^{3-} even rarer?)
Why do C^{4-} and C^{4+} never form?

<u>Ionic Compounds</u>

Ions form by *transfer* of electrons between metal atoms and nonmetal atoms to form cations and anions.
The resulting oppositely charged ions attract one another and form an ionic *crystal lattice*.
NaCl lattice model
In a lattice, *all* the cations are attracted to *all* the anions.

Ionic compounds form because the process of atoms exchanging electrons and coming together as ions is *exothermic*.
The ionic compound produced contains less energy and is therefore more stable than the unreacted elements.

Examples of Ionic Compound Formation

Na (s) (elemental) + Cl_2 (g) (elemental) → Na^+ + Cl^- Crystalline NaCl (s)
Ca (s) + F_2 (g) → CaF_2 (s)
Mg (s) + O_2 (g) → MgO (s)

(The electrostatic attraction of cations to anions is strong so ionic compounds have high mp’s)

Easy Prediction of Ionic Charges Using the Periodic Table

For some atoms, the numbers of electrons lost or gained is governed by simple rules.
Predictions can be made at the extreme right and left sides of the Periodic Table.
Use electron configurations for justification
Use the periodic table for quick reference.

Summary of Atomic Electron Levels by Period and Group and Relation to Octet rule

Period Number	*Principal* Energy Level Number	Maximum Number of Valence Electrons
First Period	1	2
Second Period	2	8
Third Period	3	8 (ignore 10)
Fourth Period	3 and 4	8 (ignore 10)
Fifth Period	4 and 5	Etc.

Summary of Results

Period One: The first period has two elements because Principal Energy Level 1 has room for just two electrons. The electrons in Principal Energy Level 1 are designated $1s^1$ and $1s^2$. The filling of a *principal energy level* confers great stability on that *electron configuration* and makes it difficult for the atom to undergo chemical change.

As a result, the He atom ($1s^2$) does not undergo chemical change because:
a) There is no room for more electrons in its $1s^2$ shell;
b) It is too difficult to remove the $1s^2$ electrons from the completed Principal Energy Level 1.

The H atom ($1s^1$) readily participates in chemical reactions.
Its main activity is to *share* its one $1s^1$ electron with another atom.
Sometimes it loses its $1s^1$ electron to become the H^+ ion ($1s^0$) called the hydrogen ion
Rarely the H atom *gains* one electron to become the H^- ion ($1s^2$) called the hydride ion

Period Two: The second period contains eight elements because the second principal energy level can contain eight electrons (in the 2s and 2p orbitals, the maximum configuration being $2s^2$, $2p^6$).
Statement of Octet Rule.
The $2s^2$ and $2p^6$ configuration, in particular the completion of the 2p shell, is exceptionally stable.
Therefore, the neon atom does not give up, share or lose electrons.
Neon has never been observed to undergo any chemical reaction.

Analogously, all elements at the far right of the periodic table have stable electron configurations that do not readily allow chemical change.
These elements are the ***Noble Gases***.
(Xe and Kr when *forced* to react with F, can form a few unstable compounds.)

- Elements in group IA each have one electron outside the “closed shell” configuration. Group IA metals lose that one electron to become M^{1+} cations. Na^+, K^+, Li^+, H^+
- Group IIA metals lose two electrons to form compounds of M^{2+}. Mg^{2+} Ca^{2+} Sr^{2+} Ba^{2+} Ra^{2+}
- Aluminum becomes the Al^{3+} cation.
- Halogens (VIIA) typically *gain* one electron to form F^-, Cl^-, Br^-, I^- mononegative anions.
- Oxygen and sulfur atoms become O^{2-} and S^{2-}.
- Hydrogen can form the hydride ion, H^-

The octet rule often correctly predicts the charges of many **Main Group** ions.
The closer an atom is to a noble gas the more likely it is to achieve an octet of electrons
Isoelectronic Species.

Ions of elements 7 through 13 all have the (stable) neon ***Electron Configuration.*** $1s^2, 2s^2, 2p^6$
Show ions of N, O, F, *Ne*, Na, Mg, Al.

Generalize this result to predict the charges of many Main Group element anions and cations.
Use periodic table to determine charges of main group ions in preparation for naming ionic compounds

Why don’t Group 14 (IVA) elements form ions?
Elements such as C, Si, P, As, etc., react by *sharing,* not losing or gaining electrons.

Nomenclature

Main group metal ions are named just like the neutral atoms.
There is no need to specify the cation charge. Examples
Main group monatomic anions assume the –ide suffix. Examples

Why can’t the ionic charges of transition metals be predicted?
Transition metals do not lose electrons in a predictable manner.
Their electrons occupy 3d (not s and p) orbitals.
Their cation charges cannot be predicted by the octet rule.
Their ion charges and names (both old and Stock names) must be learned to name ionic compounds

Learn formulas, charges, Stock names and ous/ic suffix names.

Fe^{2+} / Fe^{3+}
Cu^+ / Cu^{2+}
Sn^{2+} / Sn^{4+}
Zn^{2+} / Zn^{2+}
Hg_2^{2+} / Hg^{2+}
Zn^{2+}
Ag^+

Polyatomic Ions

Names and formulas must be learned in preparation for naming ionic compounds
No easy prediction from the periodic table of formulas and charges
Most are Polyatomic Ions are ***Polyatomic Oxyanions***
A few polyatomic ions are cations class.

Important polyatomic *cations*: $\mathbf{NH_4^+}$ $\mathbf{H_3O^+}$

Polyatomic anions with the –ide suffix: $\mathbf{CN^-}$ $\mathbf{OH^-}$ $\mathbf{O_2^{2-}}$ $\mathbf{O_2^-}$ **(cf** $\mathbf{O^{2-}}$**)**

Polyatomic Oxyanions:
Large in number and very important.
Use of –ite and –ate suffixes.
Memorization strategies:

Polyatomic Oxyanions to Learn

Memorize names, formulas and charges

$\mathbf{NO_2^-}$ / $\mathbf{NO_3^-}$
$\mathbf{SO_3^{2-}}$ / $\mathbf{SO_4^{2-}}$
$\mathbf{PO_3^{3-}}$ / $\mathbf{PO_4^{3-}}$
$\mathbf{ClO^-}$ / $\mathbf{ClO_2^-}$ / $\mathbf{ClO_3^-}$ / $\mathbf{ClO_4^-}$
$\mathbf{HSO_3^-}$ / $\mathbf{HSO_4^-}$
$\mathbf{HPO_4^{2-}}$ / $\mathbf{H_2PO_4^-}$
$\mathbf{CO_3^{2-}}$ / $\mathbf{HCO_3^-}$
$\mathbf{CrO_4^{2-}}$ / $\mathbf{Cr_2O_7^{2-}}$
$\mathbf{MnO_4^-}$
$\mathbf{C_2H_3O_2^-}$ **or** $\mathbf{CH_3COO^-}$
$\mathbf{CNO^-}$ / $\mathbf{SCN^-}$

The Covalent Bond

Nonmetal atoms form covalent compounds with each other.
If no metal is present, there is no source of donated electrons to form anions.
The octet rule still applies in most cases
The division between ionic and covalent compounds is not always sharp.
Many covalent compounds has some ***ionic character***

Electron Sharing in Diatomic Molecules
Energy diagram: H atom energies vs. separation distance
Structure of: H_2 Showing three different views of the H_2 molecule.

Pure Covalent Bonds result when both atoms are the same.
Structures of: $\mathbf{F_2}$ $\mathbf{Cl_2}$ $\mathbf{O_2}$ $\mathbf{N_2}$

Rules for writing Lewis Structures

Count the total number of *valence* electrons
Identify the central atom
Know bond orders for H, F, O, C, N, etc.
Create the most symmetrical skeleton
Count the electrons used to form the skeleton's bonds.
Remaining electrons distributed as nonbonding pairs and additional bonds as needed to complete octets.

Lewis Structures of **HCl** **HF** **H_2O** **NH_3** **H_2O_2** **CO_2**

CH_4 **C_2H_6** **C_2H_4** **C_2H_2**

Lewis Strictures of Polyatomic Oxyanions:

NO_3^- SO_3^{2-} (cf SO_3 molecule)
SO_4^{2-} and PO_4^{3-}
ClO^- and ClO_4^- (isoelectric with PO_4^{3-})
SO_4^- and HSO_4^-
CO_3^{2-}

Electronegativity

The ability of an atom to attract electrons to itself.
Electronegativity is used to determine molecular polarity
Why is molecular polarity important?
Effect of polarity on mp, bp, solubility, in water and nonpolar solvents.
Pauling's Electronegativity Values Table 6.8.
Use the Periodic Table for qualitative comparison of Electronegativity Values.
F, O N, Cl, etc.
Predict the polarity of any heteroatomic bond.
Predict the polarity of diatomic molecules.
(Some have ionic character)
Predict the polarity of polyatomic molecules based on molecular geometry
(Do not attempt to apply molecular polarity to *ions*.)

Polarity of: CO_2 CH_4 CF_4 H_2O SO_2 SO_3 CH_2F_2

Why does polarity affect the solubility of substances?
Methanol in water
NaCl in water
Hexane in water
Hexane in gasoline