CHEM 1024b: General Chemistry for Engineers

Lectures 07-08

Dr. Oleg Semenikhin

Department of Chemistry, The University of Western Ontario

Molecules (M&H6 Ch.2)

It is rare to find isolated atoms in nature, only the noble gases such as He, Ne, Ar, . . . consist of individual, nonreactive molecules.

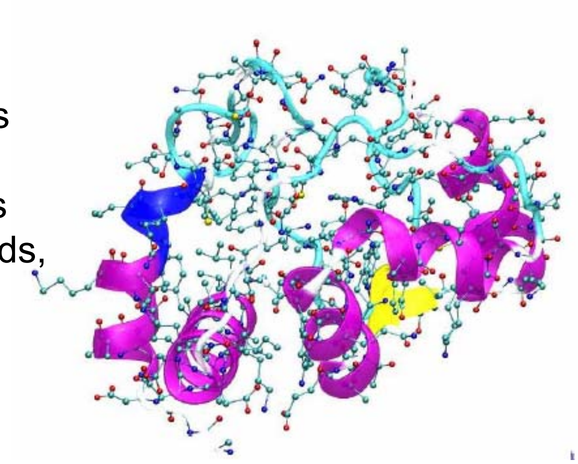
Most atoms tend to combine and form entities that are called molecules. The molecules are neutral bodies, that consist of two or more atoms.

Some molecules are simple such as the molecular elements: H_2 composed of two atoms of H, as well as N_2, O_2, Cl_2, Br_2, I_2, etc.

Others are slightly more complicated such as water (H_2O), ammonia (NH_3), methane (CH_4), etc.

Example

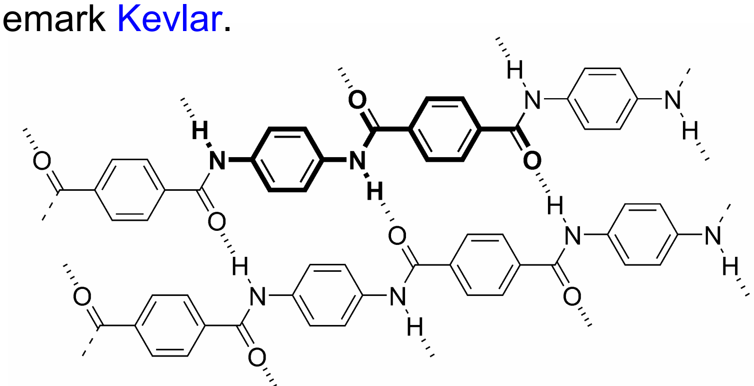
There are molecules that are way more complicated such as proteins, nucleic acids, DNA, RNA, lipids.



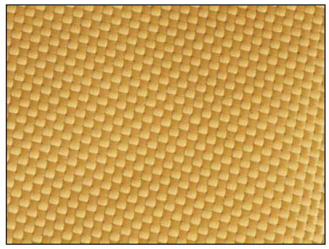
Molecular surface and ball-and-stick representations of X-Ray structure of Cytochrome C. This protein is 6,180 times larger in weight than H2.

Example

- Even bigger molecules are synthetic polymers such as rubber, polyethylene, polyamide, teflon, etc.
- One of famous polyamides is known under the trademark Kevlar.



Kevlar: Polymer tough enough to be used in bullet proof vests



Kevlar is 5 times as strong as steel on a weight for weight basis, yet it is lightweight, flexible and comfortable.

How to write down the molecules

The atoms in molecules are connected and form certain structures by chemical bonds. These bonds are formed by valence electrons of the atoms, specifically, by overlapping electron clouds.

The molecules are represented by: molecular formulae, structural formulae and condensed structural formulae.

Examples of molecular formulae:

Sugar - $C_6H_{12}O_6$

Structural formulae show the bonding pattern within the molecule.

Example: CH_3-CH=CH_2

The dashes between the atoms represent chemical bonds.

Condensed structural formulae

Condensed structural formulae suggest the bonding pattern in molecules and highlight the presence of reactive groups of atoms within the molecules.

CH_3OH CH_3NH_2

Ions

When an atom loses or gains electron(s), it becomes charged and then it is called an ion.

Typically, metal atoms tend to lose electrons to form positively charged ions called cations.

Examples: Na loses one electron and becomes Na^+, K loses one electron and becomes K^+, Ca loses two electrons and becomes Ca^{2+}, etc.

Nonmetal atoms tend to form negative ions by gaining electrons. The negative ions are called anions.

Examples: Cl gains one electron to form Cl^-, I gains one electron to form I^-, O gains two electrons to form O^{2-}.

How to predict what type of ions an atom may form?

Noble gases are unreactive because they have a stable electronic configuration.

Group	No. of Electrons in Atom	Charge of Ion Formed	Examples
1	1 more than noble-gas atom	+1	Na^{+}, K^{+}
2	2 more than noble-gas atom	+2	Mg^{2+}, Ca^{2+}
16	2 less than noble-gas atom	−2	O^{2-}, S^{2-}
17	1 less than noble-gas atom	−1	F^{-}, Cl^{-}

Atoms that are close to a noble gas in the periodic table tend to form ions that contain the same number of electrons as the neighboring noble-gas atom.

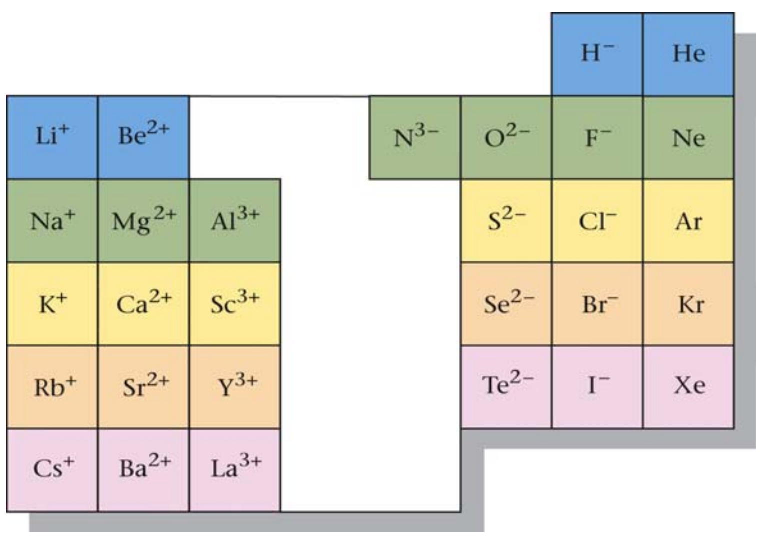
Electron Arrangements in Monatomic Ions (MH6 Ch.6.7)

- In forming an ion, electrons are ***removed from (cation)*** or ***added to (anion)*** sublevels in the highest principal energy level

Main Group Ions and Noble Gas Structures

- Cations of Group 1 form +1 ions
- Cations of Group 2 from +2 ions
- Nitrogen forms a -3 ion
- Elements in the oxygen family form -2 ions
- Halogens form -1 ions

Figure 6.13 – Noble Gas Configurations



Working with Animation to Understand The Electronic Structure of Ions

Transition Elements

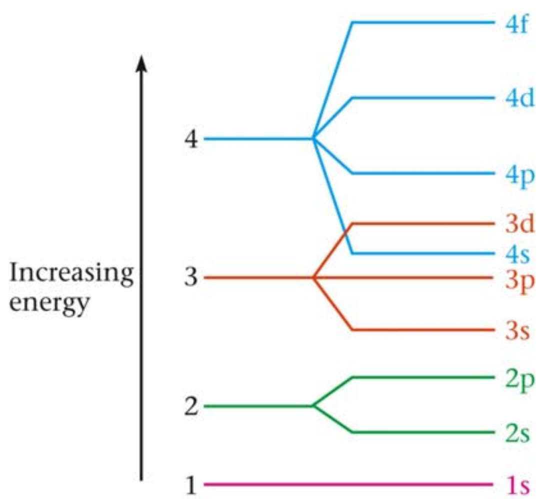
- For the transition (groups 3 to 12) and post-transition (Groups 13-15) elements the above rule does not apply exactly. In general the cations formed by these elements typically have charges +1, +2, +3 and ordinarily do not have noble-gas structure.
- Many of the transition metals form more than one cation with different number of electrons and thus with different charges, such as Fe^{2+} and Fe^{3+}, Cu^{+} and Cu^{2+}, etc.

Transition Metal Cations

- Transition metal cations do not usually form ions with noble-gas configurations
  - Cations do form, with charges ranging from +1 to higher numbers
  - The outer s electrons are lost before the d electrons; this is the first-in, first-out rule
- Consider Mn
  - Mn is $[Ar]4s^2 3d^5$
  - Mn^{2+} is $[Ar]3d^5$

Transition Metal Cations

- And why the outer s-electrons are lost before the d-electrons? This looks like a violation of the relative position of the energy levels we discussed earlier! The s-electrons were lower in energy and so d-electrons should be removed first!



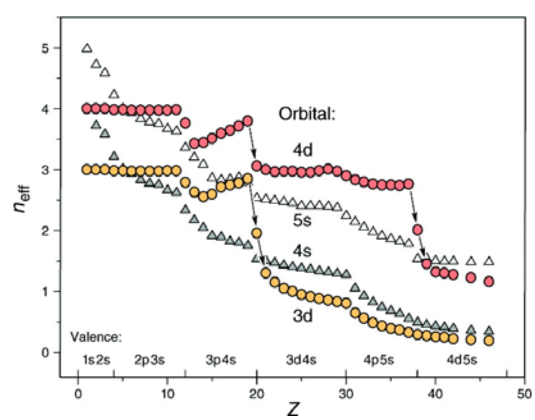
Transition Metal Cations

- There are several reasons why s-electrons are removed before d-electrons. First, the relative positions of the energy levels are not the same for empty and filled levels. For instance, empty 3d orbitals are higher in energy than 4s orbitals, whereas filled 3d orbitals become lower. This is sometimes called d-orbital collapse and is illustrated in the next slide.
- As a result, the energetic sequence of atomic orbitals changes dramatically from the alkali metals of group 1 to the alkaline-earth metals of group 2, to the earth metals of group 3, and to the heavier transition metals of the subsequent groups

$_{19}$K: 3p << 4s < 4p << 3d < …

$_{20}$Ca : 3p << 4s < 3d < 4p << …

$_{21}$Sc and subsequent : 3p << 3d < 4s < 4p << …



Energetic d-orbital collapse (indicated by arrows) of free neutral atoms at the beginning of the transition rows. *Z* is the nuclear charge; the orbital symbols above the abscissa indicate the type of the shell. The orbital energies *ε* are represented by the effective quantum numbers.

Published in: W. H. Eugen Schwarz; *J. Chem. Educ.* **2010,** 87, 444-448.
DOI: 10.1021/ed8001286

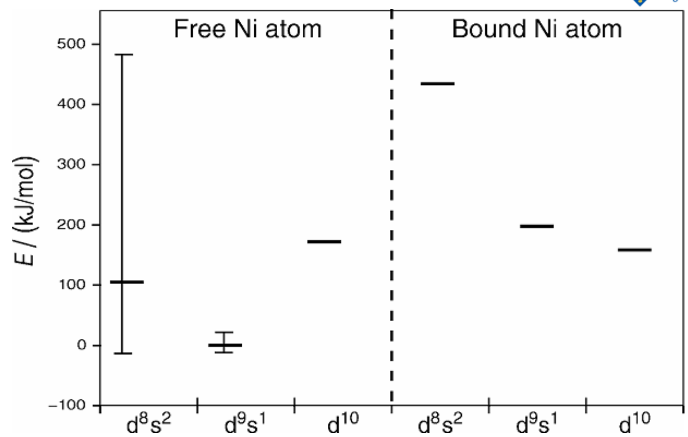
Transition Metal Cations

- The reason for the d-orbital collapse is the change in orbital shielding. If an orbital is shielded from the positive charge of the nucleus by other electrons, especially by a filled electron shell, then the energy of such an orbital increases and it becomes less energetically favorable and will be ionized first. Conversely, if an electron orbital is deshielded, its energy is lowered and it becomes more energetically favourable (stronger Coulombic interaction with the nucleus).
- The 4s orbital, being an orbital with n=4, is located further from the nucleus than 3d orbitals with n=3. Therefore, in the presence of d-electrons, the 4s orbital will be shielded by 3d electrons and thus less energetically favourable! Furthermore, the filling 3d orbitals will become deshielded as compared to K and Ca since the positive charge of the nucleus increased but the shielding did not!
- For K and Ca: no 3d electrons. The 4s orbital is not shielded by empty 3d shell, its energy is relatively lower.

Transition Metal Cations

- Yet another reason is that transition metal cations are in fact not free but rather form chemical compounds and are surrounded by other molecules or ions.
- The presence of electrons on larger 4s orbitals would not allow the other atoms to come close enough to form favourable chemical bonds. Furthermore, highly directional d electron orbitals are well suited to form chemical bonds.
- As a result, 4s electrons in transition metal cations (and actually also in neutral metal atoms that are not free but are rather parts of chemical compounds, like Ni^0 or Fe^0 carbonyls, $Ni^0(CO)_4$ and $Fe^0(CO)_5$) will be converted into 3d electrons. Such structures will have the lowest energies and thus will be most favourable, see the next slide.

ACS Publications
High quality. High impact.



Configuration energies of Ni: (right) average values of chemically bound Ni^0 and (left) free Ni^0 atoms in vacuum. The energy levels are indicated by the horizontal lines and the lowest and highest *J* levels are indicated by vertical bars. *J* is the total angular momentum, the sum of the orbital angular momentum and the intrinsic angular momentum, spin. In free atoms there could be many allowed combinations of ℓ and s.

Published in: W. H. Eugen Schwarz; *J. Chem. Educ.* **2010,** 87, 444-448.
DOI: 10.1021/ed8001286

Example 6.9

EXAMPLE 6.9

Give the electron configuration of

(a) Fe^{2+} (b) Br^-

ANALYSIS

Information given:	Identity of the ions and their charge: (Fe^{2+}, Br^-)
Information implied:	atomic number of the atoms; electron configuration of the atoms
Asked for:	electron configuration of the ions

STRATEGY

1. Write the electron configuration of each atom.
2. Add electrons (for anions) or subtract electrons (for cations) from sublevels of the highest **n**. If there is more than one sublevel in the highest **n**, add or subtract electrons in the highest ℓ of that **n**.

continued

Example 6.9 (Cont'd)

SOLUTION

(a) Fe electron configuration	$1s^22s^22p^63s^23p^64s^23d^6$
Cation with +2 charge	subtract 2 electrons
Highest **n**	4 with only one sublevel
Fe^{2+} electron configuration	$1s^22s^22p^63s^23p^64s^{2-2}3d^6 = 1s^22s^22p^63s^23p^63d^6$
(b) Br electron configuration	$1s^22s^22p^63s^23p^64s^23d^{10}4p^5$
Anion with −1 charge	add 1 electron
Highest **n**	4 with 2 sublevels (s and p)
Highest ℓ in **n**	p
Br^- electron configuration	$1s^22s^22p^63s^23p^64s^23d^{10}4p^{5+1} = 1s^22s^22p^63s^23p^64s^23d^{10}4p^6$

END POINT

The electron configuration for Br^- is the same as that for the noble gas closest to it, krypton.

Polyatomic Ions

Besides monatomic ions there are polyatomic ions with also may have a positive or negative charge:

polyatomic cations: Hg_2^{2+} , NH_4^+.

polyatomic anions: most of the polyatomic anions contain one or more oxygen atoms. Such oxygen-containing anions are called oxoanions (or oxyanions).

Working with Electronic Structures to Derive the Stoichiometry of Some Polyatomic Anions

PO_4^{3-} ; PO_3^{3-} ; SO_4^{2-} ; SO_3^{2-} ; NO_3^- ; NO_2^- ; CN^- ; CrO_4^{2-} ; CO_3^{2-} ; MnO_4^{2-} ; MnO_4^- ; ClO^- ; ClO_2^- ; ClO_3^- ; ClO_4^-

Nomenclature of Anions

Monoatomic anions

The monatomic anions are named by adding the suffix -ide to the stem of the name of the nonmetal from which they are derived.

Examples:

O^{2-} oxide

N^{3-} nitride

H^- hydride

Cl^- cloride

F^- fluoride

Nomenclature of Oxoanions

For polyatomic anions:

- When a nonmetal forms two oxoanions, the suffix -ate is used for the anion with the larger number of oxygen atoms. The suffix -ite is used for the anion containing fewer oxygen atoms.
- When a nonmetal forms more than two oxoanions, the prefix per- for the largest number of oxygen atoms and hypo- for the fewest oxygen atoms are used as well.

Nitrogen	Sulfur	Chlorine
		ClO_4^- *perchlorate*
NO_3^- nitr*ate*	SO_4^{2-} sulf*ate*	ClO_3^- chlor*ate*
NO_2^- nitr*ite*	SO_3^{2-} sulf*ite*	ClO_2^- chlor*ite*
		ClO^- *hypo*chlor*ite*

Example

Name the following oxoanions:

PO_4^{3-}
HPO_4^{2-}
$H_2PO_4^-$
PO_3^{3-}
CO_3^{2-}
CN^-
CrO_4^{2-}
MnO_4^{2-}
MnO_4^-

Example

Name the following oxoanions:

PO_4^{3-}	phosphate
HPO_4^{2-}	hydrophosphate
$H_2PO_4^-$	dihydrophosphate
PO_3^{3-}	phosphite
CO_3^{2-}	carbonate
CN^-	cyanide
CrO_4^{2-}	chromate
MnO_4^{2-}	manganate
MnO_4^-	permanganate

Nomenclature of Cations

- Monoatomic cations take the name of the metal from which they are derived.

  Example: Na^+ sodium cation, K^+ potassium cation.

  Note: In names of ionic compounds the word "cation" is omitted.

- If the same element can have several cations of different charge, the charge must be indicated in the name as a Roman numeral in parenthesis after the name of the metal.

  Example: Fe^{2+} iron (II), Fe^{3+} iron (III)

Ionic Compounds

•The ionic compounds are formed by cations and anions.

•In the chemical formula the cation is written first and the anion stands second.

•The overall charge of the compound is zero, therefore, the total charge of the cations should be equal to the charge of the anions.

•The name of the ionic compound consists of two words. The first word names the cation and the second names the anion. This is, of course, the same order in which the ions appear in the formula.

Examples : NaCl, $CaCl_2$, Na_2S, CaS, $Al(NO_3)_3$, $FeCl_2$, $CaSO_4$, Na_3PO_4.

Animation
Balancing the Charges in Ionic Compounds

Example

Write the chemical formulae for:

barium chloride

sodium nitrate

sodium hypochlorite

chromium (III) nitrate

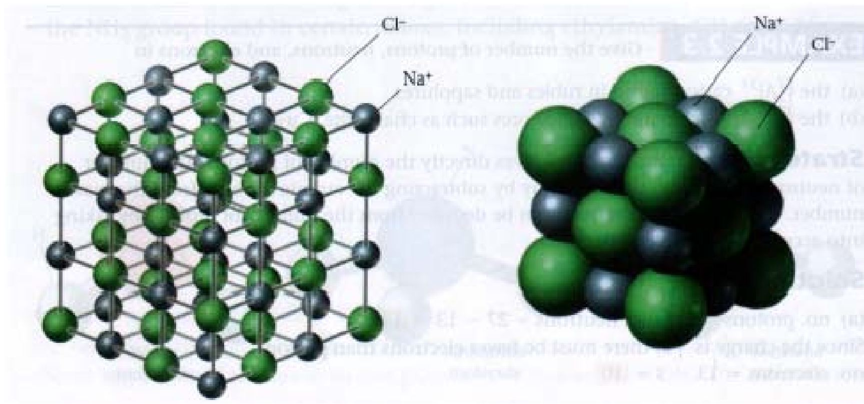
tin (II) chloride

Example

Write the chemical formulae for:

barium chloride	$BaCl_2$
sodium nitrate	$NaNO_3$
sodium hypochlorite	$NaClO$
chromium (III) nitrate	$Cr(NO_3)_3$
tin (II) chloride	$SnCl_2$

Structure of ionic compounds



In the ionic compounds one does not distinguish individual molecules.

The ions are connected by ionic bonds.

Binary molecular compounds

The name of a compound that contains two different nonmetals consists of two words.

- The first word is the name of the element that appears first in the formula; the second word is the stem of the element that appears second with the suffix -ide.
- both the first and second words take a Greek prefix designating the number of atoms of that element in the formula.

2 di-

3 tri-

4 tetra-

5 penta-

6 hexa-, 7 hepta-

Examples:

N_2O_5
N_2O_4
SO_2
Cl_2O_7

<u>Examples of differently named compounds</u>:

H_2O
H_2O_2
NH_3
CH_4
N_2H_4
PH_3
AsH_3
NO
N_2O

Examples:

N_2O_5	dinitrogen pentoxide, nitrogen (V) oxide
N_2O_4	dinitrogen tetroxide, nitrogen (IV) oxide
SO_2	sulfur dioxide, sulfur (IV) oxide
Cl_2O_7	dichlorine heptoxide, chlorine (VII) oxide

<u>Examples of differently named compounds</u>:

H_2O	water
H_2O_2	hydrogen peroxide
NH_3	ammonia
CH_4	methane
N_2H_4	hydrazine
PH_3	phosphine (IUPAC: phosphane)
AsH_3	arsine (IUPAC: arsane), arsenic trihydride
NO	nitric oxide (rather than nitrogen oxide)
N_2O	nitrous oxide (rather than dinitrogen oxide)

Acids and Bases

Traditional definition of acids and bases:

Acids are compounds that, when dissolved in water, produce an excess of hydrogen ions, H^+.

Bases are then compounds that, when dissolved in water, produce an excess of hydroxide ions, OH^-.

As we will see later, an excess of hydroxide ions means a deficiency of hydrogen ions, and vice versa. This is called the acid-base equilibrium.

There are other, more inclusive, definitions of acids and bases. We will learn them later.

Nomenclature of Acids

Similar to the names of anions: The -**ate** suffix of the anion is replaced by -**ic**. The -**ite** by -**ous**. The word **"acid"** is added. The prefixes **per**- and **hypo**- found in the name of the anion are retained.

Examples:

HNO_3(aq)	nitric acid
H_2SO_4(aq)	sulfuric acid
$HClO_4$(aq)	perchloric acid
$HClO_3$(aq)	chloric acid
$HClO_2$(aq)	chlorous acid
HClO(aq)	hypochloride acid

Nomenclature of Acids

Some hydrogen containing molecular compounds can exist in two forms: as pure substance and as water solution. They are mostly compounds of hydrogen and halogens, but may also contain other elements.

Pure substance: hydrogen + name of the anion

Examples:

HCl (g)	hydrogen chloride
HI (g)	hydrogen iodide
HCN (g)	hydrogen cyanide

Nomenclature of Acids

When passed through water, these compounds undergo dissociation into ions and they increase the concentration of H+ ions in the solution. Thus, they become acids and get different names.

Acids (water solutions): The –ide suffix of the anion is replaced by -ic. The -ite by -ous.

Examples:

HCl (aq)	hydrochloric acid
HI (aq)	hydrobromic acid
HCN (aq)	hydrocyanic acid

Nomenclature of Bases

The nomenclature of bases is derived from the names for cations, like the nomenclature of acids is based on the names of anions. The word “hydroxide” is added.

Examples:

NaOH	Sodium hydroxide
KOH	Potassium hydroxide
$Ca(OH)_2$	Calcium hydroxide