CHEMISTRY

INTRODUCTION TO CHEMISTRY

CHEMISTRY: science dealing with **MATTER**, its composition, structure and properties, and the chages in composition that matter undergoes.

Chemistry connects the MACROSCOPIC world of everyday life with The MICROSCOPIC world of molecules.

CHEMISTRY → SCIENCE → SCIENTIFIC APPROACH

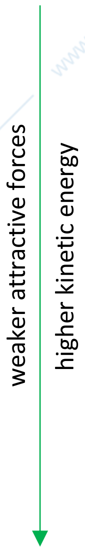
1) ***OBSERVATIONS*** on the physical world
2) ***HYPOTHESIS*** – tentative interpretation or explanation of the observations that provides a basis for further experiments.
   A good hypothesis is falsifiable, which means that it makes predic- tions that can be confirmed or refuted by further observations.
3) ***EXPERIMENTS*** – to confirm or refute a hypothesis.
4) ***THEORY*** – a well-established hypothesis proven right by other experiments.

THEORY – can be modified and altered.
SCIENTIFIC LAW – general statement on natural phenomena (no exception!). Describe how nature behaves.

MATTER – ANYTHING THAT HAS MASS AND OCCUPIES VOLUME

Classification of matter

- *PHYSICAL STATE*



  - **SOLID**
    Definite volume and shape (independent from the container).
    Particles pack closely to each other in fixed locations but can vibrate.
    Incompressible.
    Can be *CRYSTALLINE* or *AMORPHOUS*.

  - **LIQUID**
    Definite volume but indefinite shape – it depends on the shape of the container.
    Particles close together but free enough to move around and slide on each other (fluidity)
    Slightly compressible.

  - **GASEOUS**
    Indefinite volume and shape.
    Particles able to move freely – they can permeate the entire area in which they've been released but they're actual volume is very small.
    Compressible.

- ◆ *COMPOSITION*

SUBSTANCE (or PURE SUBSTANCE) – only one component.

- ○ ELEMENT: substance that cannot be broken down into simpler substances by any mean.
  ATOM: smallest unit with all chemical and physical properties.
- ○ COMPOUND: substance made of two or more elements combined in **fixed proportions** and in whole-number ratios.
  A particular compound always contains the same elements in the same proportions by mass.
  Can be broken down only by chemical means but it will lose its identity.
  MOLECULE: smallest unit with all chemical and physical properties.

MIXTURE – more than one component with **different proportions**.

- ○ HOMOGENEOUS: same composition throughout. One phase.
- ○ HETEROGENEOUS: the composition varies from one region of the mixture to another. Multiple phases.

Mixtures can be separated by PHYSICAL MEANS → use of the different properties of the components.
Examples:

- Distillation – different boiling point
- Filtration – different particles size
- Centrifugation – different particles weight

SOLUTION – clear homogenous mixture
SUSPENSION – heterogeneous mixture with solute particles that can be separated by filtration
COLLOID – mixture in which the dispersed particles are larger than the solute ions or molecules of a true solution and smaller than the particles of a suspension.
Can't be separated by filtration.

ELEMENTS

- 118 on the Periodic Table with increasing **ATOMIC NUMBER (Z)**
- 88 occur in nature – the rest is artificial and unstable
- Physical states:
    - Majority: solids
    - Hg, Br: liquids
    - H, N, O, F, Cl and noble gases: gases
- Few elements are found in their pure form – noble metals and noble gases (low reactivity)
- Some are ***POLYATOMIC MOLECULES*** (H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2, S_8, P_4)
- Most tend to combine to form ***COMPOUNDS***
- **ATOMIC MASS** – weighted average of the isotopes according to their abundance.

Classification

METALS	NONMETALS	SEMIMETALS
Good conductors	Poor conductors	Intermediate properties
Lustrous	Dull	
Malleable and ductile	Brittle	
High m.p. and high density	Low m.p. and low density	
Little tendency to combine with other metals – when it occurs, they form solids solutions called ***ALLOYS***.	Tend to combine with each other to form ***molecular compounds***.	B, Si, Ge, As, Sb, Te, At

COMPOUNDS

LAW OF DEFINITE PROPORTION – PROUST'S LAW

A compound always contains two or more elements chemically combined in a definite proportion by mass.

LAW OF MULTIPLE PROPORTION – DALTON'S LAW

Atoms of two or more elements may combine in different ratios to produce more than one compound.

- ***MOLECULAR***
  MOLECULE: smallest uncharged unit that preserves the properties of the compound
  Usually formed by two nonmetals.
  COVALENT BONDS

- ***IONIC***
  ION: charged atom or group of atoms (*CATION, ANION, POLYATOMIC ION*)
  FORMULA UNIT: the smallest, electrically **neutral** collection of ions (part of a larger lattice).
  Usually formed by a metal and a nonmetal.
  ATTRACTIVE FORCES (electrostatic forces)

NOMENCLATURE BINARY COMPOUNDS

IONIC COMPOUNDS

Alkali and alkali earth metals – only one possible charge

NaCl – sodium chloride

CaO_2 – calcium oxide

Transition metals – more than one charge possible

Stock system: Roman numeral in parenthesis to define the oxidation number of the metal.

Classical nomenclature:

- Highest oxidation number: -IC suffix
- Lowest oxidation number: -OUS suffix

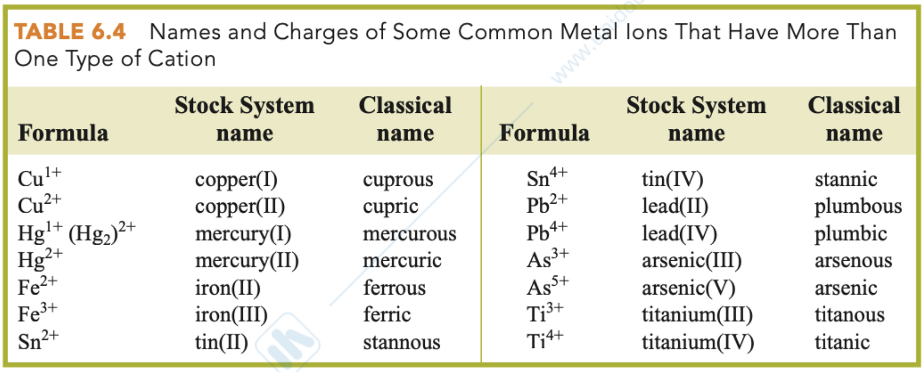


TABLE 6.4 Names and Charges of Some Common Metal Ions That Have More Than One Type of Cation

Formula	Stock System name	Classical name	Formula	Stock System name	Classical name
Cu^{1+}	copper(I)	cuprous	Sn^{4+}	tin(IV)	stannic
Cu^{2+}	copper(II)	cupric	Pb^{2+}	lead(II)	plumbous
Hg^{1+} $(Hg_2)^{2+}$	mercury(I)	mercurous	Pb^{4+}	lead(IV)	plumbic
Hg^{2+}	mercury(II)	mercuric	As^{3+}	arsenic(III)	arsenous
Fe^{2+}	iron(II)	ferrous	As^{5+}	arsenic(V)	arsenic
Fe^{3+}	iron(III)	ferric	Ti^{3+}	titanium(III)	titanous
Sn^{2+}	tin(II)	stannous	Ti^{4+}	titanium(IV)	titanic

MOLECULAR COMPOUNDS

Specify how many atoms are present in each molecule.

E.g. NO_2 nitrogen dioxide NO nitrogen monoxide N_2O dinitrogen monoxide

POLYATOMIC IONS

- Highest oxidation number: -ATE suffix
- Lowest oxidation number: -ITE suffix

BINARY ACIDS

Gaseous state: HCl hydrogen chloride

Aqueous state: HCl hydrochloric acid

OXY-ACIDS

- Highest oxidation number: -IC ACID
- Lowest oxidation number: -OUS ACID

EACH SUBSTANCE HAS UNIQUE PROPERITIES

PHYSICAL PROPERTIES – can be determined without changing the substance's composition. Displayed during PHYSICAL CHANGES → change in state but not in composition.
E.g. *boiling point, melting point, solubility*.

CHEMICAL PROPERTIES – describe the substance's ability to ***REACT*** and to form new substances. Displayed during CHEMICAL CHANGES → they result in the formation of a new substance, with different physical and chemical properties from the former.

PHYSICAL AND CHEMICAL CHANGES ARE ASSOCIATED WITH ENERGY.

Different forms of energy:

- *MECHANICAL (KINETIC + POTENTIAL)*
- *THERMAL (HEAT)*
- *RADIANT (LIGHT)*
- *NUCLEAR*

In all chemical changes matter either ABSORBS or RELELASES ENERGY.
If ***ABSORBED*** – the products will have **MORE** CHEMICAL POTENTIAL ENERGY than the reactants.

If ***RELEASED*** – the products will have **LESS** CHEMICAL POTENTIAL ENERGY than the reactants.

LAW OF CONSERVATION OF ENERGY

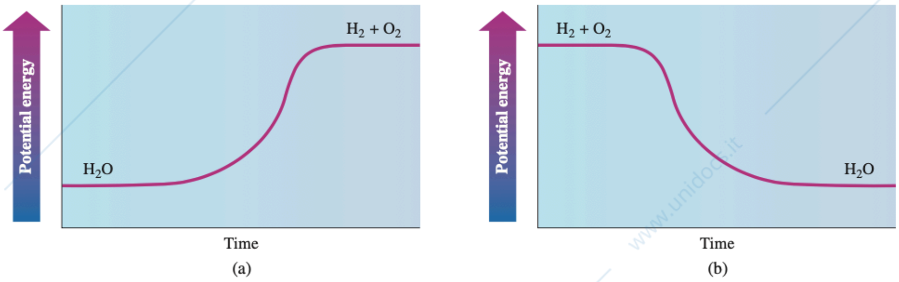


Figure 4.6

(a) In electrolysis of water, energy is absorbed by the system, so the products H_2 and O_2 have a higher potential energy. (b) When hydrogen is used as a fuel, energy is released and the product (H_2O) has lower potential energy.

CHEMICAL BONDS

Chemical bonds form between atoms that tend to attain a stable electron configuration.

OCTET RULE – for most elements the stable configuration is eight electrons in the valence shell.

IONIC BOND

TRANSFER OF ELECTRONS – from the less electronegative element to the most electronegative one. Occurs between NONMETALS and METALS.

- *METAL – CATION → ion smaller than the neutral atom*
- *NONMETAL – ANION → ion bigger than the neutral atom*

Cation and anion obtain the electronic configuration of a noble gas.
Kept together by **ELECTROSTATIC FORCES** → nondirectional (forces equally strong in all directions)

The bond doesn't exist between two single opposite ions. Each ion attracts more than one ion of opposite charge.

At solid state: **crystalline lattice** (regular three-dimensional array of alternating cations and anions)
The energy required to form the bond is supplied largely by the attraction force between the opposite ions.

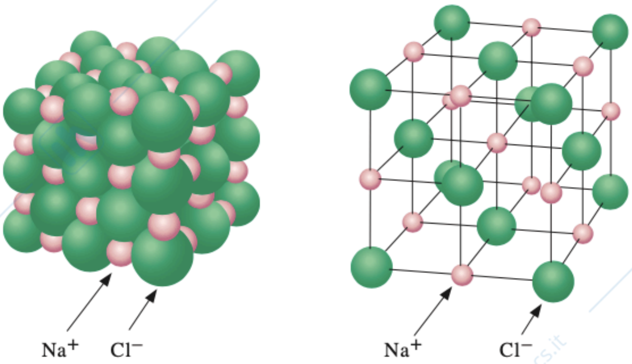


Figure 11.5
Sodium chloride crystal. Diagram represents a small fragment of sodium chloride, which forms cubic crystals. Each sodium ion is surrounded by six chloride ions, and each chloride ion is surrounded by six sodium ions. The tiny NaCl crystals show the cubic crystal structure of salt.

COVALENT BOND

SHARING OF ELECTRONS – OVERLAPPING OF ATOMIC ORBITALS

Each atom acquires a more stable structure in order to satisfy the octet rule.
Each atom contributes <u>one</u> electron of the pair – BONDING PAIR
The shared electrons have **lower potential energy** (= more stable) than they do in the isolated atoms because they interact with the nuclei of both atoms.
DIRECTIONAL BOND – it follows the orientation of the orbital
SINGLE, DOUBLE, TRIPLE BOND

Between elements with <u>either no or little difference</u> of electronegativity.
POLARITY: determined by the difference in electronegativity value

- ***OMOPOLAR*** – atoms of the same element – **APOLAR MOLECULE**
- ***HETEROPOLAR*** – atoms of different elements – **DIPOLE**: molecule electrically asymmetrical with partial charges but, in the complex, neutral.

The degree of polarity in a chemical bond depends on the electronegativity difference (ΔEN) between the two bonding atoms.
The greater the electronegativity difference, the more polar the bond.

$0.4 < \Delta EN < 1.5$	HETEROPOLAR COVALENT
$1.7 < \Delta EN < 1.9$	MORE IONIC
$\Delta EN > 2.0$	IONIC

μ - dipole moment

Quantity used to define the polarity of a bond based on the separation of positive and negative charge.
The magnitude of a dipole moment created by separating two particles of equal but opposite charges is given by the equation: $\mu = q\,r$

BOND ENERGY (or BOND ENTHALPY)

Bond energies are always positive because it always takes energy to break a bond.
COMPOUNDS WITH STRONGER BONDS = MORE STABLE = LESS REACTIVE

When bonds break, the process is endothermic (positive bond energy)
When bonds form, the process is exothermic (negative bond energy)

A reaction is exothermic when weak bonds break and strong bonds form.
A reaction is endothermic when strong bonds break and weak bonds form.

As the bond gets longer, it also becomes weaker

OVERLAPPING OF ORBITALS

→ two electrons from two half-filled orbitals: two atoms with half-filled orbitals approach each other, the half-filled orbitals overlap and the electrons occupying them align with opposite spins. This results in a net energy stabilization that constitutes a covalent chemical bond.
The resulting geometry of the molecule emerges from the geometry of the overlapping orbitals.

→ two electrons from one filled orbital overlapping with a completely empty orbital (coordinate covalent bond)

Check valence bond theory and molecular orbital theory

METALLIC BOND

ELECTRON SEA MODEL – DELOCALIZATION OF ELECTRONS

All of the atoms in a metal lattice share their valence electrons.
These pooled electrons are **delocalized over the entire metal – SEA OF ELECTRONS**
Interactions between the positively charged metal atoms and the sea of electrons.
The electron sea model also accounts for the malleability and the ductility of metals → since there are no specific "bonds" in a metal, we can deform it relatively easily by forcing the metal ions to slide past one another.

According to the molecular orbital theory electrons tend to occupy low-energy molecular orbitals (bonding orbitals).
When many metallic atoms are present, the energy levels of the molecular orbitals are so closely spaced that they fuse to form a **band**.
Half of the orbitals are bonding orbitals and contain valence electrons → **VALENCE BAND**
The other half are antibonding orbitals and are empty → **CONDUCTION BAND**
Above 0 K, electrons can easily move from the valence band to the conduction band.

In metals, the two bands are energetically continuous: the energy difference between the two is infinitesimally small. This explains the conductivity properties of metals.
In semiconductors and insulators, however, an energy gap, called the **band gap**, exists between the valence band and conduction band.

EXCEPTION TO THE OCTET RULE

- *ODD-ELECTRON SPECIES – FREE RADICALS*
    - Species with an unpaired valence electron
    - Highly chemically active → try to gain the missing electron from other species
    - Many radicals spontaneously dimerize (e.g. H → H_2)
    - Biologically dangerous because they can alter the DNA

- *INCOMPLETE OCTETS*
    - BF_3 → sestet

- *EXPANDED OCTETS*
    - SF_6 → sulfur has an expanded octet of 12 electrons
    - *HYPERVALENT COMPOUNDS*

  Elements beyond the 3rd period often exhibit expanded octets of up to 12-14 electrons.
  From the 3rd period, *d orbitals* are energetically accessible, thus expanded octets are common.

MOLECULAR SHAPE

Since Lewis structures are **inaccurate** and unable to describe important properties of compounds, such as resonance structures, partial charge in covalent bonds and bond length, they cannot provide information on the actual shape of molecules.

Another theory was needed to overcome this aspect.

VSEPR THEORY – VALENCE SHELL ELECTRON PAIR REPULSION

Basic assumptions:

1) Electrons arrange themselves in order to minimize their repulsion (maximum distance) while maintaining the same distance from the central atom
2) Electron repulsions within a molecule determine its geometry.

For molecules with just one central atom, molecular geometry depends on two factors:

- Number of electron groups around the central atom
- How many of those electron groups are bonding groups and how many are lone pairs.

TWO ELECTRON GROUPS → LINEAR GEOMETRY → 180° bond angle

E.g. $BeCl_2$ (exception to the octet rule – incomplete octet)

Same geometry in all molecules with **two electron groups and NO LONE PAIR**

2D geometry

THREE ELECTRON GROUPS → TRIGONAL PLANAR GEOMETRY → 120° bond angle

E.g. BF_3 (exception to the octet rule)

E.g. CH_2O – formaldehyde

Prediction: three electron groups = 120° bond angles.

Experimental observations: HCO bond angles are 121.9° and the HCH bond angle is 116.2°.

Explanation: the double bond contains more electron density than the single bond and therefore exerts a slightly greater repulsion on the single bonds.

2D geometry

FOUR ELECTRON GROUPS → TETRAHEDRAL GEOMETRY → 109.5°

E.g. CH_4

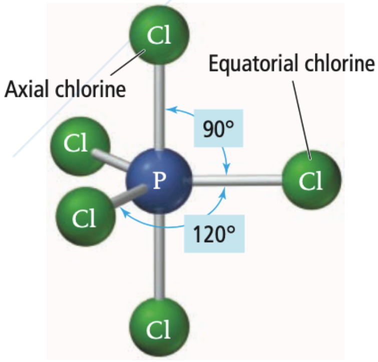
3D geometry

Lewis structure of CH_4 → square planar, with bond angles of 90° → **NOT TRUE**

FIVE ELECTRON GROUPS → TRIGONAL BIPYRAMIDAL GEOMETRY

E.g. PCl_5

- Three of the groups lie in a single plane, as in the trigonal planar configuration
- One group lies above this plane
- One group lies below this plane

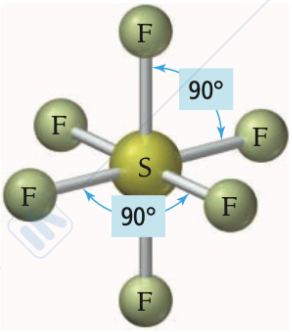


Trigonal bipyramidal geometry

The angles are not all the same:

- angles between the equatorial positions are 120°
- angle between the axial positions and the trigonal plane is 90°

SIX ELECTRON GROUPS → OCTAHEDRAL GEOMETRY



Octahedral geometry

E.g. SF_6

- Four of the groups lie in a single plane
- Fifth group above the plane
- Sixth group below the plane

The angles in this geometry are all 90°

When the number of electron pairs is the same as the number of atoms bonded to the central atom, the **electron pair arrangement and the molecular structure are the same**.

When the number of atoms and the number of electron pairs are **not the same**, the molecular structure is **different** from the electron pair arrangement.

EFFECT OF LONE PAIRS

FOUR ELECTRON GROUPS with ONE LONE PAIR

E.g. NH_3

N atom has four electron groups (one lone pair and three bonding pairs) that repel one another.

Electron pair arrangement: ***TETRAHEDRAL***

Molecular geometry: ***TRIGONAL PYRAMIDAL***

The lone pair exerts its influence on the bonding pairs → lone pairs push the atoms bonded to the central atom closer together.

If all four electron groups exerted equal repulsions → bond angles = 109.5°

Actual bond angle = 107°

The lone pair exerts a greater repulsive force on neighboring electrons and compresses the N–H bond angles.

FOUR ELECTRON GROUPS with TWO LONE PAIRS

E.g. H_2O

Water has four electron groups: two bonding pairs and two lone pairs

Electron pair arrangement: ***TETRAHEDRAL***

Molecular geometry: ***BENT GEOMETRY***

Bond angles = 104.5° → smaller than the ideal tetrahedral bond angles because of the greater repulsion exerted by the lone pair electrons.

Lone pair – lone pair → highest repulsion

FIVE ELECTRON GROUPS with ONE LONE PAIR

E.g. SF_4

S has five electron groups: four bonding pairs and one lone pair

Electron pair arrangement: ***TRIGONAL BIPYRAMIDAL***

Molecular geometry: ***SEESAW GEOMETRY***

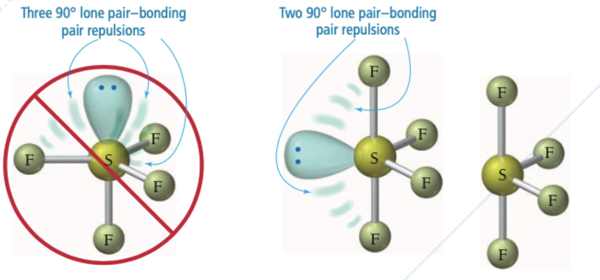
The lone pair could occupy *either an equatorial position or an axial position* within the trigonal bipyramidal electron geometry.

SINCE, lone pair-bonding pair repulsions are greater than bonding pair-bonding pair repulsions, the lone pair occupies the position that minimizes its interaction with the bonding pairs.

In an axial position, the lone pair would have three 90° interactions with bonding pairs.

In an equatorial position, it has only two 90° interactions.

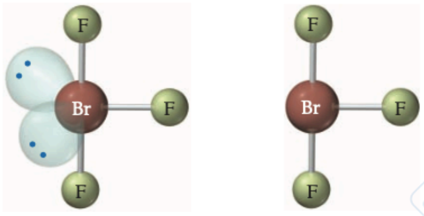
Consequently, the lone pair occupies an equatorial position.



Axial lone pair
Does not occur

Equatorial lone pair

Molecular geometry: seesaw



Electron geometry: trigonal bipyramidal

Molecular geometry: T-shaped

FIVE ELECTRON GROUPS with TWO LONE PAIRS

E.g. BrF_3

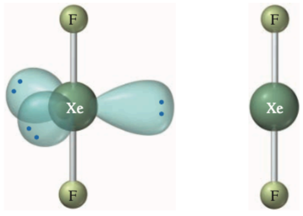
The lone pairs occupy two of the three equatorial positions minimizing 90° interactions with bonding pairs and also avoiding a lone pair-lone pair 90° repulsion.

The resulting molecular geometry is ***T-SHAPED***.

FIVE ELECTRON GROUPS with THREE LONE PAIR

E.g. XeF_2

The lone pairs occupy all three of the equatorial positions, and the resulting molecular geometry is ***LINEAR***.



Electron geometry: trigonal bipyramidal

Molecular geometry: linear

SIX ELECTRON GROUPS

With one lone pair → BrF_5

Electron pair arrangement: ***OCTAHEDRAL*** → all six positions are equivalent, thus the lone pair can be situated in any one of these positions.

Molecular geometry: ***SQUARE PYRAMIDAL***

With two lone pairs → XeF_4

Electron pair arrangement: ***OCTAHEDRAL***

Molecular geometry: ***SQUARE PLANAR***

POLARITY OF MOLECULES

Molecules can be either polar or apolar, depending on their geometry and the nature of their bonds.

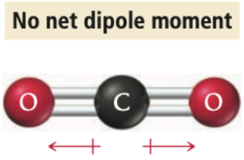
APOLAR BONDS → APOLAR MOLECULE
POLAR BONDS → POLAR MOLECULE
POLAR BONDS → APOLAR MOLECULE

→ The presence of polar bonds may or may not result in a polar molecule, depending on the molecular geometry.

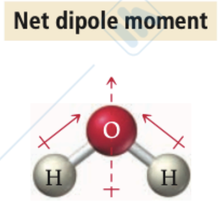
→ The polarity of the molecule depends on the vectoral sum of the dipole moments of individual polar bonds.

Thus, if the molecular geometry is such that the dipole moments of the individual polar bonds cancel each other (**SUM = ZERO**), then the molecule is **NONPOLAR**.

E.g. CO_2 → O=C=O
Bonds: two equal polar bonds with opposite direction
Geometry: LINEAR
The two dipole moments sum to zero → NONPOLAR MOLECULE



E.g. H_2O
Bonds: two equal polar bonds
Geometry: BENT
The two dipole moments do not sum to zero because of the angle between the vectors → POLAR MOLECULE



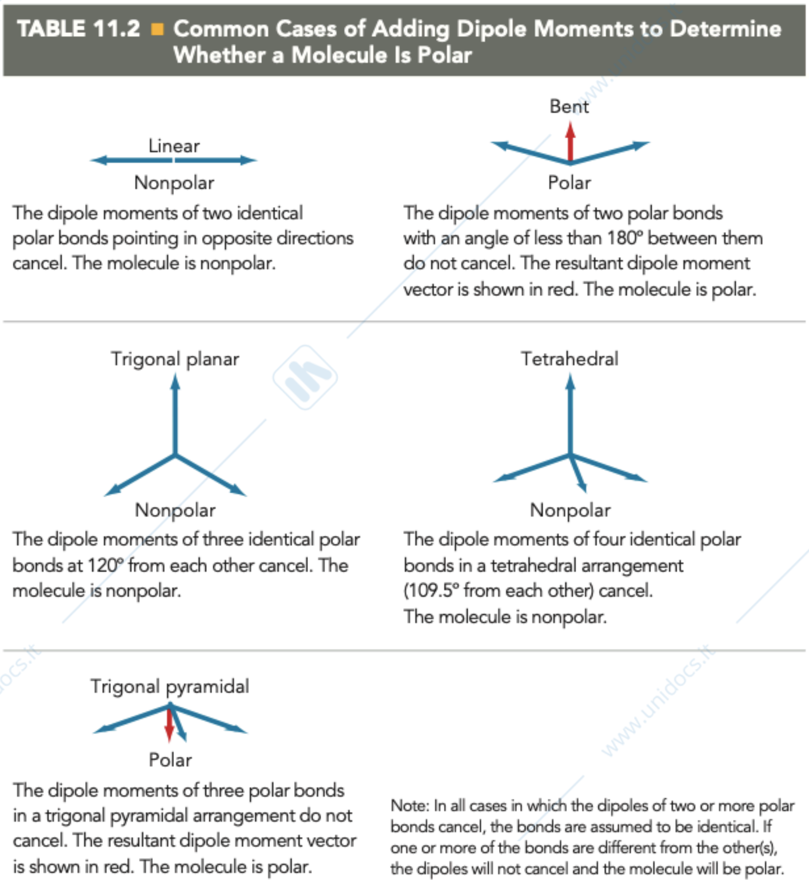


TABLE 11.2 ■ Common Cases of Adding Dipole Moments to Determine Whether a Molecule Is Polar

Linear

Nonpolar

The dipole moments of two identical polar bonds pointing in opposite directions cancel. The molecule is nonpolar.

Bent

Polar

The dipole moments of two polar bonds with an angle of less than 180° between them do not cancel. The resultant dipole moment vector is shown in red. The molecule is polar.

Trigonal planar

Nonpolar

The dipole moments of three identical polar bonds at 120° from each other cancel. The molecule is nonpolar.

Tetrahedral

Nonpolar

The dipole moments of four identical polar bonds in a tetrahedral arrangement (109.5° from each other) cancel. The molecule is nonpolar.

Trigonal pyramidal

Polar

The dipole moments of three polar bonds in a trigonal pyramidal arrangement do not cancel. The resultant dipole moment vector is shown in red. The molecule is polar.

Note: In all cases in which the dipoles of two or more polar bonds cancel, the bonds are assumed to be identical. If one or more of the bonds are different from the other(s), the dipoles will not cancel and the molecule will be polar.

VALENCE BOND THEORY

VALENCE BOND THEORY IS AN ADVANCED BONDING THEORY BASED ON THE QUANTUM-MECHANICAL MODEL OF THE ATOM.

Basic assumptions:

- Electrons reside in quantum-mechanical orbitals localized on individual atoms.
- The orbitals can be the ***standard*** *s, p, d, f orbitals*, or they may be ***hybrid*** combinations of these.
- When two atoms approach each other, their subatomic particles interact with each other.

These interactions affect the energies of the electrons in the atomic orbitals:

a) If the energy of the system is lowered because of the interactions, then a chemical bond is formed → ***overlap of two orbitals***

b) If the energy of the system is raised by the interactions, then a chemical bond does not form.

The geometry of the overlapping orbitals determines the shape of the molecule.

The overlapping results in a net energy stabilization that constitutes a covalent chemical bond. The resulting geometry of the molecule emerges from the geometry of the overlapping orbitals.

POTENTIAL ENERGY

Calculated as a function of the internuclear distance between the two bonding atoms.
Its value **depends on the distance** between the two atoms:

- Too far apart, zero energy → no interaction
- Too close, energy too high → repulsive forces
- At a certain distance, potential energy minimum → attractive forces dominate

IN ORDER TO FORM A BOND, THE POTENTIAL ENERGY MUST BE AT ITS MINIMUM

The potential energy of two atoms is lowest when they are separated by a distance that allows their orbitals a substantial degree of overlap without too much repulsion between their nuclei.

This distance, at which the system is most stable, is the ***bond length*** of molecule.

The potential energy minimum bust be higher than the thermal energy that has a disruptive influence on the bond.

Orbitals are waves, so they own wave properties such as *INTERFERENCE* → interference between atomic orbitals results in hybrid orbitals.

HYBRIDIZATION

Concept elaborated by the Valence Bond theory to explains the formation of many molecules.

ORBITALS IN A MOLECULE ARE NOT NECESSARILY THE SAME AS THE ORBITALS IN AN ATOM

Orbitals can combine themselves, forming *HYBRID ORBITALS*, in order to maximize the distance between electrons and to minimize the energy.
HYBRID ORBITALS corresponds more closely to the actual distribution of electrons in bonded atoms.

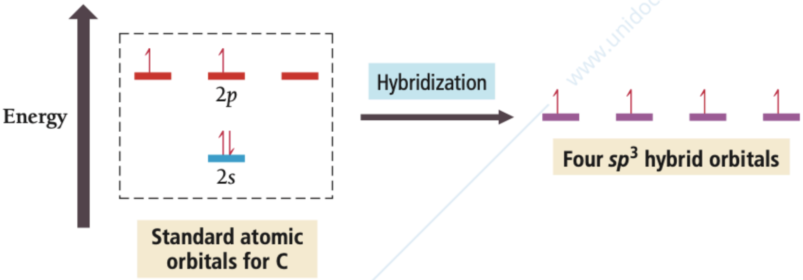
HYBRID ORBITALS

- The total number of orbitals is conserved.
- Different shapes and energies from those of standard atomic orbitals.
- Hybrid orbitals are degenerate – isoenergic.
- Higher electron probability density → **GREATER OVERLAP** with the orbitals of other atoms.
  THE GREATER THE OVERLAP, THE STRONGER THE BOND AND THE LOWER THE ENERGY
- In order to form, energy is needed → hybridization occurs only if the energy payback through bond formation is large.
  THE TENDENCY TO HYBRIDIZE INCREASES WITH THE NUMBER OF BONDS FORMED

→ Central atoms, which form the most bonds, have the greatest tendency to hybridize.
→ Terminal atoms, which form the fewest bonds, have the least tendency to hybridize.

sp^3 HYBRIDIZATION

One 2s orbital + three 2p orbitals → four sp^3 orbitals in a tetrahedral geometry with 109.5° angles.

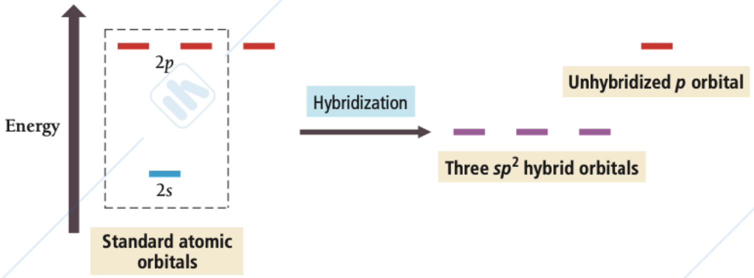


E.g. CH_4 → carbon hybridized sp^3: four valence electrons occupy the orbitals singly with parallel spins as dictated by Hund's rule. The four half-filled orbitals can bond with four hydrogen atoms. The geometry of the overlapping orbitals (the hybrids) is ***tetrahedral***, so the resulting geometry of the molecule is tetrahedral. *(VSEPR theory confirmed)*

E.g. NH_3 → nitrogen hybridized sp^3: three hybrid orbitals half-filled and one hybrid orbital fully-filled with a lone pair
The presence of the lone pair lowers the tendency of nitrogen's orbitals to hybridize.
Therefore, the bond angle in NH_3 is 107°, a bit closer to the unhybridized p orbital bond angle of 90°.

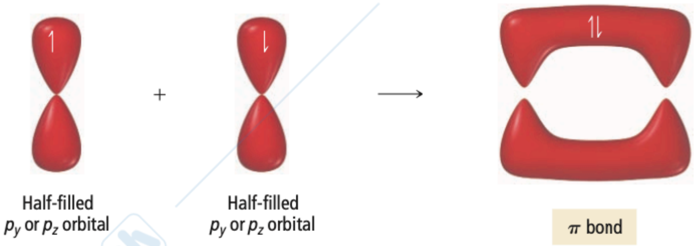
sp^2 HYBRIDIZATION

One 2s orbital + two 2p orbitals → three *sp^2 orbitals* in a trigonal planar geometry with 120° angles and the *unhybridized p orbital* is perpendicular to the three hybridized orbitals.



The unhybridized *p orbital* has a slightly higher energy.

The perpendicular half-filled *p orbital* can overlap SIDE BY SIDE with another p orbital of another atom → result: ***π bond*** → *RESTRCTIVE ROTATION*



The electron density **above** and **below** the internuclear axis → *nodal plane on the internuclear axis*

Even though we represent the two electrons in the upper lobe, they are actually spread out over both the upper and lower lobes.

σ bond

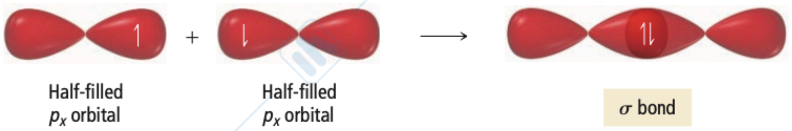
ORBITALS OVERLAP END TO END → *CYLINDRICAL SYMMETRY = FREE ROTATION*

A single bond is a σ bond.

A double bond consists of a σ bond and a π bond

A triple bond consists of a σ bond and two π bonds.

No nodal plane



In general, π bonds are weaker than σ bonds because side-to-side orbital overlap tends to be less efficient than end-to-end orbital overlap.

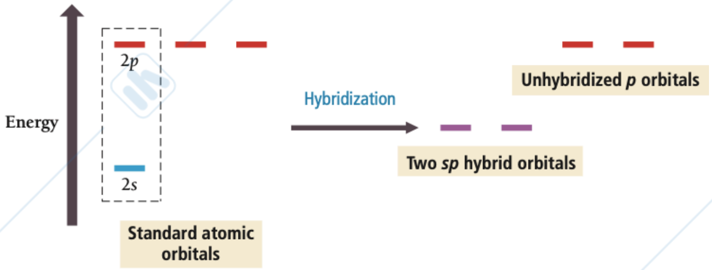
Consequently, the π bond in a double bond is generally easier to break than the σ bond.

Valence bond theory gives more insight into the bonds than the Lewis structure.

→ in the Lewis model the two bonds of the double bond appear identical

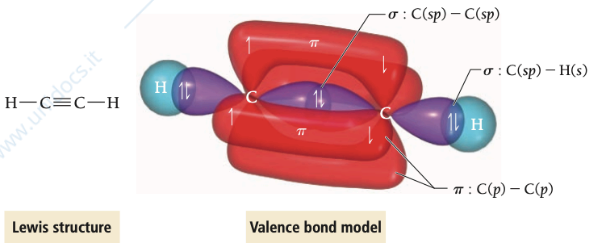
sp HYBRIDIZATION

One 2s orbital + one 2p orbital → two *sp orbitals* in a linear geometry with a 180° angle between them, and *two unhybridized p orbitals* are oriented perpendicularly to the hybridized sp orbitals



The hybrid sp orbitals form σ bonds.
The standard p orbitals form π bonds.

Triple bond: one σ bonds two π bonds



sp^{3}d and sp^{3}d^2 HYBRIDIZATION

Elements of the third row of the periodic table or below can exhibit expanded octets since they have *d orbitals* available.

d orbitals can undergo hybridization

For third-period elements, the 3d orbitals are involved in hybridization because their energies are close to the energies of the *3s* and *3p orbitals*.

sp^{3}d → five hybrid orbitals arranged in a bipyramidal geometry e.g. PF_5
sp^{3}d^2 → six hybrid orbitals arranged in an octahedral geometry e.g. SF_6

WHY CARBON MONOXIDE HAS A HIGHER AFFINITY WITH HEMOGLOBIN?

CARBON MONOXIDE → $C \equiv O$

Polar molecule – C is more electronegative due to its hybridization

CARBON → HYBRIDIZED sp:

- Two *hybrid sp* orbitals:
  - One fully occupied → **lone pair** oriented 180° respect to the O: reason why C is more electronegative
  - One empty
- Two *standard 2p* orbitals: both half-filled

OXYGEN → NO HYBRIDIZATION

- One standard 2s orbital fully occupied – no interactions
- Three 2p orbitals:
  - One double occupied → coordination bond (σ bond) with the *empty hybrid sp orbital*
  - Two half-occupied → two π bonds with the two C-electrons in the *2p orbitals*

HIGHER AFFINITY WITH HEMOGLOBIN = TOXICITY → the heme group cannot bond oxygen!

Affinity 200 times higher

REASON FOR THIS HIGHER AFFINITY

1) HYBRIDATION sp + PARTICULAR ELECTRONIC STRUCTURE → lone pair
2) TENDENCY OF CARBON TO FORM 4 BONDS
3) LINEAR GEOMETRY → it favors the coordination bond with the Fe^{2+} ion

MOLECULAR ORBITAL THEORY

Theory based on quantum mechanics and on Schrödinger equation.

The Molecular Orbital theory **compensates** for those aspects omitted by Lewis model and the Valance Bond theory.

Main points:

- ELECTRONS ARE DELOCALIZED
- Electrons occupy orbitals called MOLECULAR ORBITALS that spread throughout the entire molecule.
- Molecular orbitals are built from atomic orbitals belonging to the valence shells of the atoms in the molecule → n molecular orbitals can be constructed from n atomic orbitals.

Whereas in the Lewis and valence-bond models of molecular structure the electrons are localized on atoms or between pairs of atoms, in molecular orbital theory *all valence electrons are delocalized over the whole molecule, not confined to individual bonds.*

MOLECULAR ORBITALS ARE BUILT FROM LINEAR COMBINATIONS OF ATOMIC ORBITALS

When atomic orbitals interfere constructively, they give rise to ***BONDING ORBITALS***.

1) Two atomic orbitals overlap in the same region of space in such a way that their wavefunctions have the same signs in that region.
2) Their wavefunctions interfere constructively and give rise to a region of enhanced amplitude between the two nuclei where the probability density is higher.
3) Any electron that occupies that molecular orbital is attracted to both nuclei and so has a lower energy than when it is confined to an atomic orbital on one atom.

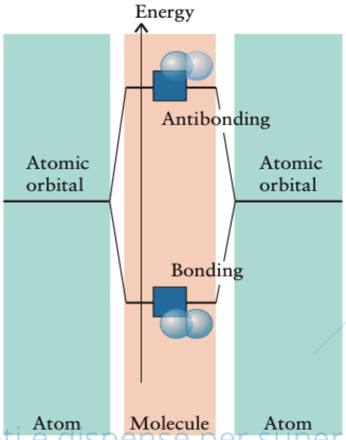
→ The **bonding orbital has a lower energy** than either of the atomic orbitals used in its construction.

When atomic orbitals interfere destructively, they give rise to ***ANTIBONDING ORBITALS***.

1) Two orbitals overlap in the same region of space in such a way that their wavefunctions have opposite signs.
2) Their wavefunctions interfere destructively and give rise to a region of diminished amplitude and a node between the two nuclei where the atomic orbitals cancel completely.
3) Any electron that occupies this molecular orbital is excluded from the internuclear region and has a higher energy than when it occupies one of the atomic orbitals alone.

→ The **antibonding orbital has a higher energy** than the forming atomic orbitals.

ELECTRONS SEEK THE LOWEST ENERGY MOLECULAR ORBITAL AVAILABLE



The molecular orbital theory accounts for the magnetic properties of compounds:

- PARAMAGNETIC COMPOUNDS: magnetic properties **due to unpaired electrons**.
  Their spin exerts a weak magnetic field that can align with an external magnetic field, creating the attraction (much as two magnets attract each other when properly oriented).

- DIAMAGNETIC COMPOUNDS: compounds with **no** magnetic properties.
  If all electrons are paired up, the magnetic fields caused by electron spin cancel each other out.

O_2 → PARAMAGNETIC MOLECULE

The two electrons shared by the double bond occupy antibonding orbitals.
These two electrons are unpaired and occupy the π^*_{2p} orbitals singly with parallel spins, as indicated by Hund's rule.

CHEMICAL REACTIONS

PROCESS IN WHICH ONE OR MORE SUBSTANCES ARE CONVERTED INTO ONE OR MORE DIFFERENT ONES

REACTANTS → PRODUCTS

The coefficients in a chemical equation specify the relative amounts in moles of each of the substances involved in the reaction.

TYPES OF REACTIONS

- COMBINATION: two reactants combine to form one product (a compound)
  E.g. alkali metal reaction with halogens.
- DECOMPOSITION: a compound is decomposed to give two or more different substances.
- SINGLE DISPLACEMENT: one element reacts with a compound and replace one of the elements and to form another compound.
- DOUBLE DISPLACEMENT: two compounds exchange partners with each other to produce two different compounds. *E.g. precipitation reaction*

Classification based on ***HEAT***
ENDOTHERMIC – requires heat to happen and to keep the reaction going.
EXOTHERMIC – releases heat (***heat of reaction***) and needs ***activation energy*** to start.

LIMITING REACTANT (or **LIMITING REAGENT**): reactant that is completely consumed in a chemical reaction and limits the amount of product. When consumed the reaction stops.

REACTANT IN EXCESS: reactant that occurs in a quantity greater than is required to completely react with the limiting reactant.

THEORETICAL YIELD: the maximum amount of product that can be made in a chemical reaction based on the amount of limiting reactant.

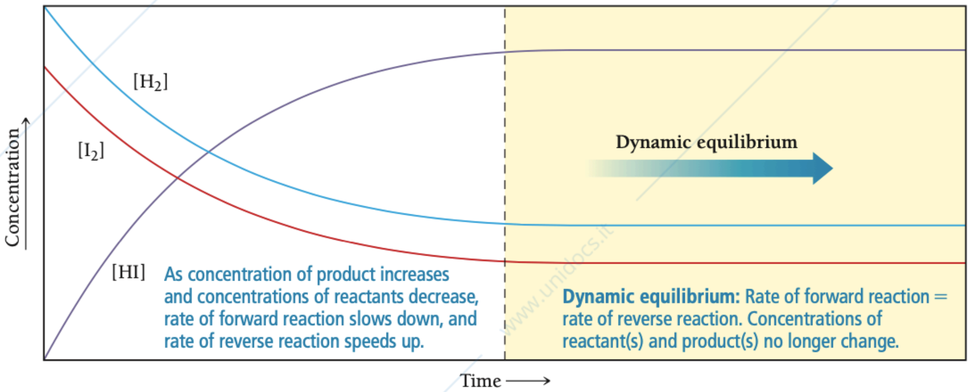
ACTUAL YIELD: the amount of product actually produced by a chemical reaction.

PERCENT YIELD: ratio of the actual yield to the theoretical yield multiplied by 100.

CHEMICAL EQUILIBRIUM

DYNAMIC EQUILIBRIUM IN WHICH THE RATE OF THE FORWARD REACTION EQUALS THE RATE OF THE REVERSE REACTION

The forward and reverse reactions are occurring at the same rate.
A chemical equilibrium corresponds to an energy minimum.



As concentration of product increases and concentrations of reactants decrease, rate of forward reaction slows down, and rate of reverse reaction speeds up.

Dynamic equilibrium: Rate of forward reaction = rate of reverse reaction. Concentrations of reactant(s) and product(s) no longer change.

EQUILIBRIUM CONSTANT (K)

THERMODYNIMAC CONSTANT – DEPENDS ONLY TEMPERATURE

Ratio – *at equilibrium* – of the concentrations of the products, raised to their stoichiometric coefficients, divided by the concentrations of the reactants, raised to their stoichiometric coefficients.

$$K = \frac{\overbrace{[C]^c[D]^d}^{\text{Products}}}{\underbrace{[A]^a[B]^b}_{\text{Reactants}}}$$

The Law of Mass Action

Only species in the same physical phase appear in the expression of K
Liquids and solids: constant concentration

K << 1 – reaction shifted toward the reactants; higher concentrations of reactants at the equilibrium.

K >> 1 – reaction shifted toward the products; higher concentrations of products at the equilibrium.

K ≈ 1 – equal concentrations of products and reactants.

If you reverse the equation, invert the equilibrium constant → **K' = 1/K**

K_c – in terms of concentration (molarity)

K_p – in terms of partial pressure → for reaction in the gaseous state.

$$PV = nRT$$

$$P = \frac{n}{V}RT$$

$$K_C = \frac{[C]^c \cdot [D]^d}{[A]^a \cdot [B]^b} = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \cdot (RT)^{a+b-c-d} = K_p \cdot (RT)^{a+b-c-d}$$

$$P = MRT$$

$$\boxed{K_p = K_c(RT)^{\Delta n}}$$

$$M = \frac{P}{RT}$$

REACTION QUOTIENT (Q)

Ratio – at any point in the reaction – of the concentrations of the products, raised to their stoichiometric coefficients, divided by the concentrations of the reactants, raised to their stoichiometric coefficients.

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \qquad Q_p = \frac{P_C^c P_D^d}{P_A^a P_B^b}$$

Difference between Q and the K:

K has only one value and it specifies the relative amounts of reactants and products at equilibrium.

Q depends on the current state of the reaction and has many different values as the reaction proceeds.

Confronting Q and K, we can predict if the reaction is at the equilibrium or in which direction it will proceed.

- Q < K – more reactants → reaction goes toward products.
- Q > K – more products → reaction goes toward reactants.
- Q = K → reaction at equilibrium.
- Q = 0 → only reactant
- Q =∞ → only products
- Q = 1 → equal concentrations of reactants and products

LE CHATELIER'S PRINCIPLE

WHEN A CHEMICAL SYSTEM AT EQUILIBRIUM IS DISTURBED, THE SYSTEM SHIFTS IN A DIRECTION THAT MINIMIZES THE DISTURBANCE.

Effect of a concentration change:

a) Increasing the concentration of a reactant: the reaction shifts in the direction of the products.
b) Increasing the concentration of a products: the reaction shifts in the direction of the reactants.
c) Decreasing the concentration of one of the species: the reaction shifts towards the formation of that species.

Effect of volume change:

a) Decreasing the volume: the reaction shifts in the direction that has the fewer moles of gas particles in order to restore the pressure that increased.
b) Increasing the volume: the reaction shifts in the direction that has the greater number of moles of gas particles in order to restore the pressure that dropped.
c) If a reaction has an equal number of moles of gas on both sides of the chemical equation, then a change in volume produces no effect on the equilibrium.

→ a change in volume causes a change of pressure, so in order to reach a new equilibrium, the system has to reestablish the pressure with an increase/decrease of moles.

Effect of a temperature change:

a) Increasing the temperature in an endothermic reaction causes the reaction to shift towards the formation of products → *K increases*

b) Increasing the temperature in an exothermic reaction causes the reaction to shift towards the formation of the reactants → *K decreases*

CATALYST – substance that increases the rate of a chemical reaction without being consumed and without shifting the equilibrium.
A catalyst lowers the activation energy of a reaction but does not change the energies of the reactants or the products.

ACTIVATION ENERGY – minimum energy for a reaction to occur.
To get from the reactant to the product, the molecule must go through a high-energy state called the **activated complex** or **transition state**.
The higher the activation energy, the slower the reaction rate (at a given temperature).

ELECTROCHEMISTRY

REDOX

Redox reactions are reactions in which **electrons transfer** from one reactant to the other.

OXIDATION – loss of electrons and, consequently, an increase in oxidation state

REDUCTION – gain of electrons and, consequently, a decrease in oxidation state

OXIDATION STATE or OXIDATION NUMBER: integer value assigned to each element in a compound or ion that allows us to keep track of electrons associated with each atom.

OXIDIZING AGENT: causes the oxidation of another substance and it is always reduced.

REDUCING AGENT: causes the reduction of another substance and it is always oxidized.

For balancing a redox: *HALF-REACTION METHOD*

ACTIVITY SERIES OF METALS

Metals have been arranged in order of decreasing tendency to lose electrons – to be oxidized.
The metals at the top have the greatest tendency to lose electrons.
The metals at the bottom have the lowest tendency to lose electrons, so they are the least reactive.

Noble metals (*Au, Ag, Pt*) are the least reactive metals, therefore they tend not to oxidize by elements in the environment (such as the oxygen in the air).

Free metals *above H* react with acids to release H_2.
Free metals *below H* do not react with acids.

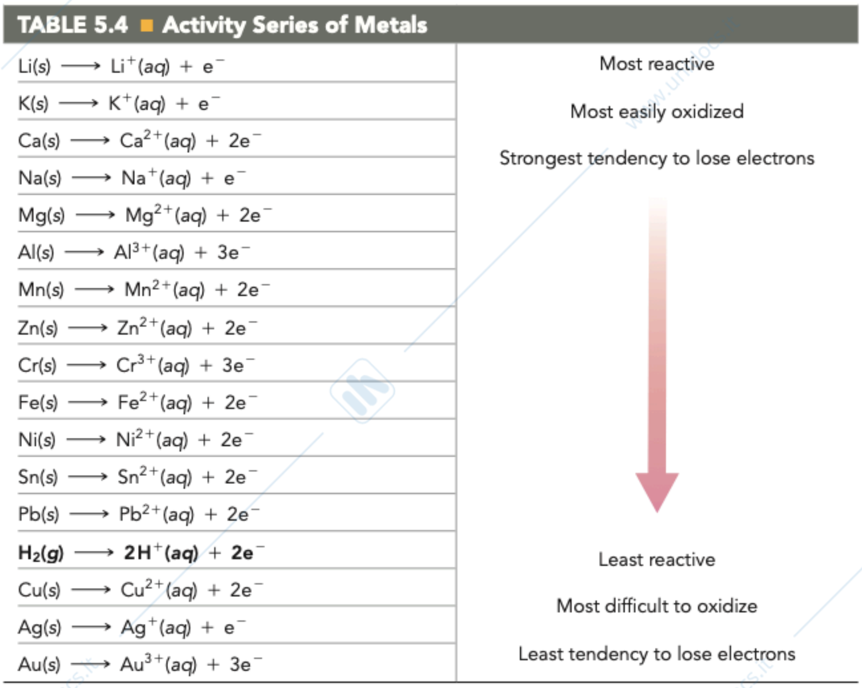


TABLE 5.4 ■ Activity Series of Metals

$Li(s) \longrightarrow Li^+(aq) + e^-$	Most reactive
$K(s) \longrightarrow K^+(aq) + e^-$	Most easily oxidized
$Ca(s) \longrightarrow Ca^{2+}(aq) + 2e^-$	Strongest tendency to lose electrons
$Na(s) \longrightarrow Na^+(aq) + e^-$	
$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$	↓
$Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$	
$Mn(s) \longrightarrow Mn^{2+}(aq) + 2e^-$	
$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$	
$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$	
$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$	
$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$	
$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$	
$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$	
$\mathbf{H_2(g) \longrightarrow 2H^+(aq) + 2e^-}$	Least reactive
$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$	Most difficult to oxidize
$Ag(s) \longrightarrow Ag^+(aq) + e^-$	
$Au(s) \longrightarrow Au^{3+}(aq) + 3e^-$	Least tendency to lose electrons

ELECTROCHEMICAL CELL

ELECTROLYSIS – process in which a chemical reaction caused by the passing of electrical energy.
The generation of electricity through redox reactions is carried out in a device called an *electrochemical cell*.

ELECTROLYTIC CELL – electrochemical cell that *consumes* electrical energy to produce a nonspontaneous redox reaction.
The cell consists of a source of direct current, a battery, connected to two electrodes immersed in solution.
CATHODE – negative electrode (cations are attracted to it), attached to the negative pole.
ANODE – positive electrode (anions are attracted to it), attached to the positive pole of the battery.

REDUCTION ALWAYS OCCURS AT THE CATHODE
OXIDATION ALWAYS OCCURS AT THE ANODE

Once the ions have reached the electrode corresponding to their charge, they gain or lose their charge in order to have an oxidation number equal to zero.

E.g. HCl
When the electric circuit is completed, positive ions (H_3O^+) migrate to the cathode, where they pick up electrons and evolve as *hydrogen gas*.
At the same time the negative chloride ions (Cl^-) migrate to the anode, where they lose electrons and evolve as chlorine gas.

VOLTAIC or GALVANIC CELL – electrochemical cell that *produces* electrical current from a spontaneous chemical reaction.
E.g. zinc–copper voltaic cell.
The cell consists of a piece of zinc immersed in a $ZnSO_4$ solution and connected by a wire through a voltmeter to a piece of copper immersed $CuSO_4$ in solution.
The two solutions are connected by a *SALT BRIDGE* that provides them electrical contact.

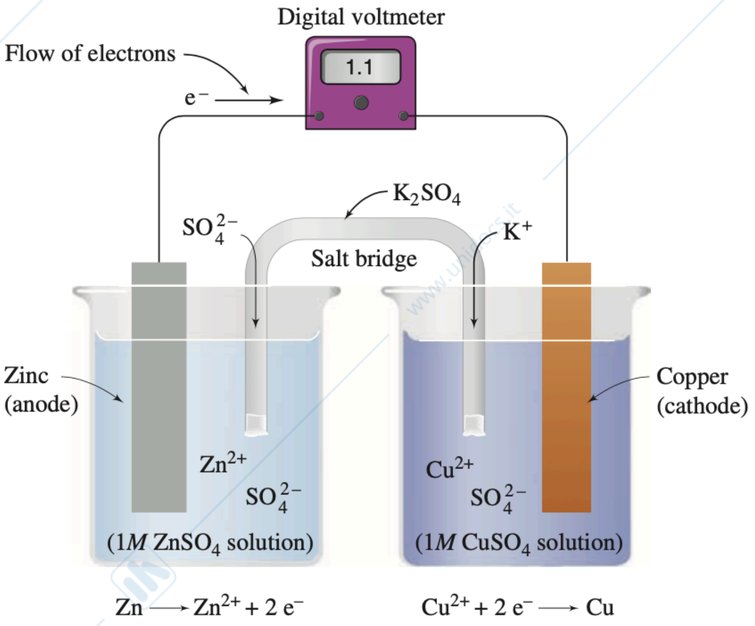
- Strips = *ELECTRODES – Zn electrode = anode – positive because it has lost electrons*
- Solutions = *HALF-CELLS*
- Wire = *EXTERNAL CIRCUIT – movement of electrons*
- Salt bridge = *INTERNAL CIRCUIT – movement of ions*

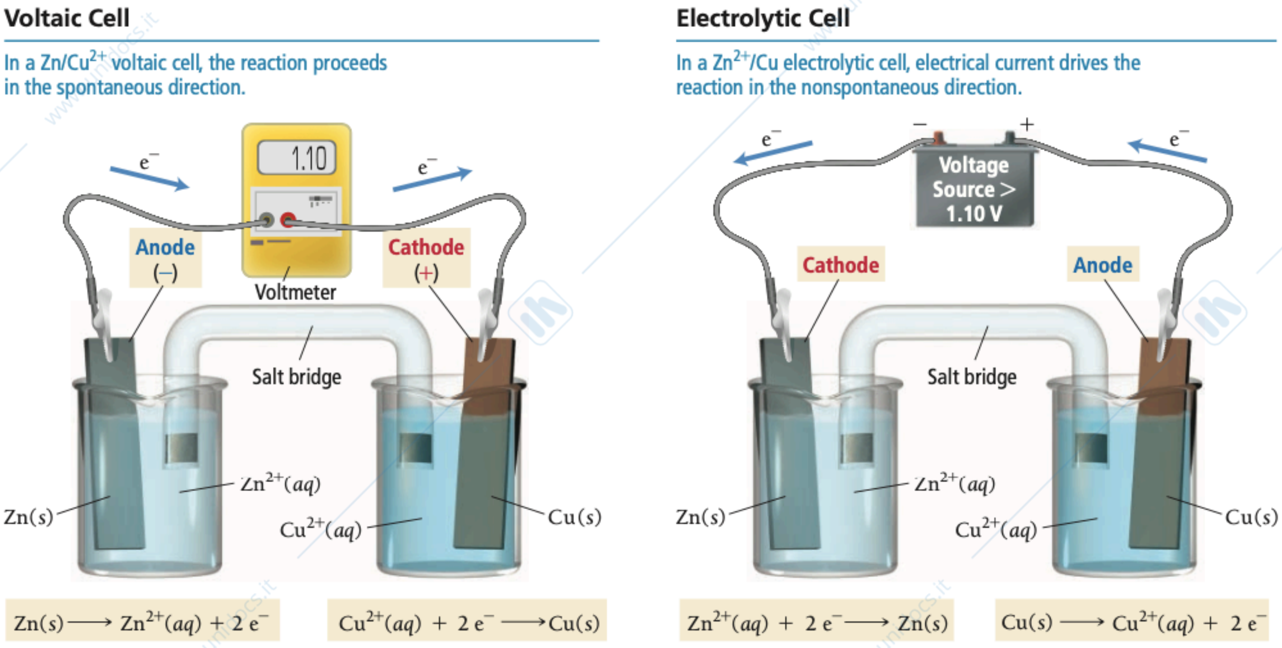
The tendency of zinc to lose electrons to copper results in a flow of electrons, thus, in electric current.

→ Zinc atoms lose electrons and are converted to zinc ions at the zinc electrode surface; the electrons flow through the wire to the copper electrode. Here copper ions pick up electrons and are reduced to copper atoms, which plate out on the copper electrode.
Sulfate ions flow from the $CuSO_4$ solution through the salt bridge to the into the $ZnSO_4$ solution to complete the circuit and neutralize the charge buildup, allowing the reaction to continue.

If the movement of electrons from anode to cathode were the only flow of charge, the buildup of the opposite charge in the solution would stop electron flow almost immediately.

The cell needs a pathway by which counterions can flow between the half-cells → salt bridge, an inverted, U-shaped tube that contains a strong electrolyte, such as KNO_3 or K_2SO_4, and connects the two half-cells. The salt bridge allows a flow of ions that neutralizes the charge buildup in the solution.




Voltaic Cell

In a Zn/Cu^{2+} voltaic cell, the reaction proceeds in the spontaneous direction.

Electrolytic Cell

In a Zn^{2+}/Cu electrolytic cell, electrical current drives the reaction in the nonspontaneous direction.

▲ **FIGURE 20.22** **Voltaic versus Electrolytic Cells**

RADIOACTIVITY

Radioactivity is the spontaneous emission of subatomic particles or high-energy electromagnetic radiation by the nuclei of certain atoms, that are said to be radioactive.
Scientists discovered that these emissions were produced by the nuclei of radioactive atoms.

RADIOACTIVITY = PROPERTY OF THE NUCLEUS

NUCLIDE – any isotope of any atom
RADIONUCLIDE – nuclide that emits radiation; such nuclei are unstable and spontaneously decompose, emitting small pieces of themselves to gain stability.

Elements with Z < 20 → stable
Elements with Z > 84 → unstable

Radioactivity is believed to be a result of an unstable ratio of neutrons to protons in the nucleus. When the neutron-to-proton ratio is too high or too low, alpha, beta, or other particles are emitted to achieve a more stable nucleus.

NUCLEAR DECAY – disintegration of the nucleus due to the strong repulsion forces between protons that overcome the force that holds the nucleons.

Each radioactive nuclide disintegrates at a specific and constant rate, which is expressed in units of *half-life*. The half-life is the time required for one-half of a specific amount of a radioactive nuclide to disintegrate.

TYPES OF RADIATION

- α decay: an unstable nucleus emits a particle composed of two protons and two neutrons that corresponds to a *He atom*.
  When an element emits an alpha particle, the number of protons in its nucleus changes, transforming the element into a different element.
- β decay: a neutron of an unstable nucleus changes into a proton and emits an electron.
  When an atom loses a beta particle from its nucleus, a different element is formed that has one proton more than the starting element.
- γ ray emission: photons of energy released along with either alpha or beta particles.
  Gamma radiation does not result in a change of atomic number or the mass of an element.

Highly energetic radiation interacts with other molecules and atoms by ionizing them.
The ability of radiation to ionize other molecules and atoms is called IONIZING POWER.