CHEMISTRY

CHEMISTRY FUNDAMENTALS

VOLUME, MATTER, AND ENERGY

Volume (*V*): Three-dimensional physical space.

Matter: Anything that has mass and occupies volume.
- Exists in three common states—**solid**, **liquid**, and **gas**.
- In a chemical reaction, matter can neither be created nor destroyed.

Mass (*m*): A measure of the amount of matter in an object.

Density (ρ): Mass per unit volume.
- Mathematically: $\rho = m/V$.

Energy: The capacity of matter to do work.
- **Potential energy:** Energy that a body possesses due to its position in space.
- **Kinetic energy:** Energy that a body possesses due to its motion.
- In a chemical reaction, energy can neither be created nor destroyed but can interconvert between potential and kinetic forms.

Temperature: A measure of the thermal energy of the molecules in a system; "hotness" or "coldness."

CHEMICAL SPECIES

Atom: The smallest unit of an element that retains the chemical properties of that element.
- **Element:** A pure substance composed of only one type of atom.

Molecule: The smallest unit of a compound that retains the chemical properties of that compound.
- **Compound:** A pure substance composed of multiple atoms chemically combined in a known ratio.

Ion: An atom or a group of bonded atoms that carries an electrical charge.
- **Cation:** A positively charged ion.
- **Anion:** A negatively charged ion.

ATOMIC STRUCTURE

COMPOSITION OF ATOMS

Protons: Positively charged (+1) particles residing in the atomic nucleus. Protons have a mass of 1 atomic mass unit (amu; 1 amu = 1.67×10^{-27} kg).

Neutrons: Chargeless particles residing in the atomic nucleus. Neutrons have a mass of 1 amu.

Electrons: Negatively charged (–1) particles that exist in "clouds" around the atomic nucleus. Electrons have a mass of approximately 1/1837 amu.

Atomic number: The number of protons in one atom of an element. For neutral atoms, the atomic number equals the number of electrons in one atom.
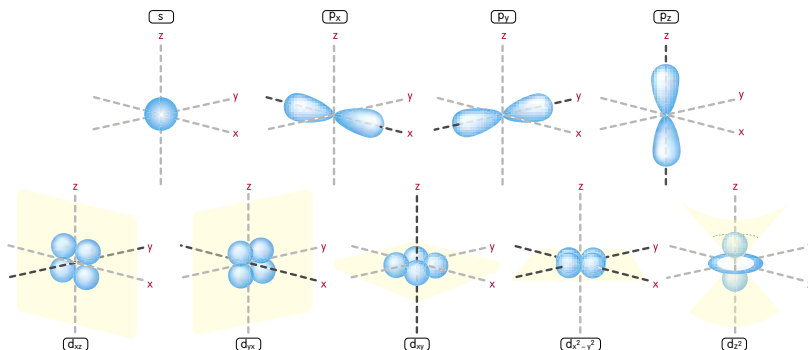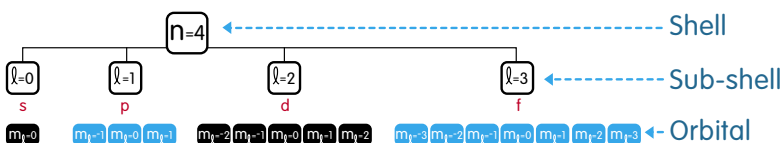
Mass number: The sum of the number of protons and the number of neutrons in one atom of a given isotope of an element.

Isotopes: Atoms with the same atomic number but different mass numbers (i.e., atoms with different numbers of neutrons).
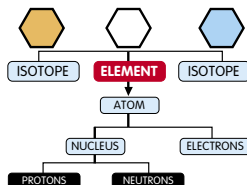
TREE DIAGRAM ILLUSTRATING THE HIERARCHY OF ELEMENTS, ISOTOPES, AND SUBATOMIC STRUCTURES.

CHARACTERISTIC SHAPES AND SPATIAL ORIENTATIONS OF *s*, *p*, AND *d* ATOMIC ORBITALS. THE ORIGIN OF THE COORDINATE AXIS SYSTEM IS THE ATOMIC NUCLEUS.

MODEL OF ATOMIC STRUCTURE

Proposed by Erwin Schrödinger in 1926:
- Electrons are both **wavelike** (similar to light) and **particle-like** (similar to matter).
- Mathematical expressions called **wavefunctions** characterize the waves that describe electron behavior.
- The probability of finding an electron at a point in space is proportional to the **square of its wavefunction** at that point.
- According to the model, electrons exist in a probabilistic haze.

Atomic orbitals: Regions of space around the nucleus that have a nonzero probability of containing an electron in a specific energy state.
- Can hold up to two electrons.
- Different types of atomic orbitals have characteristic shapes that are designated by different letters.

Quantum numbers: Integers or half-integers used to identify specific electrons in atoms.

Principal quantum number (n):
- Specifies the **most probable distance** of an electron from the nucleus. The higher the value of *n*, the more likely an electron is to be found farther from the nucleus.
- Electrons with the same value of *n* are said to belong to the same "shell" of an atom.
- Allowed values: all positive integers.

Orbital angular momentum quantum number (ℓ):
- Specifies the **shape** of the orbital (*s*, *p*, *d*, *f*, etc.).
- Electrons with the same value of ℓ are said to belong to the same "sub-shell" of an atom.
- Each sub-shell contains (2ℓ + 1) orbitals that can each hold two electrons.
- Allowed values: 0 [*s* orbital], 1 [*p* orbital], 2 [*d* orbital], … (n – 1).

Magnetic quantum number (mℓ):
- For a given sub-shell, m_ℓ specifies to which of the (2ℓ + 1) orbitals an electron belongs.
- Allowed values: 0, ±1, ±2,…, ±ℓ.

Spin magnetic quantum number (mS):
- Specifies direction of **electron spin** ("up" or "down").
- Allowed values: ±1/2.

Shielding: Electrons closer to the nucleus reduce the nuclear attractive force for electrons farther from the nucleus; these outer electrons are said to be "shielded."
- The nuclear charge experienced by an electron after the shielding effect has been taken into account is called the **effective nuclear charge**, Z_{eff}. Z_{eff} is always less than Z, the actual nuclear charge.

ELECTRON CONFIGURATION

Aufbau principle: The procedure used to find the ground-state electron configuration of an atom or ion.
1. Determine how many electrons the atom or ion has.
2. Write down the atomic sub-shells in the order in which they fill: 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, etc.
3. Fill the sub-shells in this order. Put two electrons in each *s* sub-shell, six in each *p* sub-shell, and ten in each *d* sub-shell until there are not enough electrons left to fill the next orbital.
4. Identify the next unfilled sub-shell. For unfilled *p* and *d* sub-shells, draw a box-diagram. Draw three boxes for *p* sub-shells and five for *d* sub-shells (i.e., one box for each allowed m_ℓ value).
5. Follow Hund's rule and the Pauli exclusion principle to fill the box-diagram with the remaining electrons.
- **Hund's rule:** Maximize the number of parallel spins in a sub-shell; if more than one orbital in a sub-shell is available, electrons will occupy empty orbitals before pairing up in the same orbital.
- **Pauli exclusion principle:** No two electrons in the same atom or ion can have four identical quantum numbers; two electrons occupying the same orbital must have opposite spins.
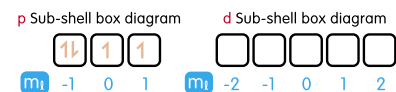
Represent electrons as ↑ (spin "up") or ↓ (spin "down")

BOX DIAGRAMS FOR PLACING ELECTRONS IN SPECIFIC ORBITALS OF THE *p* AND *d* SUB-SHELLS TO DETERMINE THE ELECTRONIC STRUCTURES OF ATOMS.

Valence electrons: The electrons in the outermost occupied shell of an atom.

Octet rule: An atom is most stable when its valence shell is completely full; an atom can obtain a full valence shell by bonding with other atoms.
- The octet rule does not always apply to atoms with electrons in *d* orbitals.

THE PERIODIC TABLE OF THE ELEMENTS

FAMILIES OF ELEMENTS

Metals: Good conductors of heat and electricity. Metals tend to lose electrons to form cations.

Nonmetals: Poor conductors of heat and electricity. Nonmetals tend to gain electrons to form anions.

Metalloids: Intermediate between metals and nonmetals. Metalloids have physical and chemical properties in common with both.

PERIODIC TRENDS

Atomic radius: Half the distance between nuclei of neighboring atoms in a sample of an element.
- *Decreases traveling across a period.* While atomic number (and therefore nuclear charge) is increasing, added electrons go into the same shell and do not contribute to shielding other electrons from the nucleus; valence electrons are more strongly attracted to the nucleus, so the atom becomes more compact.
- *Increases traveling down a group.* Although atomic number (and therefore nuclear charge) is increasing, added

TREE DIAGRAM ILLUSTRATING THE HIERARCHY OF QUANTUM NUMBERS IN THE *n* = 4 ELECTRON SHELL. EACH ORBITAL CAN HOLD TWO ELECTRONS (ONE WITH m_S = 1/2 AND ONE WITH m_S = −1/2).

CHEMISTRY

THE PERIODIC TABLE OF THE ELEMENTS.
ROWS IN THE TABLE ARE CALLED PERIODS; COLUMNS ARE CALLED GROUPS.

Periodic table legend: ATOMIC NUMBER 47, SYMBOL Ag, ATOMIC MASS 107.9. ■ METALS, □ METALLOIDS, ▥ NONMETALS.

1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.70	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (97.9)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57★ La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.0	89★ Ac 227.0	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Ns (262)	108 Hs (265)	109 Mt (266)									

LANTHANIDE SERIES ★

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0

ACTINIDE SERIES ★

90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)

electrons go into new shells that are shielded by the inner shells; Z_{eff} decreases and nuclear attraction is weaker for valence electrons, so the atom becomes less compact.

Ionization energy: The energy required to remove an electron from the highest-energy shell of an atom.
- *Increases traveling across a period* for the same reason that atomic radius decreases traveling across a period; removing electrons from full shells is especially difficult.
- *Decreases traveling down a group* for the same reason that atomic radius increases traveling down a group.

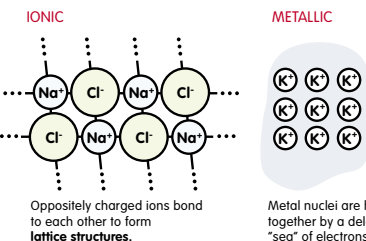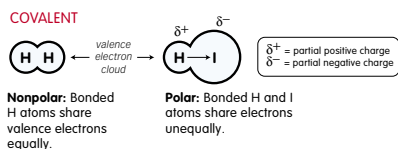**Electronegativity:** The ability of an atom in a molecule to attract electrons.
- Related to ionization energy; periodic trends follow those of ionization energy.

BONDING AND INTER-MOLECULAR INTERACTIONS

TYPES OF BONDS

Covalent: Formed when two elements share valence electrons so that both gain full valence shells. Covalent bonds can be single (two shared electrons), double (four shared electrons), or triple (six shared electrons).

TYPES OF CHEMICAL BONDING.

COVALENT

H H ← valence electron cloud   δ+ H—I δ−

δ+ = partial positive charge
δ− = partial negative charge

Nonpolar: Bonded H atoms share valence electrons equally.

Polar: Bonded H and I atoms share electrons unequally.

IONIC

Na⁺ Cl⁻ Na⁺ Cl⁻ / Cl⁻ Na⁺ Cl⁻ Na⁺

Oppositely charged ions bond to each other to form **lattice structures.**

METALLIC

K⁺ K⁺ K⁺ / K⁺ K⁺ K⁺ / K⁺ K⁺ K⁺

Metal nuclei are held together by a delocalized "sea" of electrons.

Ionic: Formed when the electronegativities of bonded atoms are significantly different. Both shared electrons are almost completely associated with the more electronegative atom, which becomes an anion while the other atom becomes a cation.

Metallic: Metals involved in bonding exist as cations held together in a regular crystal lattice by a cloud of delocalized valence electrons.

BOND CHARACTERISTICS

Bond order: Half the number of electrons shared in a covalent bond. The higher the bond order, the shorter the bond compared to a lower order bond between the same two atoms; e.g., a C=C bond is shorter than a C–C bond.

Bond polarity: In bonds between atoms of unequal electronegativities, shared electrons are more likely to be found near the more electronegative atom; such a bond is said to be polar.

LEWIS STRUCTURES

Lewis structure: A representation of a molecule that depicts covalent bonds and nonbonding valence electrons.

Drawing Lewis structures:
1. For a given compound, write down the chemical symbols of its constituent atoms and position them to show their rough layout in the molecule (Lewis theory alone cannot predict molecular shape).
2. Draw the valence electrons around each atom as dots.
3. Draw covalent bonds by connecting valence electrons on neighboring atoms.
4. Redraw the molecule so that shared electrons are not explicitly shown.
5. Organize non-bonding valence electrons (usually there is an even number) into pairs on each atom. These electron pairs are called lone-pairs.

ETHANE C₂H₆

LEWIS STRUCTURE OF ETHANE. DOTS REPRESENT ELECTRONS AND LINES REPRESENT COVALENT BONDS.
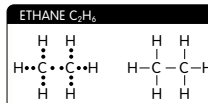
Counting electrons to show that the octet rule is obeyed: Electrons used to make a covalent bond are associated with both atoms participating in the bond and are therefore counted for both atoms involved in the bond. For example, unbonded H has one valence electron and unbonded Cl has seven; in HCl, Cl shares one of its electrons with H so that H has two valence electrons (full valence shell), and H shares its electron with Cl so that Cl has eight valence electrons (full valence shell).

Resonance structures: Some Lewis structures have multiple distinct, but equivalent, ways of arranging multiple bonds and electrons while still obeying the octet rule. Each equivalent arrangement is called a resonance structure.
- In reality, molecules exist as the average of all their different resonance structures. Individual resonance structures cannot be isolated because electrons in a molecule are actually delocalized and multiple bond characteristics can be spread out over the entire molecule.

NITRATE ION NO₃⁻

BENZENE C₆H₆
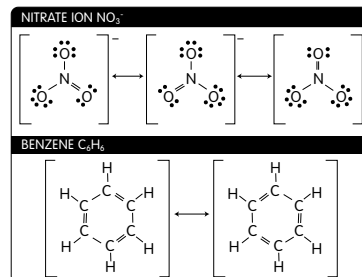
RESONANCE STRUCTURES OF NITRATE ION AND BENZENE. THE ACTUAL MOLECULES ARE AN AVERAGE OF THEIR INDIVIDUAL RESONANCE STRUCTURES.

Formal charge: The formal charge on an atom equals the number of valence electrons in the unbonded atom minus the sum of the number of electrons the atom has in lone-pairs and the number of covalent bonds to the atom.
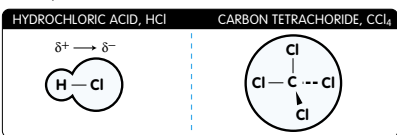- A nonzero formal charge indicates that an atom has a different number of valence electrons than it would have if it were unbonded and neutral.
- The sum of the individual formal charges in a molecule equals the overall charge of the molecule; formal charges give a sense of where charge is localized within a molecule.

CARBON MONOXIDE, CO

:C≡O: −1 on C, +1 on O

	Carbon	Oxygen
Unbonded	4 valence electrons	6 valence electrons
In CO molecule	2 lone-pair electrons, 3 covalent bonds	2 lone-pair electrons, 3 covalent bonds
Formal charge	4 - 2 - 3 = -1	6 - 2 - 3 = +1

FORMAL CHARGES ON THE ATOMS IN CARBON MONOXIDE. THE NET CHARGE ON THE MOLECULE IS −1 + 1 = 0.

Molecular polarity: Asymmetric distribution of charge within a molecule.
- A single polar bond in a molecule can make the whole molecule polar; e.g., HCl is polar.
- If a molecule has more than one polar bond, then these bonds may cancel each other out and make the molecule nonpolar.

HYDROCHLORIC ACID, HCl	CARBON TETRACHLORIDE, CCl₄
$\delta^+ \longrightarrow \delta^-$ H—Cl	Cl—C—Cl with Cl top and Cl bottom

POLARITIES OF HCl AND CCl₄ MOLECULES.
HCl contains a single polar H–Cl bond, which gives an asymmetric distribution of electron density througout the molecule. As a result, the HCl molecule is polar. In contrast, CCl₄ has four symmetrically arranged polar C–Cl bonds, which give a symmetric distribution of electron density throughout the molecule. Consequently, the CCl₄ molecule is nonpolar.

GEOMETRY

Valence shell electron pair repulsion (VSEPR) theory: A model for predicting molecular geometry. Based on the idea that, in a molecule, electron pairs arrange themselves as far apart as possible to minimize electron-electron repulsion.
- The shape of a molecule is determined by the number of electron pairs (bonding pairs and lone-pairs) associated with the central atom of the molecule.
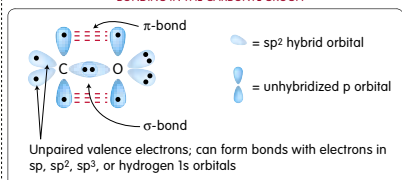
Valence-bond theory: A theory of bonding that states that bonds form through the spatial overlap of orbitals containing valence electrons. Valence-bond theory is consistent with the geometric predictions of VSEPR theory.
- **Hybridization:** Formation of hybrid orbitals, which are mixtures of individual atomic orbitals.
  - The number of atomic orbitals used to create a set of hybrid orbitals equals the number of orbitals generated by hybridization.
  - Hybrid orbitals can hold up to two electrons; half-filled hybrid orbitals can share electrons with other half-filled orbitals to form a covalent bond.

HYBRID ORBITALS AND THEIR CORRESPONDING VSEPR GEOMETRIES.

Atomic orbitals combined	Hybrid orbits formed	Bonding electron pairs and lone-pairs around central atom	VSEPR geometry
1 s orbital & 1 p orbital	sp hybrid (2 orbitals)	2	linear
1 s orbital & 2 p orbitals	sp² hybrid (3 orbitals)	3	trigonal planar
1 s orbital & 3 p orbitals	sp³ hybrid (4 orbitals)	4	tetrahedral
1 s orbital & 3 p orbitals & 1 d orbital	dsp³ hybrid (5 orbitals)	5	trigonal bipyramidal
1 s orbital & 3 p orbitals & 2 d orbitals	d²sp³ hybrid (6 orbitals)	6	octahedral

HYBRIDIZED AND UNHYBRIDIZED ORBITALS AND BONDING IN THE CARBONYL GROUP.

π-bond
= sp² hybrid orbital
= unhybridized p orbital
σ-bond

Unpaired valence electrons; can form bonds with electrons in sp, sp², sp³, or hydrogen 1s orbitals


- **Sigma (σ) bonds:** Bonds formed by the head-on overlap of *sp*, *sp²*, or *sp³* hybrid orbitals with each other or with hydrogen 1s orbitals.
- **Pi (π) bonds:** Bonds formed by the sideways overlap of *p* orbitals.

INTERMOLECULAR (COHESIVE) FORCES

London (dispersion) forces: Attractive forces between transient dipoles caused by random changes in the electron distribution of a molecule (one part of a molecule temporarily becomes slightly positively charged while another part becomes slightly negatively charged).
- Affect all molecules.
- Weakest type of cohesive force.

How London forces arise

(a) (b) (c)

δ^+ = partial positive charge δ^- = partial negative charge
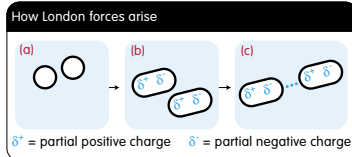
(a) Nonpolar molecules have a symmetric charge distribution throughout; i.e., they have no permanent partially positive or negative end.
(b) Movement of electrons can make nonpolar molecules temporarily polar.
(c) In these temporarily polar molecules, the distribution of electron density can rearrange itself to create stabilizing interactions between oppositely charged ends of neighboring molecules.

Dipole-dipole interactions: Attractive forces between the permanent dipoles of polar molecules (a given polar molecule will always have partially positively charged and partially negatively charged regions).
- Stronger than London forces.

How dipole-dipole interactions arise
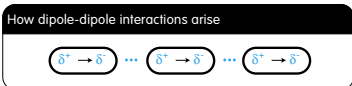
Neighboring polar molecules will orient themselves to create stabilizing interactions between oppositely charged ends.

Hydrogen bonding: A type of dipole-dipole interaction involving molecules containing hydrogen attached to a highly electronegative element (e.g., oxygen or nitrogen) with electron lone-pairs. These hydrogen atoms carry a partial positive charge and can interact with lone-pairs on electronegative atoms from other molecules.

How hydrogen bonding arises
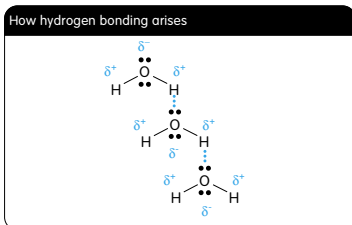
Hydrogen bonding as seen in water (H₂O). Partially positively charged H atoms will orient themselves to create stabilizing interactions between themselves and electronegative atoms on neighboring molecules.

Electrostatic interactions: Interactions in which oppositely charged species (ions) attract each other.
- Strongest type of cohesive force.

# STOICHIOMETRY AND CHEMICAL REACTIONS

RELATIONSHIP BETWEEN MOLES AND MOLECULES

Mole: 6.02×10^{23} (**Avogadro's number**) particles (e.g., atoms, molecules, electrons, etc.)

Molar mass (*M*): Mass of one mole of particles.
- E.g., the molar mass of carbon-12 is 12.000 g; a 12.000 gram sample of carbon-12 contains 1 mole of carbon-12 atoms.
- A naturally occurring sample will usually be a mixture of different isotopes. The quoted molar mass of an element is the average mass (weighted by the relative amount of each isotope present) of an atom in a naturally occurring sample of the element.

Molecular mass: Mass (in amu) of one molecule of a compound.

MASS OF SAMPLE m
MOLES OF SAMPLE n
MOLAR MASS M
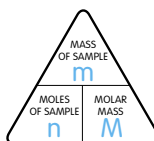
$m = n \times M$

$n = \dfrac{m}{M}$

$M = \dfrac{m}{n}$

CHEMICAL FORMULAS

Molecular formula: The chemical formula that shows the actual number of atoms of each element present in a molecule; e.g., the molecular formula of glucose is $C_6H_{12}O_6$.

Empirical formula: The chemical formula that shows the relative number (ratio) of atoms of each element present in a molecule; e.g., the empirical formula of glucose is CH_2O.

CHEMICAL REACTIONS

Chemical reaction: A process by which chemical bonds can be broken or made.

- **Addition (combination) reactions:** Multiple reactants combine to give a single product.
  - E.g., $C + O_2 \longrightarrow CO_2$.
- **Decomposition reactions:** A compound breaks down into multiple simpler compounds.
  - E.g., $CaCO_3 \longrightarrow CaO + CO_2$.
- **Metathesis (displacement) reactions:** Two reactants exchange component parts.
  - E.g., $CaCl_2(aq) + 2AgNO_3(aq) \longrightarrow 2AgCl(s) + Ca(NO_3)_2(aq)$.

State symbols: Symbols used in chemical equations to denote whether a reactant or product is a solid *(s)*, a liquid *(l)*, a gas *(g)*, or an ion in aqueous solution *(aq)*.

Balancing chemical equations:
1. Write the unbalanced equation.
2. Count the number of each type of atom on both sides of the equation.
3. Find the stoichiometric coefficients (numbers that multiply entire molecular or ionic formulas in equations) that equalize the number of each type of atom on both sides of the equation.

Limiting reactant: The reactant that is supplied in an amount smaller than required by the stoichiometric relation for any of the other reactants to be consumed completely.
- Determines the maximum yield of product in the reaction.
- To find the limiting reactant and calculate the amount of reactants used or products formed:
  1. Calculate the number of moles of each reactant present.
  2. For each reactant, divide the number of moles by the stoichiometric coefficient of that reactant in the reaction equation; the reactant that gives the smallest number is the limiting reactant. If the number is the same for each reactant, then there is no limiting reactant, and all reactants can be consumed completely.
  3. The number of moles of a particular reactant consumed or of a product formed is equal to the stoichiometric coefficient of that reactant or product multiplied by the number obtained in Step 2 for the limiting reactant.

Theoretical yield: The amount of a given product formed if all of the limiting reactant is consumed by the reaction.

Percent yield: Fraction of the theoretical yield obtained experimentally.
- $Percent\ yield = 100 \times \dfrac{(Experimental\ yield)}{(Theoretical\ yield)}$.

GASES

KINETIC MOLECULAR THEORY

Kinetic molecular theory: A theory that explains the behavior of gases on a molecular level.

Energy: The average kinetic energy (E_k) of a gas is proportional to its absolute temperature (*T*).
- Mathematically: $E_k = 3RT/2$.
- R = ideal gas constant = 8.314 J mol⁻¹ K⁻¹ = 0.0821 L bar mol⁻¹ K⁻¹

Velocity: The average velocity (*v*) of a gas molecule is proportional to the square root of its absolute temperature and inversely proportional to the square root of its molar mass.
- Mathematically: $v = \sqrt{3RT/M}$.

Diffusion: Mixing of two or more gases by random molecular motion.

Effusion: Escape of a gas by random molecular motion from one container into another through a permeable barrier.

Graham's law of effusion: The ratio of the rates of effusion of two different gases is inversely proportional to the square roots of their molar masses.
- Mathematically:

$\dfrac{(rate\ of\ diffusion\ of\ A)}{(rate\ of\ diffusion\ of\ B)} = \sqrt{\dfrac{M_B}{M_A}}$.

IDEAL GASES

Ideal gas: A gas that is described perfectly by kinetic molecular theory.

Properties of ideal gas molecules:
- Do not interact with each other except when they collide, in which case all collisions are elastic (do not decrease the energy of the system).
- Individual molecules have no volume and are in constant, random motion.
- Real gases behave like ideal gases at low pressure (fewer molecules per unit volume, therefore fewer intermolecular interactions) and high temperature (reduces the effect of inelastic collisions).

Boyle's law: At constant temperature (T), the pressure of a gas (P) is inversely proportional to its volume (V).
- Mathematically: $P_1V_1 = P_2V_2$ = constant.

Charles' law: At constant pressure, the volume of a gas is directly proportional to its temperature (T).
- Mathematically: $V_1/T_1 = V_2/T_2$ = constant.

Avogadro's law: The volume occupied by an ideal gas at constant temperature and pressure is proportional to the number of moles (n) of gas present.

Ideal gas law: The previous three laws combined.
- Mathematically: $PV = nRT$.

REAL GASES

Van der Waals equation: Models the intermolecular interactions that cause non-ideality.
- Mathematically: $(P + a(n/V)^2)(V - nb) = nRT$.
  - a and b are experimentally determined constants that depend on the identity of the gas.
  - a accounts for the effect of intermolecular interactions.
  - b accounts for the fact that real gas molecules have nonzero volumes.

GAS MIXTURES

Mole fraction (X): Ratio of the number of moles of a particular gas in a mixture to the total number of moles of gas in the mixture.

Partial pressure: Pressure due to an individual gas in a mixture of different gases. The partial pressure of a gas equals its mole fraction times the total pressure of the mixture.

Dalton's law of partial pressures: The total pressure of a mixture of gases is the sum of the pressures that each individual gas would exert alone.

THERMOCHEMISTRY

LAWS OF THERMODYNAMICS

First law of thermodynamics: Energy can neither be created nor destroyed, only interconverted between heat and work.
- **Heat** (q): Thermal energy resulting from the motion of atoms, molecules, or ions.
- **Work** (w): Force acting on an object over a distance.

Second law of thermodynamics: The entropy of the universe increases in a spontaneous process; i.e., the entropy of the universe is always increasing.
- **Entropy** (S): A measure of disorder in a system.
- **Spontaneous process:** Process that occurs without any external intervention.

Third law of thermodynamics: The entropy of a pure substance in a perfect crystalline state is zero at absolute zero.
- **Absolute zero:** Zero on the Kelvin temperature scale; the lowest physically possible temperature; approximately equal to –273°C.

THERMODYNAMIC QUANTITIES

Enthalpy (H): A measure of energy that can be released as heat.
- **Reaction enthalpy** ($\Delta_r H$): At constant pressure, the change in enthalpy observed when reactants are converted into products.
  - A reaction for which $\Delta_r H > 0$ is **endothermic** (heat is consumed).
  - A reaction for which $\Delta_r H < 0$ is **exothermic** (heat is released).
- **Standard enthalpy of formation** ($\Delta_f H°$): Under standard conditions (P = 1 atm, T = 298 K), the enthalpy change observed when one mole of a compound is formed from its constituent elements.
- **Hess's law:** The overall enthalpy of a reaction is the sum of the reaction enthalpies of the steps into which that reaction can be divided.

Gibbs free energy (G): The thermodynamic driving force of a reaction.
- **Gibbs free energy change** ($\Delta_r G$): The change in Gibbs free energy observed when reactants are converted to products.
  - Mathematically: $\Delta_r G = \Delta_r H - T\Delta_r S$.
  - For spontaneous reactions, $\Delta_r G < 0$.
  - For nonspontaneous reactions, $\Delta_r G > 0$.
  - For reactions at equilibrium, $\Delta_r G = 0$.

SOLUTIONS

**Solution:** A homogeneous mixture of more than one substance in one phase.
- **Solute:** Minor component of a solution.
- **Solvent:** Major component of a solution.

"Like dissolves like":
- A solute dissolves when the attraction of solvent molecules to solute molecules (or ions) overcomes the intermolecular forces (or ionic bonds) holding solute molecules (or ions) together.
- For a solute to dissolve in a solvent, the cohesive forces that hold the solute molecules together (e.g., London forces, dipole-dipole interactions) should be the same as those that hold the solvent molecules together.
- Non-polar solvents dissolve non-polar solutes, while polar solvents dissolve polar solutes.

Concentration: Amount of solute per unit volume or mass in a solution.
- **Molarity:** Moles of solute per liter of solution.
- **Molality:** Moles of solute per kilogram of solvent.
- **Normality:** Molar equivalents of solute per liter of solution.
- **Mass percent:** One hundred times mass of solute divided by mass of solution.
- **Mole fraction** (X): Ratio of the number of moles of a substance in a solution to the total number of moles in the solution.

$$n = c \times V$$
$$c = \frac{n}{V}$$
$$V = \frac{n}{c}$$

(Triangle diagram: CONCENTRATION c, MOLES OF SOLUTE n, VOLUME OF SOLVENT V)
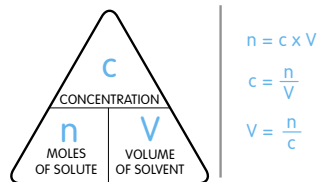
Henry's law: The concentration of a gas (c_g) in a solution is directly proportional to the partial pressure (P_g) of the gas above the solution.
- Mathematically: $c_g = k_H P_g$.
- k_H = proportionality constant (depends on solute and solvent).

Colligative properties: Properties of a solution that depend only on the number of solute molecules and not the identity of the solute.
- **Raoult's law:** In a solution, the vapor pressure of a solvent ($P_{solvent}$) is proportional to its mole fraction.
  - Mathematically: $P_{solvent} = X_{solvent} \times P°_{solvent}$.
  - $P°_{solvent}$ = vapor pressure of the pure solvent.
- **Boiling point elevation:** The boiling point of a solvent is raised by the presence of a solute.
  - Mathematically: $\Delta T_{boil} = k_b \times m_{solute}$.
  - ΔT_{boil} = change in solvent boiling-point.
  - k_b = proportionality constant (depends on solvent).
  - m_{solute} = molality of solute.
- **Freezing point depression:** The freezing point of a solvent is lowered by the presence of a solute.
  - Mathematically: $\Delta T_{freeze} = k_f \times m_{solute}$.
  - ΔT_{freeze} = change in solvent freezing point.
  - k_f = proportionality constant (depends on solvent).
  - m_{solute} = molality of solute.
- **Osmotic pressure** (Π): The pressure that results from solvent flow in osmosis (the net flow of solvent through a selectively permeable membrane from a solution of high concentration to a solution of low concentration).
  - Mathematically: $\Pi = M_{solute}RT$.
  - M_{solute} = molarity of solute.
  - R = ideal gas constant.
  - T = temperature (K).

CHEMICAL EQUILIBRIUM

Equilibrium: State reached by a reversible reaction when forward and reverse reaction rates are equal; represented in chemical equations by $\rightleftharpoons$ instead of $\longrightarrow$.
- Chemical equilibrium is said to be dynamic because reactants and products are continually being formed and re-formed.
- $\Delta_r G = 0$ for a reaction at equilibrium.

Equilibrium constant (K_{eq}): A measure of the relative amounts of reactants and products in a reaction system at equilibrium.
- For the reaction aA + bB $\rightleftharpoons$ pP + qQ,
  $K_{eq} = [P]^p[Q]^q/[A]^a[B]^b$.

Solubility product constant (K_{sp}): Equilibrium constant for the dissolution of a compound.
- For the dissolution reaction
  $A_aB_b(s) \rightleftharpoons aA^{b+}(aq) + bB^{a+}(aq)$,
  $K_{sp} = [A^{b+}]^a[B^{a+}]^b$.
- Concentrations of solids do not appear in the expression for K_{sp}.

Le Châtelier's principle: When a system at dynamic equilibrium is perturbed, the system will adjust itself to minimize the effects of the perturbation.

Concentration:
- Adding reactant to or removing product from a system at equilibrium will drive the reaction in the forward direction.
- Removing reactant from or adding product to a system at equilibrium will drive the reaction in the reverse direction.

Temperature:
- Increasing temperature will drive the reaction in the direction that is endothermic.
- Decreasing temperature will drive the reaction in the direction that is exothermic.

Pressure:
- Increasing pressure will drive the equilibrium toward the side of the reaction that has fewer moles of gas.
- Decreasing pressure will drive the equilibrium toward the side of the reaction that has more moles of gas.

Catalysts:
- Catalysts reduce the time needed for a reaction to reach equilibrium, but they do not affect the composition of the equilibrium mixture.

PHASE EQUILIBRIUM

Phase: Physically distinct state of a substance; e.g., gas, liquid, or solid.

Phase diagram: Plot showing which phase of a substance is most stable at a given combination of temperature and pressure.

Phase boundaries: Lines on a phase diagram; the two phases on either side of a phase boundary are in equilibrium (coexist) at the phase-boundary.

Triple point: Point on a phase diagram where all three phases are in equilibrium.

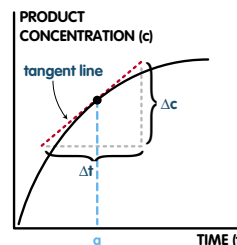**Critical point:** Temperature and pressure above which a substance cannot condense into a liquid.
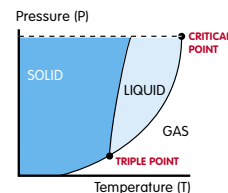
A TYPICAL PHASE DIAGRAM OF A PURE SUBSTANCE.

KINETICS

REACTION RATE

Reaction rate: The rate of change in concentration in a reactant or product over time.

Instantaneous rate: The rate of reaction at a given instant; may vary as a reaction proceeds.

GRAPH OF PRODUCT CONCENTRATION VERSUS TIME. THE INSTANTANEOUS RATE OF REACTION AT TIME a IS $\Delta c/\Delta t$.

Rate law: Equation that expresses the instantaneous rate of reaction as a function of reactant concentrations.
- Mathematically: for a reaction between A and B, rate = $k[A]^p[B]^q$.
  - k = rate constant, an experimentally determined proportionality constant.
  - [A] = concentration of A.
  - [B] = concentration of B.
  - p = reaction order in A.
  - q = reaction order in B.
- The sum of the individual reaction orders equals the overall reaction order.

Integrated rate law: Formula that gives the concentration of reactants or products at any time (t) after the start of a reaction.
- For a reaction involving a single type of compound, A:

Reaction order	Rate law	Integrated rate law
0	**Rate = k**	**$[A]_t = [A]_0 - kt$**
1	**Rate = $k[A]$**	**$\ln[A]_t = \ln[A]_0 - kt$**
2	**Rate = $k[A]^2$**	**$1/[A]_t = 1/[A]_0 + kt$**

- $[A]_0$ = initial concentration of A.

Half-life ($t_{1/2}$): Time required for the concentration of a reactant to fall to one half of its initial value.
- Calculated by substituting the value $0.5[A]_0$ for $[A]$ in the integrated rate equation and solving for t.

REACTION COORDINATE DIAGRAM

Reaction coordinate diagram: A plot of energy versus reaction progress.

Activation energy (E_a): Energy barrier that the reactants must overcome in order to react; the energy difference between the reactants and the activated complex.

Activated complex: Species intermediate between reactants and products; results from the collision of reactants; can either proceed to form products or revert to reactants.

Catalyst: A substance that lowers activation energy but is not consumed in a reaction.

TYPICAL REACTION COORDINATE DIAGRAMS FOR THE GENERIC REACTION
A + B ⟶ AB.

Exothermic Reaction

Endothermic Reaction

Uncatalyzed vs. Catalyzed Reaction
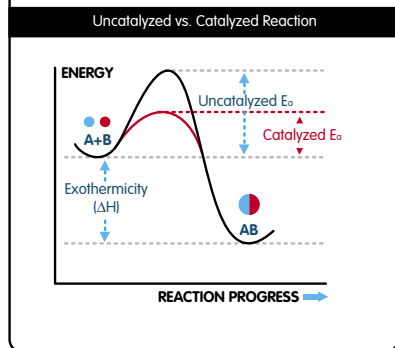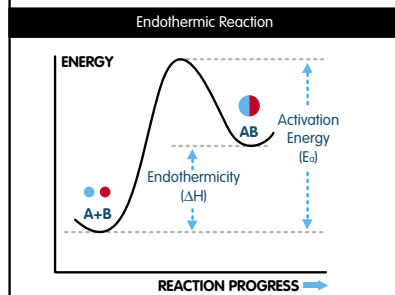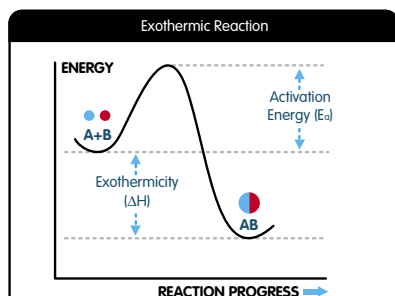
EFFECT OF TEMPERATURE ON RATE

Arrhenius equation:
$\ln k = \ln A - E_a/RT$,
- k = rate constant.
- A = frequency factor (depends on reaction).
- E_a = activation energy.
- R = ideal gas constant.
- T = temperature (K).

ACIDS AND BASES

DEFINITIONS OF ACIDS AND BASES

Arrhenius:
- *Acids*: Compounds that produce H_3O^+ in water.
- *Bases*: Compounds that produce OH^- in water.

Lewis:
- *Acids*: Electron-pair acceptors.
- *Bases*: Electron-pair donors.

Brønsted-Lowry:
- *Acids*: Proton (H^+) donors.
- *Bases*: Proton (H^+) acceptors.

Conjugate acid: For a base, B^-, its protonated form, HB, is said to be the "conjugate acid" of B^-.

Conjugate base: For an acid, HA, its deprotonated form, A^-, is said to be the "conjugate base" of HA.

**Amphiprotic species:** A compound that can both donate and accept protons.

Amphoteric species: A compound that can accept both electron pairs and protons.

Polyprotic acid: A Brønsted acid that can donate more than one proton per molecule.
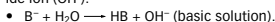
HYDROLYSIS REACTION

Hydrolysis reaction: A reaction between a Brønsted acid or base and water to produce an acidic or basic solution.

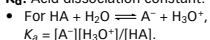A Brønsted acid can donate a proton to water to give hydronium ion (H_3O^+).
- $HA + H_2O \longrightarrow A^- + H_3O^+$ (acidic solution).
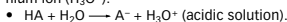
A Brønsted base can accept a proton from water to give hydroxide ion (OH^-).
- $B^- + H_2O \longrightarrow HB + OH^-$ (basic solution).

DISSOCIATION CONSTANTS

K_a: Acid dissociation constant.
- For $HA + H_2O \rightleftharpoons A^- + H_3O^+$,
  $K_a = [A^-][H_3O^+]/[HA]$.

K_b: Base dissociation constant.
- For $B^- + H_2O \rightleftharpoons BH + OH^-$,
  $K_b = [BH][OH^-]/[B^-]$.
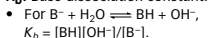
pK_a and pK_b:
- $pK_a = -\log_{10}(K_a)$.
- $pK_b = -\log_{10}(K_b)$.
- The lower the value of K_a (or K_b) the higher the value of pK_a (or pK_b).
- The higher the pK_a of a compound, the more difficult it is to deprotonate.

Strong acid (or base): An acid (or base) that ionizes completely in water; pK_a (or pK_b) < 0.

Weak acid (or base): An acid (or base) that does not ionize completely in water; pK_a (or pK_b) > 0.

Ion product constant (K_w):
- Because water is amphoteric, $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$
  $K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$ mol^2 l^{-2}.
- For any conjugate acid-base pair, $K_a \times K_b = K_w$.

pH AND pOH

pH: A measure of the acidity of a solution.
- Mathematically: $pH = -\log_{10}[H_3O^+]$.
- For an acidic solution, $pH < 7$.
- For a basic solution, $pH > 7$.

pOH: A measure of the basicity of a solution.
- Mathematically: $pOH = -\log_{10}[OH^-]$.
- For a basic solution, $pOH < 7$.
- For an acidic solution, $pOH > 7$.
- From the definition of K_w, $pH + pOH = 14$.
- For pure water, a neutral solution, $pH = pOH = 7$, since $[H_3O^+] = [OH^-] = 10^{-7}$.

Relationship between pH and pK_a:
- $K_a = [A^-][H_3O^+]/[HA]$.
- When half of the acid molecules in an aqueous solution are ionized, $[A^-] = [HA]$; as a result, $K_a = [H_3O^+]$; taking the negative logarithm of both sides of this equation gives $pK_a = pH$ when $[A^-] = [HA]$.
- If $pH > pK_a$, then $[A^-] > [HA]$.
- If $pH < pK_a$, then $[HA] > [A^-]$.

Buffer solution: Solution of a weak acid (or base) and its conjugate base (or acid) that is resistant to changes in pH; works by reacting with any added acid or base to restore the equilibrium of the weak acid (or base) and neutralize the added acid or base.
- **Henderson-Hasselbalch equation:**
  For a buffer solution of a weak acid [HA] and its conjugate base $[A^-]$,
  $pH = pK_a + \log([A^-]/[HA])$.

TITRATION

Titration: A method for determining the concentration of an acid (or base) by neutralization of a known volume of that acid (or base) with a known volume of base (or acid) at a known concentration.

Indicator: Substance used to detect the end-point of a titration, generally by changing the color of the titration mixture.

Titration curve: Plot of pH versus titrant volume.
- Shape depends on the relative strengths of the acid and base used.
- Yields information about the pK_a or pK_b values of the acid or base being titrated.
- Titration curves for polyprotic acids show multiple buffering regions and equivalence points, which indicate the stepwise manner in which polyprotic acids are deprotonated.

Equivalence point: Midpoint of the vertical part of a titration curve; indicates when the acid (or base) being titrated is exactly neutralized by the added base (or acid).

TYPICAL TITRATION CURVES FOR TITRATIONS OF ACIDS
WITH A STRONG BASE.

Strong acid titrated with strong base

Weak acid titrated with strong base

Titration of a polyprotic acid
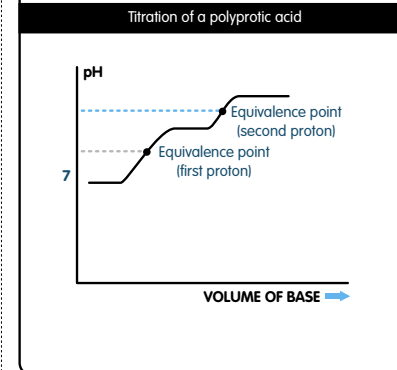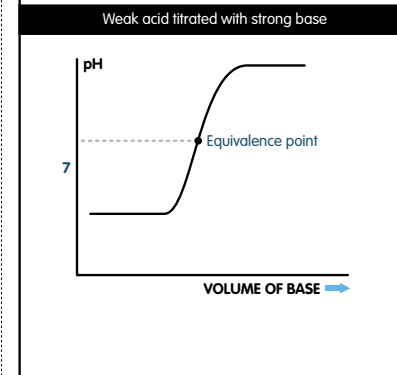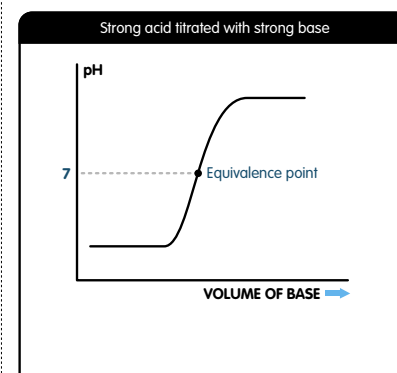
ELECTROCHEMISTRY

ELECTROCHEMISTRY

Electrochemistry: The study of chemical reactions that produce electricity, and the use of electricity to facilitate nonspontaneous chemical reactions.

Electrochemical cell: Device that uses an electrochemical reaction to generate an electric current at a constant voltage.

Voltage: Electric potential energy per unit charge.

Current: Flow of charge past a point in an electric circuit per unit time

OXIDATION AND REDUCTION

Oxidation: Electron loss; associated with an increase in oxidation number.

Reduction: Electron gain; associated with a decrease in oxidation number.

Oxidation number: The oxidation number of an atom or monatomic ion is the same as its charge.

REDOX REACTIONS

Redox reaction: A reaction in which one reactant is reduced when it oxidizes the other reactant.

Oxidizing agent: The reactant in a redox reaction that gains electrons and becomes reduced.

Reducing agent: The reactant in a redox reaction that donates electrons and becomes oxidized.

Half-reactions: Chemical equations that show oxidation and reduction separately and can be combined to give the overall equation for a redox reaction.

- **To balance half-reactions:**
  1. For each half-reaction, choose stoichiometric coefficients that balance each type of atom *except* oxygen and hydrogen.
  2. Balance oxygen by adding the appropriate number of H_2O molecules.
  3. Balance hydrogen by adding the appropriate number of H^+ ions.
     - **3a.** For reactions in basic solution, add one OH^- ion to both sides of the equation for every H^+ ion added to either side of the equation and combine H^+ and OH^- ions on the same side of the equation to give H_2O.
  4. Balance the charge of each half-reaction by adding the appropriate number of electrons to the side with the greater charge.
  5. Equalize the number of electrons in both half-reactions by multiplying each half-reaction by an appropriate integer.
  6. Add half-reactions together to obtain the overall balanced equation.

Galvanic cell: Electrochemical cell in which a spontaneous redox reaction is used to generate an electrical current.
- Reduction and oxidation occur at separate electrodes.
  - **Anode:** Negatively charged electrode; where oxidation occurs.
  - **Cathode:** Positively charged electrode; where reduction occurs.
  - The electrodes are in electrical contact through an electrolyte (ionic solution that conducts electricity), while a salt bridge maintains the balance of ion charges in each half of the cell.

Cell potential: Voltage produced by an electrochemical cell.
- **Standard cell potential** (E^o): cell potential generated by a redox reaction under standard conditions .
  - Calculated by summing the potentials for the two half-reactions of a cell.
  - The absolute potential for a half-reaction cannot be determined, but the potential for a half-reaction relative to another half-reaction can be determined; the tabulated standard potentials for half-reactions are relative to the H_2/H_3O^+ half-reaction, which is arbitrarily assigned a standard potential of zero.

- **To calculate the standard potential of a cell:**
  1. Determine the value of E^o for the reduction half-reaction.
  2. Reverse the oxidation half-reaction and determine the value of E^o for the reversed half-reaction; change the sign of E^o to obtain the standard potential for the oxidation half-reaction.
  3. Even if the stoichiometric coefficients of the half-reactions are not the same, do not multiply E^o values, as they do not depend on stoichiometry.
  4. Add the standard reduction potential and the "standard oxidation potential" to obtain the overall E^o value for the cell.

Electrolytic cell: Electrochemical cell that reverses the direction of a galvanic cell by using a supply of electricity (e.g., a battery).

Thermodynamics of redox reactions:
- Cell potential is related to $\Delta_r G$.
- Mathematically: $\Delta_r G^o = -nFE$.
  - n = moles of electrons transferred between electrodes.
  - F = Faraday constant = 96485 C mol^{-1}.
  - E = cell potential (V).

NUCLEAR CHEMISTRY

RADIOACTIVITY

Radioactivity: Emission of high-energy particles from unstable nuclei.

- α–**particles:** Helium nuclei; composed of two protons and two neutrons.
- β–**particles:** Fast-moving electrons.
- γ–**radiation:** High-frequency electromagnetic radiation.
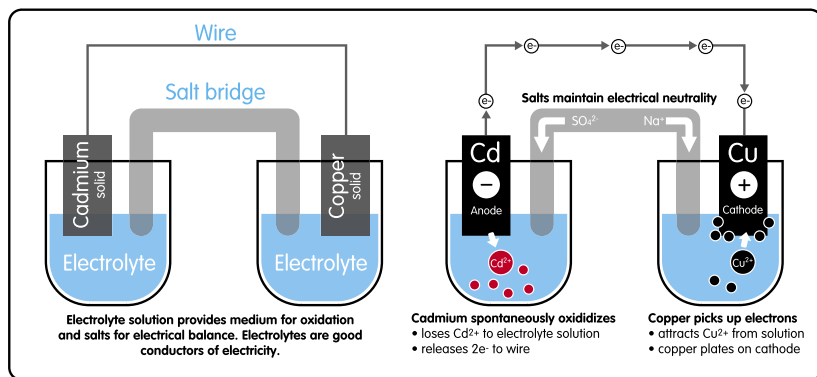
NUCLEAR REACTIONS

Nuclear decay: Breakdown of the nucleus; the origin of radioactivity.
- α–**decay:** Emission of an α–particle from the nucleus; mass number decreases by four and atomic number decreases by two.
- β–**decay:** Emission of a β–particle from the nucleus; mass number is unchanged, but atomic number increases by one.
- γ–**decay:** Emission of a γ–particle from the nucleus; does not affect mass number or atomic number of the nucleus.
- When α– or β–particles are lost, the identity of the nucleus changes (becomes a different element).
- **Half-life:** Time needed for half the radioactive nuclei in a sample to decay. Equivalent to the half-life of the first order chemical reaction.

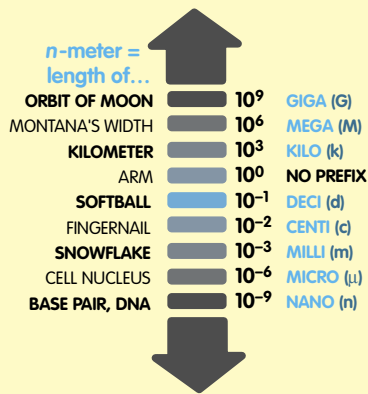**Fission:** Splitting of large, unstable nuclei into smaller, more stable ones.

Fusion: Combination of small nuclei into larger ones.

COMMON MEASUREMENTS

METRIC PREFIXES AND THEIR ABBREVIATIONS

n-meter = length of…

ORBIT OF MOON	10^9	GIGA (G)
MONTANA'S WIDTH	10^6	MEGA (M)
KILOMETER	10^3	KILO (k)
ARM	10^0	NO PREFIX
SOFTBALL	10^{-1}	DECI (d)
FINGERNAIL	10^{-2}	CENTI (c)
SNOWFLAKE	10^{-3}	MILLI (m)
CELL NUCLEUS	10^{-6}	MICRO (μ)
BASE PAIR, DNA	10^{-9}	NANO (n)

COMMON UNITS

MEASUREMENT	UNIT (AND ABBREVIATION)
Distance	meter (m)
Volume	liter (L): 1 L = 1000 cm^3
Mass	gram (g)
Time	second (s)
Energy	joule (J); 1 J = 1 kg m^2/s^2
Temperature	Kelvin (K)

TEMPERATURE SCALES

	FAHRENHEIT (°F)	CELSIUS (°C)	KELVIN (K)
Boiling point of water	212 °F	100 °C	373 K
Freezing point of water	32 °F	0 °C	273 K
Absolute zero	−460 °F	−273 °C	0 K
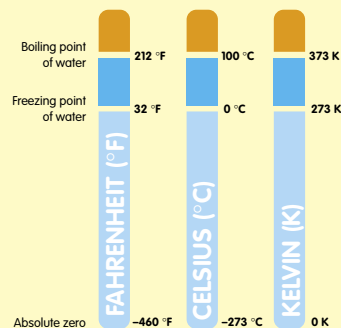
Conversion between scales:
- **Celsius to Fahrenheit:** Multiply °C by 9/5 and add 32
- **Fahrenheit to Celsius:** Subtract 32 from °C and multiply by 5/9
- **Celsius to Kelvin:** Add 273 to °C
- **Kelvin to Celsius:** Subtract 273 from K

GALVANIC CELL USING THE SPONTANEOUS REDUCTION OF Cu^{2+} BY Cd TO GENERATE AN ELECTRIC CURRENT.

Wire
Salt bridge
Cadmium solid
Copper solid
Electrolyte
Electrolyte

Electrolyte solution provides medium for oxidation and salts for electrical balance. Electrolytes are good conductors of electricity.

Salts maintain electrical neutrality
SO_4^{2-} Na^+
Cd − Anode   Cu + Cathode

Cadmium spontaneously oxidizes
- loses Cd^{2+} to electrolyte solution
- releases 2e- to wire

Copper picks up electrons
- attracts Cu^{2+} from solution
- copper plates on cathode

SPARKCHARTS™