

ATOMIC STRUCTURE, ELECTRONS, AND PERIODICITY

All matter is made of atoms. There are a limited number of types of atoms; these are the elements. (EU 1.A)

Development of Atomic Theory

Atoms are so small that they are difficult to study directly; atomic models are constructed to explain data on collections of atoms (EU 1.D). As with all scientific models, any model of the atom is subject to refinement and change, therefore atomic models are regarded as theoretical constructs that fit a set of experimental data, not as exact descriptions. (EK 1.D.1).

Know the experiments and the contributions to atomic theory of the following scientists:

- Dalton
- Thomson
- Millikan
- Rutherford
- Planck
- Einstein
- Bohr
- DeBroglie
- Schrodinger

Law of Conservation of Mass (Lavoisier): The total mass remains constant during a chemical reaction.

Law of Definite Proportions (Proust): A given compound always contains exactly the same proportions of elements by mass (ie: Because the molecules of a particular compound are always composed of the identical combination of atoms in a specific ratio, the ratio of the masses of the constituent elements in any pure sample of that compound is always the same EK.1.A.1.a).

Law of Multiple Proportions: Pairs of elements that form more than one type of molecule are nonetheless limited by their atomic nature to combine in whole number ratios. This discrete nature can be confirmed by calculating the difference in mass percent ratios between such molecule types.

Ex: The following data were collected for several compounds of nitrogen and oxygen:

	Mass of Nitrogen That Combines With 1 g of Oxygen
Compound A	3.500 g
Compound B	1.750 g
Compound C	0.8750 g

Show how these data illustrate the Law of Multiple Proportions.

Basic Atomic Structure:

- Review the subatomic particles, their charges, relative masses and locations.
- Review atomic number and mass number.
- Review ions and isotopes.

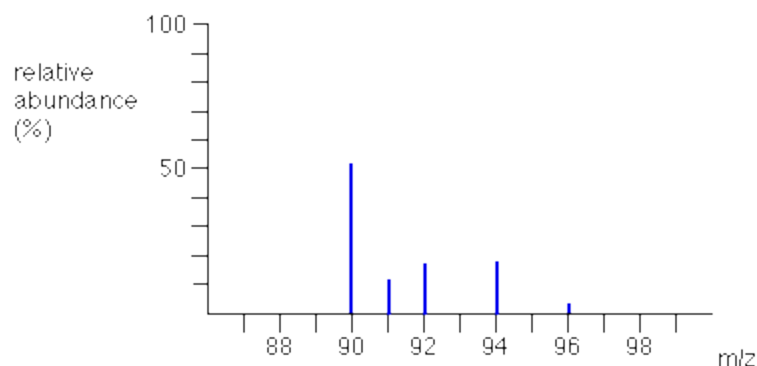
Mass Spectrometry:

- Mass spectrometer separates positive gaseous ions depending on their mass to charge ratio
- Ions are deflected into circular paths, lighter ions are deflected the most, forming tighter circles.
- Gives a mass spectrum which shows the relative number of each atom of each mass in the sample (used to determine average atomic masses).
- Data from mass spectrometry give evidence that Dalton's model of the atom is incorrect, therefore requiring a modification of the atomic model.
- Data from mass spectrometry also demonstrate direct evidence of the existence of different isotopes for the same element.

Calculating Average Atomic Mass:

Ex: A sample of naturally occurring carbon contains 98.892% carbon-12 and 1.108 % carbon-13. What is the average atomic mass of carbon?

Ex: Given the mass spectrum for zirconium (below) calculate the average atomic mass for zirconium.



zirconium-90	51.5
zirconium-91	11.2
zirconium-92	17.1
zirconium-94	17.4
zirconium-96	2.8

Electron Arrangement

- The attraction of the electrons to the nucleus is the basis of the structure of the atom. Coulomb's Law is qualitatively useful for understanding the structure of the atom (EK 1.B.1)

Coulomb's Law:

The force between 2 charged particles is proportional to the magnitude of each of the charges (q_1 and q_2) and inversely proportional to the square of the distance between them (r)

$$F = k \frac{q_1 q_2}{r^2}$$

For Chemistry, a modified version of Coulomb's Law is often used where the energy (E) of 2 stationary charged particles is given by the equation

$$E = \frac{k q_1 q_2}{r}$$

k is a positive-valued proportionality constant

q_1 and q_2 are the charges on the particles (Ex: q_1 = the + charge of the nucleus, q_2 = the charge of the electron, -1)

r is the separation of the particles (in pm) ie: the distance between them

- Note that if the two charges are of opposite sign, the value for energy is negative and they are attracted to each other; if they are of the same sign, the energy is positive and they repel each other.
- The amount of energy an electron has depends on its distance from the nucleus.

- The greater the charge of the nucleus, the more energy an electron will have.
- Coulomb's Law leads to an understanding of ionization energies and an understanding of the electron arrangements inside an atom. It will also lead to an understanding of bonding and bond lengths.

The Wave Nature of Light:

- **Wavelength (λ)** - the distance between two crests (or troughs) - measured in nm (10^{-9} m) or angstroms ($1 \text{ \AA} = 10^{-10}$ m)
- **Frequency (ν)** - the number of cycles of a wave that pass a point in a certain time - measured in hertz (Hz) - $1 \text{ Hz} = 1 \text{ s}^{-1}$.
- **Amplitude** - the height of the wave from origin to crest.
- **Speed (c)** - in a vacuum the speed of light = $2.998 \times 10^8 \text{ m s}^{-1}$
 $c = \lambda\nu$

Ex: Calculate the frequency in Hertz of an X-ray that has a wavelength of 8.21 nm.

- **Electromagnetic spectrum** - shows complete range of wavelengths and frequencies for electromagnetic radiation.
- **Continuous spectrum** - all wavelengths and frequencies (rainbow)
- **Line spectrum** - only certain wavelengths and colors represented.
- **Emission spectra** - line spectra from analyzing light emitted by elements excited by heat or electricity - unique for each element (atomic fingerprint).

Planck's Quantum Hypothesis:

- Energy can only be absorbed or emitted as a quantum (or multiples of a quantum).
- $E = h\nu$ $E = \text{energy (J)}$ $h = \text{Planck's constant } (6.626 \times 10^{-34} \text{ Js})$ $\nu = \text{frequency } (\text{s}^{-1})$

The Photoelectric Effect:

- When a photon of light with the correct energy hits the surface of a substance, an electron is ejected.
- Energy of photon : $E = h\nu$
- Energy of one mole of photons: $E = 6.022 \times 10^{23} \times h \times \nu$

Ex: Calculate the energy in joules of a photon of violet light that has a frequency of $6.15 \times 10^{14} \text{ s}^{-1}$.

Ex: Calculate the energy, in joules per photon, of ultraviolet light with a wavelength of 235 nm.

Ex: A laser produces red light of wavelength 632.8 nm. Calculate the energy, in kilojoules, of one mole of photons of this red light.

- Different types of molecular motion lead to absorption or emission of photons in different spectral regions. Infrared radiation is associated with transitions in molecular vibration and so can be used to detect the presence of different types of bonds. Ultraviolet/ visible light radiation is associated with transitions in electronic energy levels and so can be used to investigate electronic structure.

Bohr's Model of the Hydrogen Atom

- Using the quantum theory, Bohr predicted that electrons orbit the nuclei at specific fixed radii, or energy levels.
- When atoms absorb energy in the form of electromagnetic radiation, electrons jump to a higher energy level (excited state).
- When electrons drop from higher to lower energy levels (their ground state) they emit energy in the form of electromagnetic radiation.

- Since the energy level changes of electrons for a particular element are always the same, atoms can be identified by their emission and absorption spectra.

Shell Model of the Atom:

- Each electron in an atom has a different ionization energy, which can be qualitatively explained through Coulomb's Law (EK 1.B.2 a).
- In atoms with multiple electrons, the electrons can be thought of as being in "shells" and "subshells" as indicated by the relatively close ionization energies associated with some groups of electrons.
- Inner electrons are called **core electrons**.
- Outer electrons are called **valence electrons**.
- Core electrons "shield" the valence electrons from the full electrostatic attraction of the nucleus.
- Differences in electron-electron repulsion are responsible for the differences in energy between electrons in a different orbital in the same shell.



Shell model of lithium

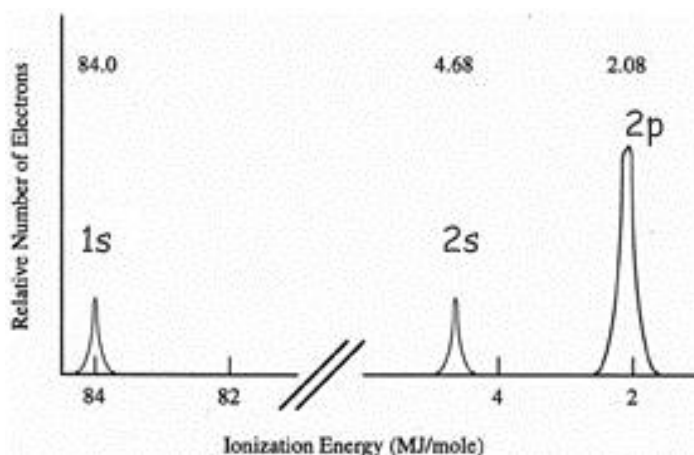
Photoelectron Spectroscopy (PES)

- Determines the energy needed to eject an electron from a material.
- Measurement of the energies gives direct evidence for the shell model of the atom.
- The intensity of the photoelectron signal at a given energy is a measure of the number of electrons in that energy level.
- The electronic structure of atoms with multiple electrons can be inferred from PES evidence.

Ionization Energy:

- The minimum energy needed to remove an electron from an atom or ion (is equivalent to the binding energy for the electron) and is measured in joules (J) or electron volts (eV).
- Coulomb's Law suggests that the farther an electron is from the nucleus, the lower its ionization energy.
- If two species have the same arrangement of electrons, then the higher the nuclear charge, the higher the ionization energy of an electron in a given subshell.

Example: PES for neon.



- Note that the higher ionization energies are to the left of the x-axis
- The relative size of the peaks gives the relative number of electrons.
- The 1s electrons are often missing from the PES diagram because their IE is so high.

Quantum Mechanical Model of the Atom

- The electronic structure of the atom can be described using an electron configuration that reflects the concept of electrons in quantized energy levels or shells; the energetics of the electrons in the atom can be understood by consideration of Coulomb's Law (EK 1.B.2)
- The currently accepted best model of the atom.
- Addresses known problems with the shell model and is consistent with electronic structures corresponding to the periodic table.
- Coulomb's Law is the basis for describing the energy of interaction between protons and electrons.
- Electron configurations provide a method for describing the distribution of electrons in an atom or ion.
- Electrons do not follow specific orbits, they are in regions of space in the atom called orbitals.
- Electrons in an atom have a spin which can result in atoms having a magnetic moment.
- Shells in an atom reflect quantization.
- Each electron has a unique set of 4 quantum numbers.
- The quantum mechanical model can be approximately solved using computers and serves as a basis for software that calculates the structure and reactivity of molecules.
- **DeBroglie's equation:** $\lambda = h / mv$ $m = \text{mass}$
- All matter exhibits wavelike behavior
- Led to development of electron microscope.
- **Schrodinger's equation** describes wave functions - gives the **probability** of finding an electron in a particular volume of space in the atom.
- **Heisenberg uncertainty principle:** We cannot determine both the position and momentum of a small particle simultaneously.

Writing Electron Configurations:

1. Electrons occupy the lowest energy level orbitals available (learn the fill order). The **Aufbau principle** describes the order.
2. No two electrons in the same atom have the same four quantum numbers (**Pauli Exclusion Principle**) ie: an orbital can hold up to two electrons and they must have opposite spins.
3. With degenerate orbitals, electrons enter empty orbitals whenever possible (**Hund's rule**). Electrons in half-filled orbitals have parallel spins.

Orbital Filling Order;

- Can be obtained from the periodic table.

Row	Orbital Filling Order
1	1s
2	2s - 2p
3	3s - 3p
4	4s - 3d - 4p
5	5s - 4d - 5p
6	6s - 4f - 5d - 6p
7	7s - 5f - 6d - 7p

spdf notation: Ex - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$

Abbreviated (noble-gas-core) Configurations: Ex: $[\text{Kr}] 5s^2$

Orbital diagrams:

- Depict each orbital as a box or straight line and each electron as an arrow.

Exceptional configurations: Cr, Mo, Cu, Ag (you are not expected to memorize exceptions for the AP Exam)

Electron Configurations of Ions:

- **Negative ions** - add the same number of electrons as the charge on the ion to the last orbital being filled.
- **Positive ions** - subtract the same number of electrons as the charge on the ion from the last orbital filled EXCEPT if the element has d orbitals, take the electrons from the last s orbital before removing them from the d orbital.

Isoelectronic Species: Have the same electron configuration. Ex: Na^+ , Mg^{2+} , Al^{3+} , F^- , Ne

Paramagnetism and Diamagnetism:

- An atom or ion is **diamagnetic** if it has no unpaired electrons. (it is weakly repelled by a magnetic field)
- An atom or ion is **paramagnetic** if it has one or more unpaired electrons (it is attracted into a magnetic field).

Ex: Which of the following would be attracted into a magnetic field:

- K, Hg, Ba^{2+} , N^- , F^- , Cu^{2+}

Periodicity

- The structure of the periodic table is a consequence of the pattern of electron configurations and the presence of shells (and subshells) of electrons in atoms.
- For many atomic properties, trends within the periodic table can be qualitatively understood using Coulomb's law, the shell model, and the concept of shielding/ effective nuclear charge.
- Periodicity is a useful tool when designing new molecules or materials; replacing an element of one group with another of the same group may give a new substance with similar properties.

You should know the definitions and periodic trends for the following:

Atomic radius

- The distance between the nuclei of two atoms
- Effective nuclear charge = actual nuclear charge- screening effect
- Smallest atomic radius is in the top right corner.

Ionic radius

- Cations are smaller than the neutral atom
- Anions are larger than the neutral atom.
- For isoelectronic species, the greater the nuclear charge, the smaller the ion.

Ionization energy

- Energy required to remove an electron from an atom or ion in its gaseous state.
- First ionization energy is lowest.

- A large increase in ionization energy occurs between the removal of the last valence electron and the removal of the first core electron.
- Highest ionization energy is in the top right.

Electron affinity

- Energy change that occurs when an electron is added to a gaseous atom.
- If EA is negative, the addition of the electron is exothermic.
- Most negative EA is in the top right corner.
- Second EA will be a positive value

Electronegativity

- The greater the electronegativity of an atom in a molecule, the more strongly it attracts the electrons in a covalent bond.
- Highest EN is in top right corner.

Metals/nonmetals/metalloids

- Most non-metallic is in top right
- Most metallic is in bottom left.
- The more readily an atom gains an electron, the more non-metallic the character.

Flame colors

- Only atoms with low first ionization energies will be excited in a Bunsen flame – those of group 1A and heavier group 2A metals.

Halogens as oxidizers

- Oxidizing agents cause other substances to be oxidized (oxidation # increases) and are themselves reduced (oxid # decreases).
- Strength as oxidizing agents decreases sharply down the group.

S block elements

- Oxidize (are reducing agents)
- Lower IE = more easily oxidized, better reducing agent.