1. Atomic Structure and Periodicity (8 hours)

1.1 The concept of the atom

Historical preview

Exploring the unseen world often relies on indirect reasoning. Useful deductions led early philosophers and scientists to make conclusions about the possible existence of atoms

Initial attempts to know composition of matter were made by Greek philosophers.

- As early as 600 B.C., philosophers developed a view that the **world** was made of a few basic "elements"—**earth, air, water, and fire**.
  - ★ **Aristotle** and **Plato**
    - Believed that matter is infinitely divisible
  - ★ **Democritus** and **Lucretius** (300 BC)
    - Proposed that matter consists very small, indivisible particles called '**atoms'** (meaning indivisible)
    - Limitation of Democritus atomic theory
      - ⇨ The ideas were not widely accepted due to lack of experimental evidences.
        - ✓ only theoretical views
      - ⇨ Does not have any information about subatomic particles (electron, proton and neutron)
- Antoine **Lavoisier** (1774) From his repeated measurements, he concluded that
  - The total mass of substances present after a chemical reaction is the same as the total mass of substances before the reaction.
  - the *total mass of the reactants is equal to the total mass of the products*.
    - ⇨ matter is neither created nor destroyed in a chemical reaction.
      - ↳ the law of conservation of mass.
  - ⇨ laid the experimental foundation of modern chemistry.
- ⇨ Joseph **Proust** (1799) studied the composition of various minerals
  - ⇨ the components of the compound were always present in the same ratio, by mass.
    - ⇨ law of definite composition, or law of constant composition

Dalton's Atomic Theory

- John **Dalton** (1766-1844),
    - His findings were based on
        - ⇨ experiments or experimental observations and
        - ⇨ laws of chemical combination
            - ✓ basis of an atomic theory
                - ↳ Law of conservation of mass
                - ↳ Law of constant or definite composition
                - ↳ Law of multiple proportions
    - Proposed Dalton's Atomic Theory
        - ⇨ the theory involves many assumptions/ postulates

        a) All matter is composed of tiny, indivisible particles called "atoms" (meaning indivisible).
            - ⇨ An atom is an extremely small particle of matter that retains its identity during chemical reactions

        b) Atoms of the same element are identical but, atoms of different elements are different (in size, mass and other properties)
            - ⇨ doesn't recognize isotopes

        c) Atoms are indivisible, they can neither created nor destroyed

        d) Atoms take part in chemical reactions

        e) An **element** is a type of matter composed of only one kind of atoms

        f) Atoms of different elements combine in a definite ratio to form **compounds**

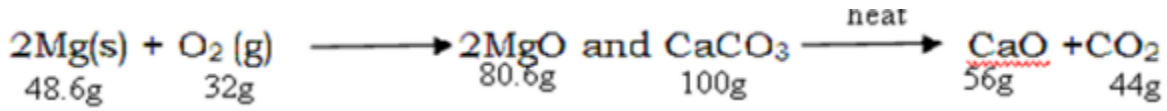
Laws of Chemical Combination

Various chemical reactions take place according to certain laws, known as the Laws of chemical combination. There are three common laws of chemical combinations

A. **Law of conservation of mass/the law of mass action:**

- states that "**matter** is neither created nor destroyed in the course of chemical reaction rather it may change from one form to other".

⇨ “During any physical or chemical changes, the total mass of product equals to the total mass of reactants”



$2Na + Cl2 \rightarrow 2NaCl,$

$2x23+2x35.5=117 \rightarrow 2(23+35.5)=117$

B. Law of constant or **definite composition:**

states that in a given **compound**, the constituent elements are always combined in the same proportions by mass, regardless of the origin or mode of preparation of the compound.

⇨ when elements react chemically, they combine in specific proportions, not in random proportions.

Example 1: A sample of **pure water** which obtains from river, sea, well, spring whatever the source, always contains **88.9%** by mass of **oxygen** and **11.1%** by mass of **hydrogen**.

Example 2: If we analyze the composition of two different samples of iron(II) sulfide or FeS, we find that their mass ratios are identical

Result from Analysis of Two Samples of Iron(II) Sulfide

⇨ Sample A: Compound mass = 42.0 g
⇨ Sample B: Compound mass = 100.0

Mass Ratios

⇨ Sample A: 26.7 g Fe/15.3 g S = 1.74:1.00 → ratio of g Fe to g S
⇨ Sample B: 63.5 g Fe/36.5 g S = 1.74:1.00 → ratio of g Fe to g S

Exercises

1. Suppose that you collected two samples of pure bottled water.

   a. If you separated the water into hydrogen and oxygen and obtained the following results, what would you report as the ratio of the mass of oxygen to that of hydrogen in each sample?

Sample 1: 37.3 g of oxygen; 4.67 g of hydrogen

Sample 2: 69.3 g of oxygen; 8.67 g of hydrogen

b. Do these data support the law of definite composition?

c. If you obtained another sample of water and found it to contain 17.0 g of oxygen, how many grams of hydrogen would you expect to obtain?

C. Law of multiple proportions:

states that when two elements A and B combine to form more than one chemical compound then different weights of A, which combine with a fixed weight of B, are in proportion of simple whole numbers. Or

when two/more elements combine to form two/more compounds, the mass of one element combines with a fixed mass of another element.

Example 3:

- ✓ Carbon monoxide (CO): 12 parts by mass of carbon combines with 16 parts by mass of oxygen.
- ✓ Carbon dioxide (CO_2): 12 parts by mass of carbon combines with 32 parts by mass of oxygen.
    - Ratio of the masses of oxygen that combines with a fixed mass of carbon (12 parts) is 16: 32 or 1: 2

Model:

A **model** is a representation of a system in the real world. **Atomic model** represents what the structure of an atom could look like, based on what we know about how atoms behave. It is not necessarily a true picture of the exact structure of an atom.

Dalton model is known as the solid sphere model (like billiard balls)



Dalton's concept of the atom as the "billiard ball model; (the model of the atom in 1809). The atom, as Dalton pictured it, was a tiny, solid, indestructible sphere.

Limitations of Dalton's atomic theory

- ✓ Dalton considered atoms to be the ultimate particles of matter
  - Does not have any information on subatomic particles (electron, proton and neutron).
  - Does not include the existence of the nucleus
  - Does not explain the existence of ions or isotopes
- ✓ It does not explain why do atoms of same element combine with each other.
- ✓ The low of definite proportion fails if different isotopes are involved.

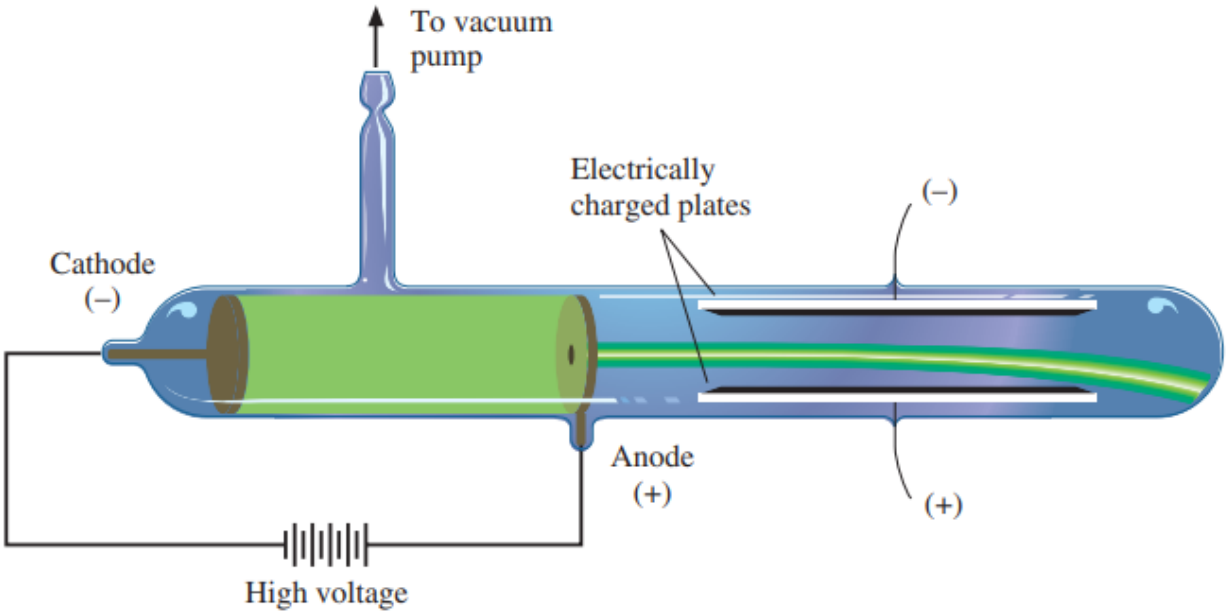
1.2 Discoveries of subatomic particles

Although Dalton had postulated that atoms were **indivisible** particles, experiments conducted around the beginning of the last century showed that atoms themselves consist of particles. These experiments showed that an atom consists of two kinds of particles:

- ★ A **nucleus**,
  - the atom's central core,
  - is positively charged and
  - contains most of the atom's mass.
- ★ An **electron**
  - is a very light,
  - is negatively charged particle
  - exists in the region around the atom's positively charged nucleus.

1.2.1 Discovery of the Electron—Thomson's cathode rays experiment

1897 the British physicist J. J. Thomson conducted a series of experiments that showed that atoms were not indivisible particles.



A cathode-ray tube Gas discharge tube

Apparatus used: gas discharge tube (made of hard glass fitted with metal electrodes) with high voltage. In this apparatus, two electrodes from a high-voltage source are sealed into a glass tube from which the air has been evacuated.

- The negative electrode is called the **cathode**;
- the positive electrode is called the **anode**.

★ At normal pressure, the gas remains non-conducting

★ When pressure is reduced (10^{-2} - 10^{-3} mm hg), the gas becomes conducting

- When the high-voltage current is turned on,
  - ✓ light is emitted by the residual gas in the discharge tube.
  - ✓ The color of light depends upon the nature of the residual gas used.

★ At very low pressure (10^{-2} - 10^{-4} mm Hg), the glass tube emits a greenish light. Experiments showed that this greenish light is caused by the interaction of the glass with cathode rays, which are rays that originate from the cathode

- After the cathode rays leave the negative electrode, they move toward the anode, where some rays pass through a hole to form a beam

★ . This beam bends ***away from the negatively charged plate*** and ***toward the positively charged plate.***

★ From his experiments, Thomson could also calculate the ratio of the electron's mass, me, to its electric charge, e^-.

In 1909 the U.S. physicist Robert Millikan performed a series of ingenious experiments in which he obtained the charge on the electron by **oil-drop experiment**

★ From this experiment,
  - the charge on the electron is found to be 1.602×10^{-19} coulombs
  - mass of an electron is 9.109×10^{-31} kg

Properties of cathode rays

1. Cathode rays travel from the negatively charged electrode to the positively charged electrode
2. The particles that compose the cathode rays travel in straight lines
3. Cathode rays are independent of the composition of the material from which they originate
4. Cathode rays are composed of particles carrying a negative electrical charge

Conclusion: Thomson concluded that

- atoms of any element can be made to emit tiny negative particles
  - ⇨ cathode ray particles are present in all types of matter
  - ⇨ all atoms must contain these negative particles
- cathode rays are composed of stream of negatively charged particles called **electrons**.
  - ⇨ atoms do contain subatomic particles – or
  - ⇨ atoms are divisible into smaller particles.

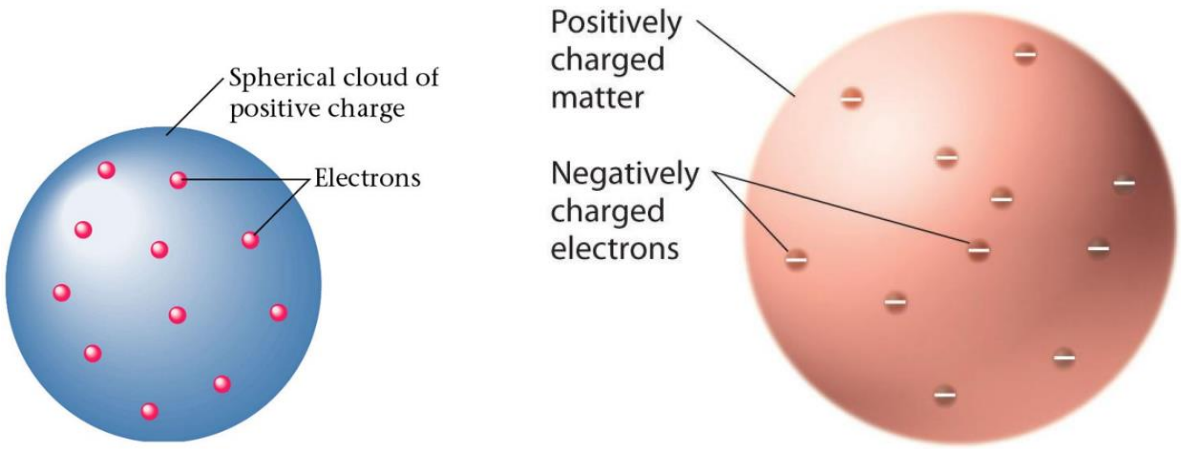
J.J.Thomson measured the **charge to mass ratio** of the cathode ray particle by deflecting them using electric and magnetic fields

⇨ The charge to mass ratio of cathode ray particles does not depend on the nature of the **residual gas** and the **cathode material** used

Robert Millikan: performed an "**oil-drop experiment**" to determine an accurate value for the **charge** (and therefore the mass also) of the electron.

Thomson provided the first model of the structure of the atom, known as the **plum pudding model**

- ⇨ States that negative electrons were embedded into a positively charged spherical cloud.



The plum pudding model of the atom.

Thomson viewed the atom as a positively charged sphere embedded with sufficient numbers of electrons to balance (neutralize) the total charge; (the atomic model in 1903).

- ↳ in this model, the entire sphere carries a uniform, positive charge.

Self-Assessment Exercises

1. Explain the operation of a cathode-ray tube. Describe the deflection of cathode rays by electrically charged plates placed within the cathode-ray tube. What does this imply about cathode rays?
2. Explain Millikan's oil-drop experiment.

1.2.2. Radioactivity

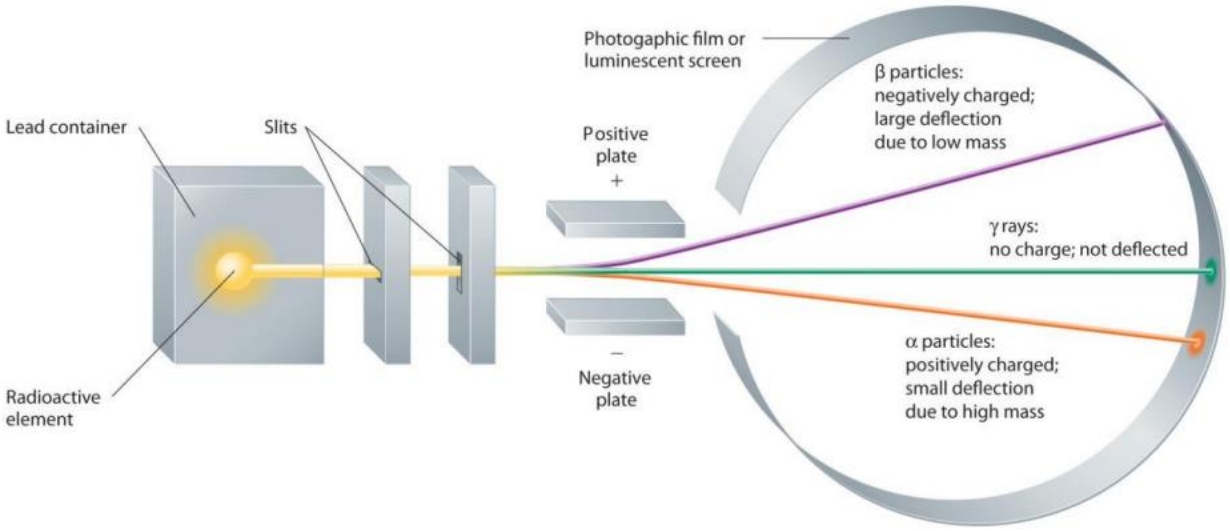
Radioactivity is the spontaneous emission of radiation from the **unstable nuclei** of certain isotopes. Isotopes that are radioactive are called radioactive isotopes or radioisotopes. For example,

$^{55}_{24}Cr$, $^{226}_{88}Ra$, $^{14}_{6}C$, $^{238}_{92}U$

three types of rays emitted from radioactive substances are

i. **alpha (α) particles** are known to be a doubly-ionized helium atom, that is, He^{2+}
ii. **beta (β) particles** are known to consist of negatively-charged particles
iii. **gamma (γ) ray** is a form of electromagnetic radiation much like the X-rays but of even higher energy.
    - ⇨ unlike alpha and beta particles, gamma rays are a form of energy and not a form of matter.

Effect of an Electric Field on α Particles, β Particles, and γ Rays

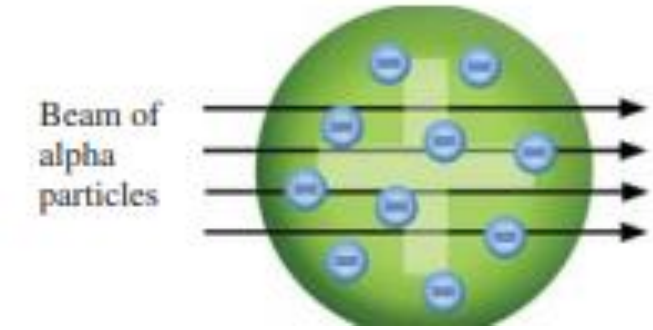


1.2.3. Discovery of Nucleus— Rutherford's *α*-particles scattering experiment

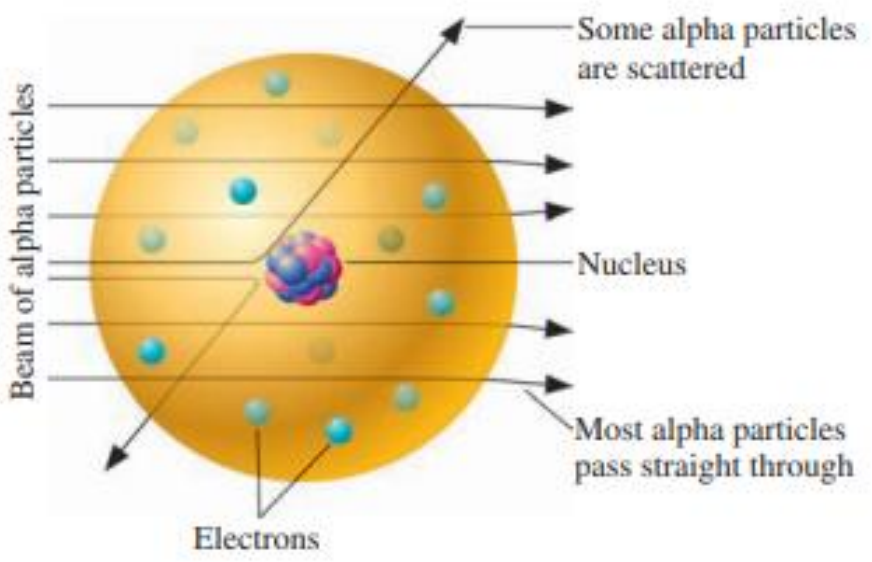
Rutherford carried out a series of experiments using very thin foils of gold and other metals as targets for α-particles from a radioactive source. **Alpha particles** are much **lighter** than **gold atoms**. (Alpha particles are helium nuclei.)

Expectation

- Based on Thomson's plum-pudding model, Rutherford expected that most particles in a beam of α-particles would pass through thin sections of matter largely **undeflected**, but that some α-particles would be **slightly scattered or deflected** as they encountered **electrons**. By studying these scattering patterns, he hoped to deduce something about the distribution of electrons in atoms.



If the **plum pudding model** of the atom were accurate, a beam of massive alpha particles would penetrate right through the atom with little or no deflections.



Observation/ Explanation

- The majority of particles penetrated the foil undeflected by the lightweight electrons.
  - ⇨ undeflected straight-line paths exhibited by most of the particles
- Some particles experienced slight deflections.
  - ⇨ slight deflections of particles passing close to electrons
- A few (about 1 in every 20,000) suffered rather serious deflections as they penetrated the foil.
  - ⇨ severe deflections of particles passing close to a nucleus
- A similar number did not pass through the foil at all, but bounced back in the direction from which they had come.\
  - ⇨ reflections from the foil of particles approaching a nucleus head-on
  - ⇨ The observation that some of the alpha particles were deflected backward implied that the positive charge in the atom must be confined to a **highly dense region** inside the atom known as the nucleus

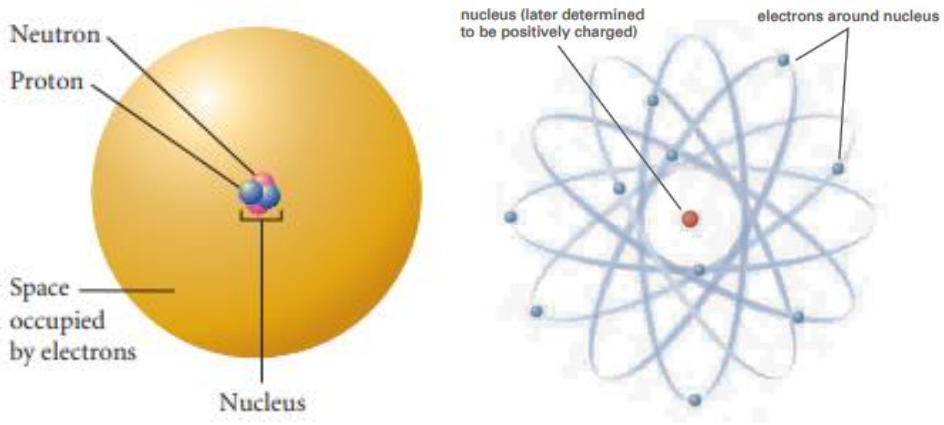
Explanation/conclusion

- Most of the mass and all of the positive charge of an atom are centered in a very small region called the ***nucleus***. The remainder of the atom is mostly ***empty space***.

- The magnitude of the positive charge is different for different atoms and is approximately one-half the atomic weight of the element.
- There are as many electrons outside the nucleus as there are units of positive charge on the nucleus. The atom as a whole is electrically neutral.
- When an alpha particle does happen to hit a metal-atom **nucleus**, however, it is scattered at a wide angle because **it is deflected by the massive, positively charged nucleus**

In 1919, Rutherford discovered that hydrogen nuclei, or what we now call **protons**, form when alpha particles strike some of the lighter elements, such as nitrogen.

- A **proton** is a nuclear particle having a **positive charge** equal to that of the electron and a mass more than 1800 times that of the electron
    - ⇨ His explanation led to a new model of the atom in which a small region of very concentrated positive charge existed within a large area of mostly empty space containing negatively charged electrons
        - ⇘ According to **Rutherford's model**, most of the mass of the atom (99.95% or more) is concentrated in a positively charged center, or nucleus, around which the negatively charged electrons move.



Rutherford's model of the atom or the nuclear model of the atom

- ⇨ The atomic model in 1911, disk-shaped model with electrons orbiting a positively charged nucleus

Self-Assessment Exercises

1. Describe the nuclear model of the atom. How does this model explain the results of alpha-particle scattering from metal foils?

2. Explain the important distinctions between each pair of terms:

    (a) cathode rays and X-rays

    (b) protons and neutrons

    (c) nuclear charge and ionic charge

3. Cathode rays

    (a) may be positively or negatively charged

    (b) are a form of electromagnetic radiation similar to visible light

    (c) have properties identical to particles

    (d) have masses that depend on the cathode that emits them

4. The scattering of particles by thin metal foils established that

    (a) the mass of an atom is concentrated in a positively charged nucleus

    (b) electrons are fundamental particles of all matter

    (c) all electrons carry the same charge

    (d) atoms are electrically neutral

5. Which of the following have the same charge and approximately the same mass?

    (a) an electron and a proton;

    (b) a proton and a neutron;

    (c) a hydrogen atom and a proton;

    (d) a neutron and a hydrogen atom;

(e) an electron and an ion

1.2.4. Discovery of Neutrons —*α*-particles scattering experiment

When beryllium metal is irradiated with alpha rays, a strongly penetrating radiation is obtained from the metal.

In 1932 the British physicist James Chadwick (1891–1974) showed that this penetrating radiation consists of neutral particles, or neutrons.

- ⇨ The **neutron** is a nuclear particle having a mass almost identical to that of the proton but no electric charge
- ⇨ When beryllium nuclei are struck by alpha particles, neutrons are knocked out.

Table 1 Properties of the proton, electron and neutron.

		Proton	Electron	Neutron
Charge	C	$+1{:}602 \times 10^{-19}$	$-1{:}602 \times 10^{-19}$	0
Charge number (relative charge)		+1	−1	0
Rest mass	kg	$1{:}673 \times 10^{-27}$	$9{:}109 \times 10^{-31}$	$1{:}675 \times 10^{-27}$
Relative mass	amu	$1.0073 \approx 1$	$1/1837=0.0005486$	$1.0087 \approx 1$

1.2.5. Atomic Number, Mass number, and Isotopes

Atomic number (Z). is the number of protons in the nucleus of an atom

- ⇨ The identity of the atom is determined by the quantity of protons in the nucleus
  - ⇨ Z value determines the identity of the atom.
- ⇨ A neutral atom must contain the same number of positive and negative charges, so the number of protons equals the number of electrons.

Mass number (A) (or nucleon number) is the total number of protons and neutrons in a nucleus of an atom. The number of neutrons is therefore the difference between the mass number and the atomic number: A – Z = number of neutrons.

⇨ $A - Z = n$

⇨ Atoms are electrically neutral if they contain the same number of positively charged protons and negatively charged electrons. When the numbers of these subatomic particles are not equal, the atom is electrically charged and is called an ion.

A **nuclide** is an atom characterized by a definite atomic number and mass number. A **shorthand notation** of nuclide lists the symbol for the element, accompanied by the atomic number and the mass number of the atom.

mass number → $^{A}_{Z}E$ ← atomic number

element symbol →

e.g. $^{59}_{27}Co$

Isotopes

⇨ are atoms whose nuclei have the **same atomic number** but different mass numbers;

⇨ that is, the nuclei have the **same number of protons** but **different numbers of neutrons**.

Isotopes of an element have the same atomic number, Z, but different atomic masses, A.

⇨ isotopes behave in the same way during chemical reactions because they have the same number of electrons on their outer shell

Nuclide Notation	Relative Natural Abundance (%)	Name of Isotope	Protons	Neutrons	Electrons
$^{1}_{1}H$	99.985%	hydrogen	1	0	1
$^{2}_{1}H$	0.015	deuterium	1	1	1
$^{3}_{1}H$	10^{-18}	tritium	1	2	1
$^{12}_{6}C$	98.93	carbon-12	6	6	6
$^{13}_{6}C$	1.07	carbon-13	6	7	6
$^{14}_{6}C$	2×10^{-10}	carbon-14	6	8	6
$^{16}_{8}O$	99.762	oxygen-16	8	8	8
$^{17}_{8}O$	0.038	oxygen-17	8	9	8
$^{18}_{8}O$	0.200	oxygen-18	8	10	8

Element	Symbol	Atomic No.	No of Protons	No of Neutrons	Mass (amu)	% Natural Abundance
Lithium	$^{6}_{3}Li$	3	3	3	6.0151	7.59
	$^{7}_{3}Li$	3	3	4	7.0160	92.41
Berylliu m	$^{9}_{4}Be$	4	4	5	9.0122	100
Boron	$^{10}_{5}B$	5	5	5	10.0129	19.9
	$^{11}_{5}B$	5	5	6	11.0093	80.1
Carbon	$^{12}_{6}C$	6	6	6	12.0000	98.89
	$^{13}_{6}C$	6	6	7	13.0034	1.11
	$^{14}_{6}C$	6	6	8	14.0032	— (trace)

Self-Assessment Exercises

1. Fill in the information missing from the following table:

Isotope	Protons	Neutrons	Electrons	Charge
carbon-12		6	6	0
	13	14	10	
chlorine-35		18		−1
calcium-40	20		18	
	14	14		0
sulfur-32		16	14	

2. Which of the following are isotopes of Cl-35? (a) $^{17}_{35}Cl$ (b) $^{35}_{17}Cl$ (c) $\mathrm{Cl}^{37}_{17}Cl$
3. Indicate whether each of these phrases describes the proton, neutron, or electron. (You may need to assign more than one term to each phrase.)
    a. Determines the identity of an atom.

b. Has about the same mass as a proton.

c. The number of particles can be changed without changing the identity of the atom.

Ans. a. proton; b. neutron; c. neutrons or electrons

4. Assume that an atom contained 1 proton and 1 electron. By what percentage would the mass of this atom increase if 10 electrons were added to the atom?

Ans. 0.54%

5. In a neutral atom, the number of electrons must equal the number of protons. However, if an atom had two more protons than electrons, what would you report as its charge? Would this ion be called an anion or a cation?

Ans. +2, cation

6. Explain the meaning of each of the following terms: (a) nucleus (b) electron (c) atomic mass
7. For the element ${}^{234}_{92}U$ (uranium), use standard notation to describe:

a) the isotope with 2 fewer neutrons

b) the isotope with 4 more neutrons

1.2.6. Relative atomic mass

The mass of an atom is expressed in atomic mass units.

Atomic mass units are a relative measure, defined by the mass of carbon-12.

One atomic mass unit (amu or u) is a mass unit equal to exactly one-twelfth the mass of a carbon-12 atom

- Note: 1/12 of the mass of one carbon-12 atom = 1 amu
- The actual value of 1 atomic mass unit is 1.67 x 10−24g or 1.67 x 10−27kg

The masses of all other atoms are defined by their relationship to carbon-12. For example, oxygen-16 has a mass that is 133% of the mass of carbon-12. Hence the mass of an atom of oxygen-16 is 133/100 × 12.000 u =**16.0 amu** = **16.0 u**.

Relative atomic mass is the average mass of all the naturally occurring isotopes of a particular element, (symbol A_r)

- ⇨ is the average mass of the naturally occurring isotopes of an element
- ⇨ average of the masses of all the element's isotopes
  - ⇘ expressed in **atomic mass units**
- ⇨ is the mass that is given for each element in the **periodic table**

On this modern scale, the atomic mass of an element is **the average atomic mass for the naturally occurring element, expressed in atomic mass units**.

$$A_r = \frac{\text{average mass of isotopes of the element}}{\frac{1}{12} \times \text{mass of 1 atom of carbon-12}}$$

$$\text{average mass} = \sum_i (\text{fractional abundance} \times \text{isotopic mass})_i$$

Isotopic abundance is the relative amount in which each isotope is present in an element

- ⇨ is the a **percent** or **fraction** of the total number of atoms that is composed of a particular isotope.
- ⇨ It can be expressed as a percent or as a decimal fraction
  - ⇘ **Percentage or fractional abundance**

Example-1: chlorine has two isotopes:

	$^{35}_{17}Cl$	$^{37}_{17}Cl$
% abundance	75	25

Hence the 'average mass' or A_r of a chlorine atom is:

$$\frac{(75 \times 35) + (25 \times 37)}{75 + 25} = 35.5$$

$$A_r = \frac{35.5}{1} = 35.5 \text{ amu}$$

Example-2: Calculate the relative atomic mass of naturally occurring magnesium if the distribution of isotopes is 78.7% $^{24}_{12}Mg$, 10.1% $^{25}_{12}Mg$, and 11.2% $^{26}_{12}Mg$,, and the accurate masses of the isotopes are 24.0, 25.0 and 26.0.

$$\text{Relative atomic mass} = \left(\frac{78.7}{100} \times 24.0\right) + \left(\frac{10.1}{100} \times 25.0\right) + \left(\frac{11.2}{100} \times 26.0\right)$$ the relative atomic mass =**24.3 amu**

Self-Assessment Exercises

1. There are two isotopes of lithium found on earth. Isotope ^{6}Li (6.01512 mu) accounts for 7.42% of the total, and isotope ^{7}Li (7.01600 mu) accounts for the remaining 92.58%. What is the average atomic mass of lithium?

The Modern Atomic Theory

i. All matter is made up of tiny particles called atoms. Each atom is made up of smaller subatomic particles: protons, neutrons, and electrons
   - Although an atom is divisible, it is still the smallest particle of an element that has the properties and identity of the element

ii. The atoms of one element cannot be converted into the atoms of any another element by a chemical reaction
   - **Nuclear reactions** (changes that alter the composition of the atomic nucleus) may, in fact, convert atoms of one element into atoms of another.

iii. Atoms of one element have the same properties, such as average mass and size. These properties are different from the properties of the atoms of any other element
   - Different isotopes of an element have different numbers of neutrons and thus different masses. scientists treat elements as if their atoms have an average mass.

iv. Atoms of different elements combine in specific proportions to form compounds
   - This idea has remained basically unchanged.

Self-Assessment Exercises

1. Cathode rays

    (a) may be positively or negatively charged

    (b) are a form of electromagnetic radiation similar to visible light

    (c) have properties identical to particles

    (d) have masses that depend on the cathode that emits them

2. The scattering of particles by thin metal foils established that

    (a) the mass of an atom is concentrated in a positively charged nucleus

    (b) electrons are fundamental particles of all matter

    (c) all electrons carry the same charge

    (d) atoms are electrically neutral

3. Briefly describe

    (a) the law of conservation of mass

    (b) Rutherford s nuclear atom

    (c) weighted-average atomic mass

4. Explain the important distinctions between each pair of terms:

    (a) cathode rays and X-rays

    (b) protons and neutrons

5. When 10.0 g zinc and 8.0 g sulfur are allowed to react, all the zinc is consumed, 14.9 g zinc sulfide is produced, and the mass of unreacted sulfur remaining is

    (a) 2.0 g (b) 3.1 g (c) 4.9 g

    (d) impossible to predict from this information alone

6. Which of the following have the same charge and approximately the same mass?

    (a) an electron and a proton;

    (b) a proton and a neutron;

    (c) a hydrogen atom and a proton;

    (d) a neutron and a hydrogen atom;

    (e) an electron and an H^- ion.

7. Atom **A** has 5 protons and 5 neutrons, and atom **B** has 6 protons and 5 neutrons. These atoms are...

    (a) allotropes (b) isotopes (c) isomers

(d) atoms of different elements

8. What is the correct symbol for the species that contains 18 neutrons, 17 protons, and 16 electrons?
9. Compare protons, neutrons, and electrons in terms of their charge, their mass, and their size.
10. Explain the difference between an atom and an element.
11. The two stable isotopes of boron exist in the following proportions: 19.78% $^{10}_{5}B$ (10.01 u) and 80.22% $^{11}_{5}B$ (11.01 u). Calculate the average atomic mass of boron.

1.3 The Bohr Theory of the hydrogen atom

Rutherford's atomic model solved problems inherent in **Thomson's atomic model**, but it also raised others.

Limitations/ Problems with Rutherford's atomic model**:**

a) Rutherford's nuclear atom could not adequately explain the **total mass** of an atom.
b) Rutherford's atomic model contradict the laws of physics.
   - an electron in motion around a central body must continuously give off radiation (lose energy). As a result of this radiation, the radius of its orbit should continuously decrease in size until it spirals into the nucleus.
c) it could not explain the very interesting observation that atoms only emit light at certain wavelengths or frequencies

Rutherford's model allows electrons to **move anywhere** within the volume of space around the nucleus. Bohr's atomic model, however, imposes certain **restrictions on the movement and energy of** electrons**.** Bohr's atomic model pictures electrons in **orbit** around a central nucleus. ***Assumptions of Bohr's atomic model:***

1. The atom has only specific, allowable energy levels, called stationary states (orbit or shell). Each stationary state corresponds to the atom's electrons occupying fixed, circular orbits around the nucleus.

$$E_n = -\frac{R_H}{n^2} = -2.18 \times 10^{-18}\text{J}\left(\frac{1}{n^2}\right) \qquad \text{n} = 1, 2, 3, \ldots \text{(for H atom)}$$

Here n is called the principal quantum number

$$E_1 = -\frac{R_H}{1^2} = -R_H = -2.18 \times 10^{-18}\text{J} = -13.6\text{ eV}$$

$$E_2 = -\frac{R_H}{2^2} = -2.18 \times 10^{-18}\text{J}\left(\frac{1}{4}\right) = -0.545 \times 10^{-18}\text{J} = -13.6\text{ eV}\ \left(\frac{1}{4}\right)$$

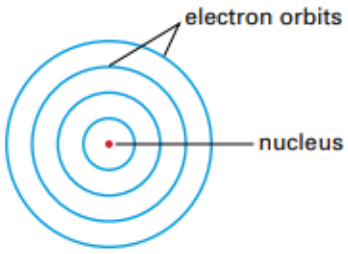
$$E_3 = -\frac{R_H}{3^2} = -2.18 \times 10^{-18}\text{J}\left(\frac{1}{9}\right) = -0.242 \times 10^{-18}\text{J} = -13.6\text{ eV}\ \left(\frac{1}{9}\right)$$

2. While in one of its stationary states, atoms do not emit energy. That is, even though it violates the ideas of classical physics, the atom does not change energy while the electron moves within an orbit.
3. An atom changes stationary states by emitting or absorbing a specific quantity of energy that is exactly **equal to the difference in energy** between the two stationary states.
   - The electron moves to another stationary state (orbit) only by absorbing or emitting a photon whose energy equals the difference in the energy between the two states.

$$E_{photon} = h\nu = \Delta E = E_{final} - E_{initial} = -2.18 \times 10^{-18}\text{J}\left(\frac{1}{n^2{}_{final}} - \frac{1}{n^2{}_{initial}}\right)$$

The subscripts f and i represent the final and the initial states, respectively.

- If an electron **jumps down** from a higher energy level to a lower energy level, then **light is emitted** from the atom.
- The **energy of the light emitted** is the same as the **gap in the energy** between the two energy levels.



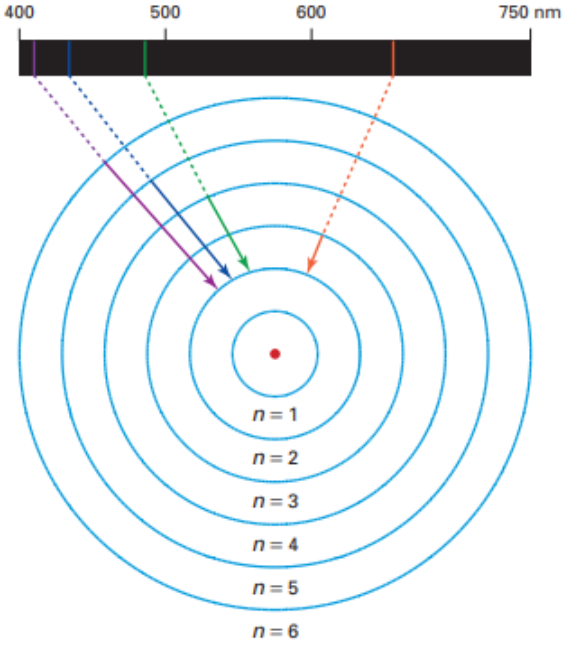
The Bohr Atomic Model. The model of the atom in 1913. The Bohr Atomic Model

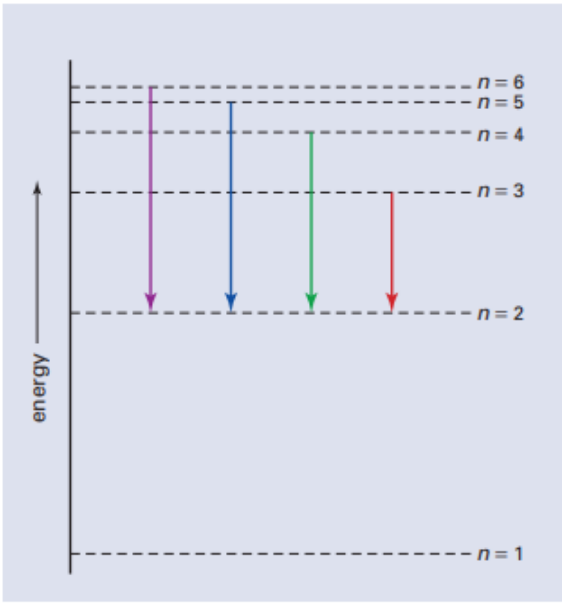
Self-Assessment Exercises

1. Of the following possible transitions of an electron in a hydrogen atom, which emits light of the highest energy?
    a) Transition from the n = 1 to the n = 3 level
    b) Transition from the n = 1 to the n = 2 level
    c) Transition from the n = 3 to the n = 1 level
    d) Transition from the n = 2 to the n = 1 level
    e) Transition from the n = 5 to the n = 4 level
2. A hydrogen atom with an electron in its ground state interacts with a photon of light with a wavelength of 1.22 x10^{-6} m. Could the electron make a transition from the ground state to a higher energy level? If it does make a transition, indicate which one. If no transition can occur, explain.

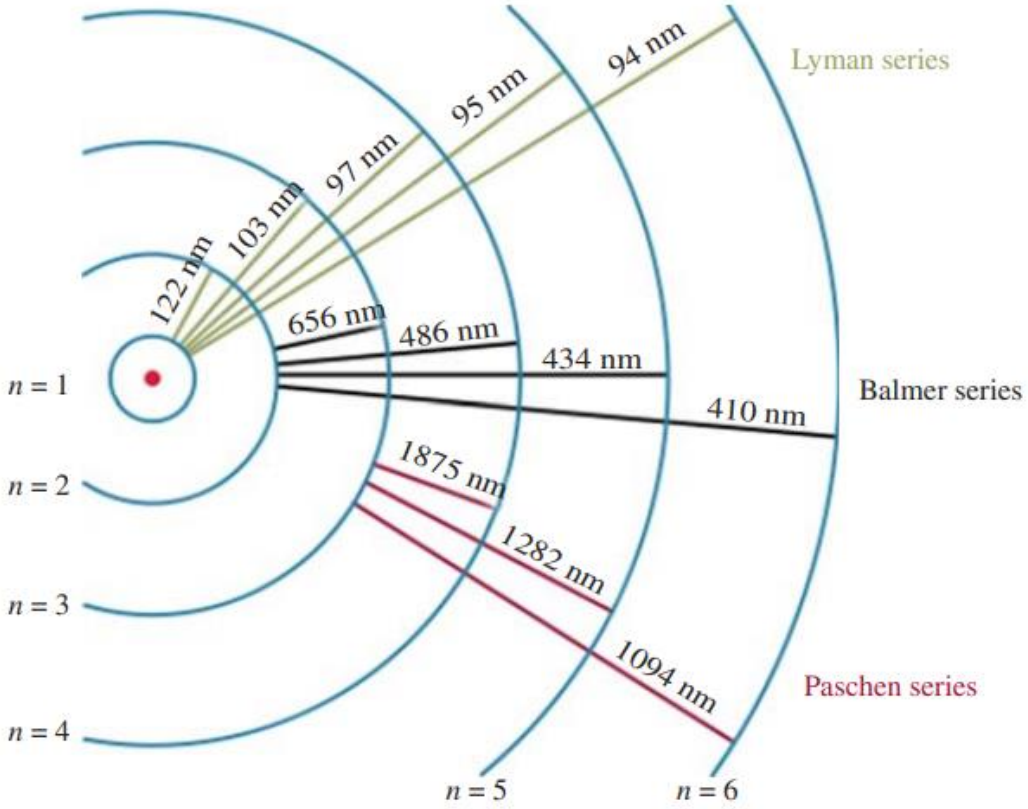
How Bohr's Atomic Model Explains the Spectrum for Atomic Hydrogen

When the electron of a hydrogen atom that has been excited to the third energy level falls to the second energy level, it emits light of certain energy. Specifically, an electron that makes a transition from the third energy level to the second energy level emits a photon of red light with a wavelength of 656 nm. Because line spectra result when atoms in an excited state emit photons as they fall to a lower energy level, these spectra are also called emission spectra.





When an excited electron falls from a higher energy level to a lower energy level (shown by the downward-pointing arrows), it emits a photon with a specific wavelength that corresponds to one of the coloured lines in the spectrum



According to the Bohr model of the atom, the lines in the emission spectrum of hydrogen result from transitions between stationary orbits. The first several transitions and their corresponding wavelengths are shown for each series of lines in the line spectrum of hydrogen

Limitations of the Bohr Atomic Model

1. it successfully explained only one-electron systems. That is, it worked fine for hydrogen and for ions with only one electron, such as He^{+}, Li^{2+}
    - Bohr's model was unable, however, to explain the emission spectra produced by atoms with two or more electrons
    - Mathematically, Bohr's model fails to explain electronic repulsions in multielectronic atoms.
2. It does not explain the distribution of electrons in orbits.

3. It does not explain the splitting of spectral lines under the influence of electric (Stark effect) and magnetic field (Zeeman effect).
4. It does not provide mathematical support to assumption mvr=n x h/2π

1.4 The quantum mechanical model of the atom

5. Louis **de Broglie's hypothesis** of matter waves
    - ↳ The Discovery of Matter
6. Erwin Schrödinger
    - ↳ combine de Broglie's idea of matter waves and Einstein's idea
7. Heisenberg's uncertainty principle
8. Schrödinger proposed a new atomic model
    - ↳ quantum mechanical model of the atom

- Based on the uncertainty principle, Bohr's atomic model is flawed because you cannot assign fixed paths (orbits) to the motion of electrons
- the wave function gives information about an electron's **energy** and **location** within an atom. Chemists call these wave functions **orbitals**
- Scientists cannot determine the **actual paths** of the moving electrons. However, orbitals indicate where there is a high **probability of finding electrons**.

1803



Dalton proposes the indivisible unit of an element is the atom.

1904



Thomson discovers electrons, believed to reside within a sphere of uniform positive charge (the plum pudding model).

1911



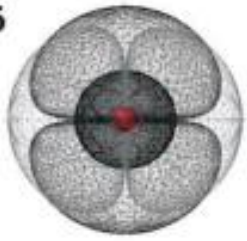
Rutherford demonstrates the existence of a positively charged nucleus that contains nearly all the mass of an atom.

1913



Bohr proposes fixed circular orbits around the nucleus for electrons.

1926



In the current model of the atom, electrons occupy regions of space (orbitals) around the nucleus determined by their energies.

The Evolution of Atomic Theory, as Illustrated by Models of the Oxygen Atom

Quantum Numbers and Orbitals

- **Quantum numbers** are numbers that describe the energies of electrons in atoms; they are derived from quantum mechanical treatment. The allowed values and general meaning of each of the four quantum numbers of an electron in an atom are as follows:

Principal Quantum Number (n)

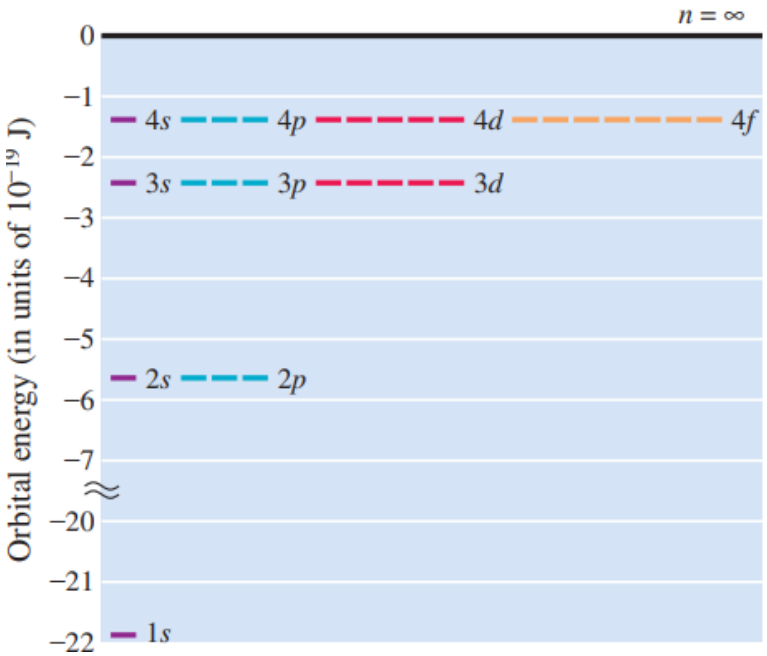
- is the one on which the energy of an electron in an atom principally depends;
- The size of an orbital also depends on n
- it can have any positive value: 1, 2, 3, and so on. T

Letter	K	L	M	N …
n	1	2	3	4 …

Angular Momentum Quantum Number (l) (Also Called Azimuthal Quantum Number)

- distinguishes orbitals of given n having different shapes; it can have any integer value from 0 to n-1
- Within each shell of quantum number n, there are n different kinds of orbitals, each with a distinctive shape denoted by an l quantum number.
- the energy also depends somewhat on the *l* quantum number (except for the H atom).
- Orbitals of the same n but different *l* are said to belong to different subshells of a given shell.

Letter	s	p	d	f	g …
l	0	1	2	3	4 …



Orbital energies of the hydrogen atom. The lines for each subshell indicate the number of different orbitals of that subshell

Magnetic Quantum Number (m_l)

This quantum number distinguishes orbitals of given n and *l*—that is, of given energy and shape but having a different orientation in space; the allowed values are the integers from *-l* to *+l.*

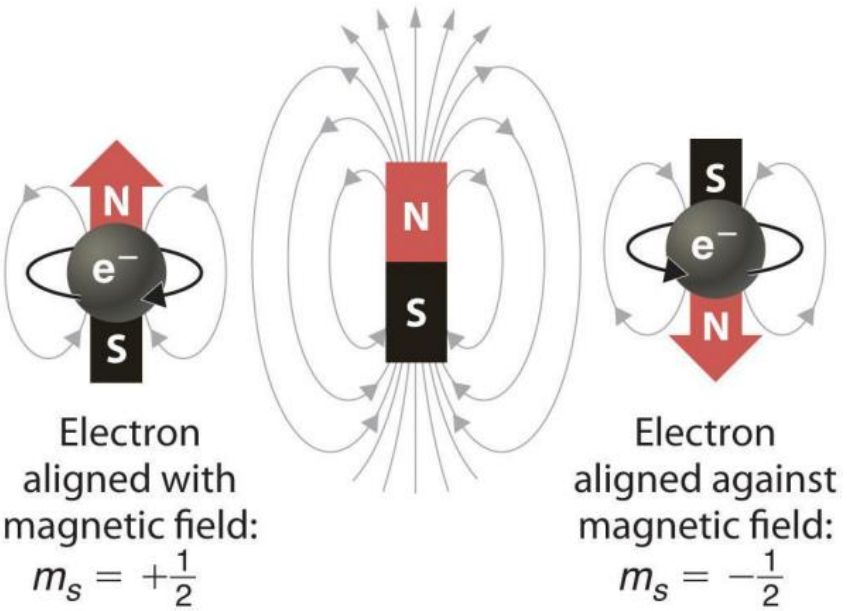
- there are 2l + 1 orbitals in each subshell of quantum number l

TABLE 7.1 | Permissible Values of Quantum Numbers for Atomic Orbitals

n	l	m_l*	Subshell Notation	Number of Orbitals in the Subshell
1	0	0	1*s*	1
2	0	0	2*s*	1
2	1	−1, 0, +1	2*p*	3
3	0	0	3*s*	1
3	1	−1, 0, +1	3*p*	3
3	2	−2, −1, 0, +1, +2	3*d*	5
4	0	0	4*s*	1
4	1	−1, 0, +1	4*p*	3
4	2	−2, −1, 0, +1, +2	4*d*	5
4	3	−3, −2, −1, 0, +1, +2, +3	4*f*	7

Spin Quantum Number (m_s)

This quantum number refers to the two possible orientations of the spin axis of an electron; possible values are – 1/2 and + 1/2 .



Permissible Values of the Quantum Numbers Through n = 4

n	ℓ	m_ℓ	m_s	Electron Capacity of Subshell = $4\ell + 2$	Electron Capacity of Shell = $2n^2$
1	0 (1*s*)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	2
2	0 (2*s*)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	8
	1 (2*p*)	$-1, 0, +1$	$\pm\frac{1}{2}$ for each value of m_ℓ	6	
3	0 (3*s*)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	18
	1 (3*p*)	$-1, 0, +1$	$\pm\frac{1}{2}$ for each value of m_ℓ	6	
	2 (3*d*)	$-2, -1, 0, +1, +2$	$\pm\frac{1}{2}$ for each value of m_ℓ	10	
4	0 (4*s*)	0	$+\frac{1}{2}, -\frac{1}{2}$	2	32
	1 (4*p*)	$-1, 0, +1$	$\pm\frac{1}{2}$ for each value of m_ℓ	6	
	2 (4*d*)	$-2, -1, 0, +1, +2$	$\pm\frac{1}{2}$ for each value of m_ℓ	10	
	3 (4*f*)	$-3, -2, -1, 0, +1, +2, +3$	$\pm\frac{1}{2}$ for each value of m_ℓ	14	

Self-Assessment Exercises

1. State whether each of the following sets of quantum numbers is permissible for an electron in an atom. If a set is not permissible, explain why

a. $n = 1, l = 1, m_l = 0, m_s = +\frac{1}{2}$

b. $n = 3, l = 1, m_l = -2, m_s = -\frac{1}{2}$

c. $n = 2, l = 1, m_l = 0, m_s = +\frac{1}{2}$

d. $n = 2, l = 0, m_l = 0, m_s = 1$

2. Explain why each of the following sets of quantum numbers is not permissible for an orbital.

a. $n = 0, l = 1, m_l = 0, m_s = +\frac{1}{2}$

b. $n = 2, l = 3, m_l = 0, m_s = -\frac{1}{2}$

c. $n = 3, l = 2, m_l = +3, m_s = +\frac{1}{2}$

d. $n = 3, l = 2, m_l = +2, m_s = 0$

3. What is the maximum number of electrons in an atom that can have the following quantum numbers?

a) n =3;
b) n=3 and l=1;
c) n=3, l= 1, and m_l=1;
d) n= 3, l=1, m_l= -1, and m_s = -1/2

4. What are the values of n and l for the following sub-shells?

a) 1s;
b) 4s;
c) 3p;
d) 3d;
e) 4f

5. Write the possible values of l when n=5.

6. Write the allowed number of orbitals

a) with the quantum numbers n=4, l =3;
b) with the quantum number n =4;
c) with the quantum numbers n=4, l =2, m_l = 0;
d) with the quantum numbers n=6, l =5

7. Write the subshell notations that correspond to

a) n=3, l =0;
b) n =3, l =1;
c) n =7, l =0;
d) n=3, l =2

8. Indicate the number of each in the following:

a) orbitals in the 3d sublevel
b) sublevels in the n = 1 energy level
c) orbitals in the 6s sublevel

d) orbitals in the n = 3 energy level

9. In each pair of subshells for a hydrogen atom, which has the higher energy? Give the principal and the azimuthal quantum number for each pair.
    a) 1s, 2p
    b) 2p, 2s
    c) 2s, 3s
    d) 3d, 4s
10. If a given atom or ion has a single electron in each of the following subshells, which electron is easier to remove?
    a) 2s, 3s
    b) 3p, 4d
    c) 2p, 1s
    d) 3d, 4s
11. How many subshells are possible for n = 3? What are they?
12. How many orbitals and subshells are found within the principal shell n = 6? How do these orbital energies compare with those for n = 4?

1.5. The electromagnetic radiation and atomic spectra

1.6. Electronic Configuration and Periodic Table

Electron Configurations Guidelines

A. ***Aufbau (“building up”) Principle***

. In describing ground state electron configuration, the guiding idea is that the total energy of the atom is as low as possible. To determine these configurations, we use the **Aufbau Principle** as a guide:

- A guide for predicting the order in which electrons fill subshells and shells in atoms.

Two general rules help us to predict electron configurations

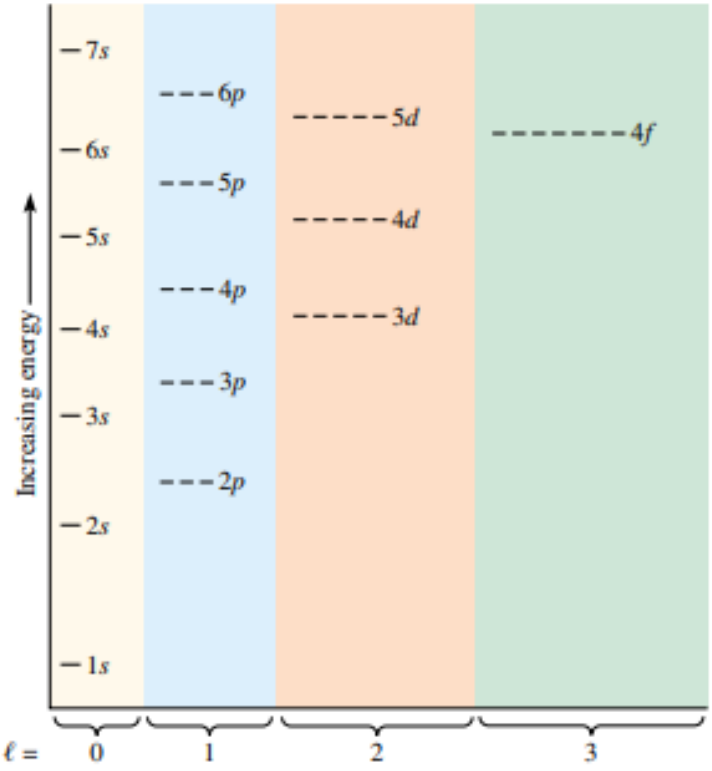
rule 1: Electrons are assigned to orbitals in order of increasing value of (n +ℓ).

rule 2: For subshells with the same value of (n +*l*), electrons are assigned first to the subshell with lower n

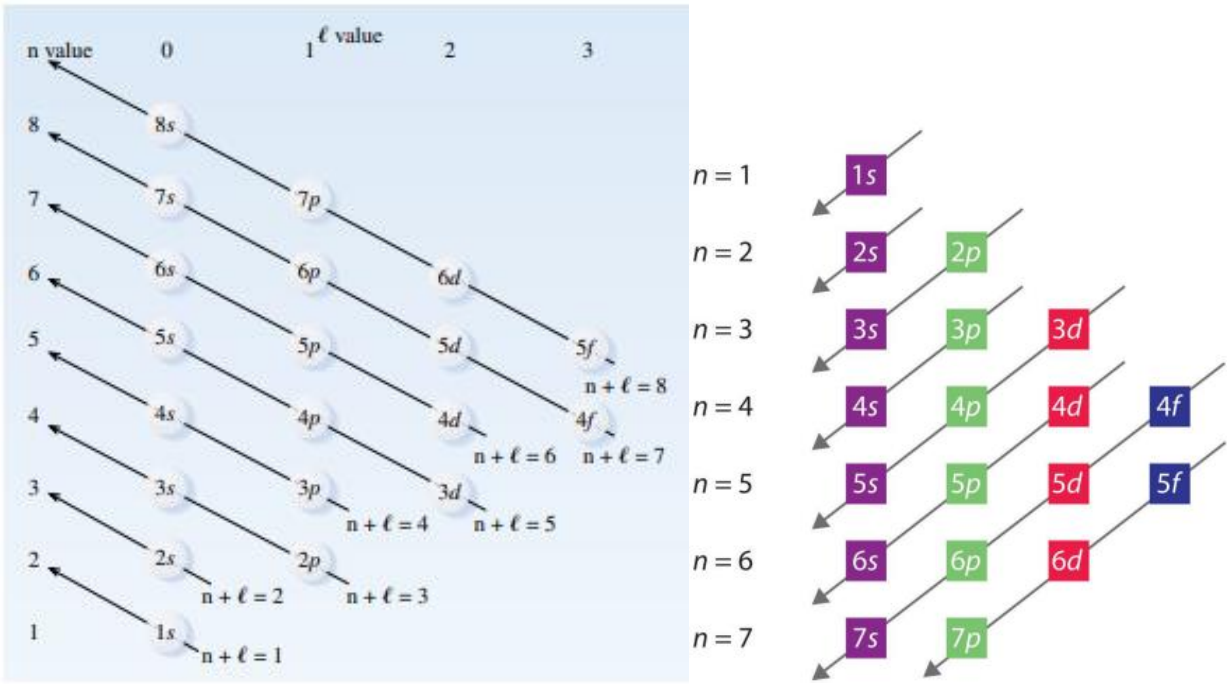
For example,

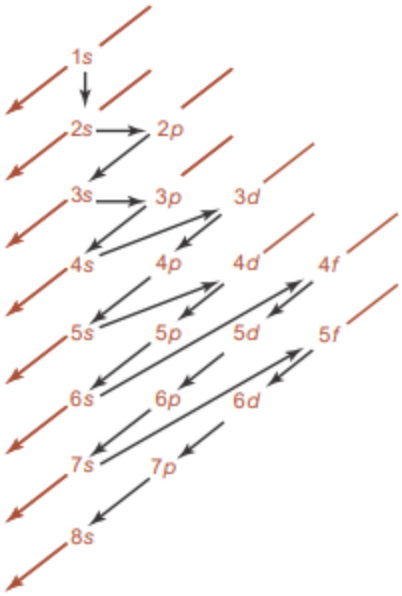
- the 2s subshell has (**n +ℓ =2 + 0 = 2**), and the 2p subshell has (**n +ℓ =2 + 1 = 3**), so we would expect to fill the 2s subshell before the 2p subshell (**rule 1**).
- This rule (**rule 1**) also predicts that the 4s subshell (**n +ℓ =4 + 0 = 4**) will fill before the 3d subshell (**n +ℓ =3 + 2 = 5**).
- Rule 2 reminds us to fill 2p (**n +ℓ =2 + 1 = 3**) before 3s (**n +ℓ =3 + 0 = 3**), because 2p has a lower value of **n**.

The usual order of energies of orbitals of an atom and a helpful device for remembering this order are shown below.



The usual order of filling (Aufbau order) of the orbitals of an atom.





An aid to remembering the usual order of filling of atomic orbitals

Some of these anomalies occur as the 3d orbitals are filled. For example, the **observed** ground state electron configuration of chromium is $[Ar]4s^1 3d^5$ rather than the **predicted** $[Ar]4s^2 3d^4$. Similarly, the **observed** electron configuration of copper is $[Ar]4s^1 3d^{10}$ **instead** of $[Ar]s^2 3d^9$. The actual electron configuration may be rationalized in terms of an added stability associated with a half-filled (ns^1, np^3, nd^5, nf^7) or filled (ns^2, np^6, nd^{10}, nf^{14}) subshell.

- ⇨ Additional **stability** is associated with **half-filled** or **filled** subshells

B. Pauli Exclusion Principle

The electronic structures of atoms are governed by the Pauli Exclusion Principle

- ⇨ No two electrons in an atom may have identical sets of four quantum numbers
  - ↳ two electrons can occupy a given atomic orbital (with the same values of n, l, and m_l) only if their spins are **paired** (have opposite values of m_s).

C. Hund's Rule

- Electrons occupy all the orbitals of a given subshell singly before pairing begins. These unpaired electrons have parallel spins.

- Each orbital of a given subshell is occupied by a single electron before pairing begins

	Orbital Notation			Simplified Notation		
	1*s*	2*s*	2*p*			
$_{3}$Li	↑↓	↑		$1s^2 2s^1$	or	[He] $2s^1$
$_{4}$Be	↑↓	↑↓		$1s^2 2s^2$		[He] $2s^2$
$_{5}$B	↑↓	↑↓	↑ _ _	$1s^2 2s^2 2p^1$		[He] $2s^2 2p^1$
$_{6}$C	↑↓	↑↓	↑ ↑ _	$1s^2 2s^2 2p^2$		[He] $2s^2 2p^2$
$_{7}$N	↑↓	↑↓	↑ ↑ ↑	$1s^2 2s^2 2p^3$		[He] $2s^2 2p^3$
$_{8}$O	↑↓	↑↓	↑↓ ↑ ↑	$1s^2 2s^2 2p^4$		[He] $2s^2 2p^4$
$_{9}$F	↑↓	↑↓	↑↓ ↑↓ ↑	$1s^2 2s^2 2p^5$		[He] $2s^2 2p^5$
$_{10}$Ne	↑↓	↑↓	↑↓ ↑↓ ↑↓	$1s^2 2s^2 2p^6$		[He] $2s^2 2p^6$

	Orbital Notation		Simplified Notation
	3*s*	3*p*	
$_{11}$Na	[Ne] ↑		[Ne] $3s^1$
$_{12}$Mg	[Ne] ↑↓		[Ne] $3s^2$
$_{13}$Al	[Ne] ↑↓	↑ _ _	[Ne] $3s^2 3p^1$
$_{14}$Si	[Ne] ↑↓	↑ ↑ _	[Ne] $3s^2 3p^2$
$_{15}$P	[Ne] ↑↓	↑ ↑ ↑	[Ne] $3s^2 3p^3$
$_{16}$S	[Ne] ↑↓	↑↓ ↑ ↑	[Ne] $3s^2 3p^4$
$_{17}$Cl	[Ne] ↑↓	↑↓ ↑↓ ↑	[Ne] $3s^2 3p^5$
$_{18}$Ar	[Ne] ↑↓	↑↓ ↑↓ ↑↓	[Ne] $3s^2 3p^6$

		Orbital Notation			Simplified Notation
		3*d*	4*s*	4*p*	
$_{19}$K	[Ar]		↑		[Ar] $4s^1$
$_{20}$Ca	[Ar]		↑↓		[Ar] $4s^2$
$_{21}$Sc	[Ar]	↑ _ _ _ _	↑↓		[Ar] $3d^1 4s^2$
$_{22}$Ti	[Ar]	↑ ↑ _ _ _	↑↓		[Ar] $3d^2 4s^2$
$_{23}$V	[Ar]	↑ ↑ ↑ _ _	↑↓		[Ar] $3d^3 4s^2$
$_{24}$Cr	[Ar]	↑ ↑ ↑ ↑ ↑	↑		[Ar] $3d^5 4s^1$
$_{25}$Mn	[Ar]	↑ ↑ ↑ ↑ ↑	↑↓		[Ar] $3d^5 4s^2$
$_{26}$Fe	[Ar]	↑↓ ↑ ↑ ↑ ↑	↑↓		[Ar] $3d^6 4s^2$
$_{27}$Co	[Ar]	↑↓ ↑↓ ↑ ↑ ↑	↑↓		[Ar] $3d^7 4s^2$
$_{28}$Ni	[Ar]	↑↓ ↑↓ ↑↓ ↑ ↑	↑↓		[Ar] $3d^8 4s^2$
$_{29}$Cu	[Ar]	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑		[Ar] $3d^{10} 4s^1$
$_{30}$Zn	[Ar]	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓		[Ar] $3d^{10} 4s^2$

as we fill the 3d set of orbitals, from $_{21}$Sc to $_{30}$Zn, we see that these orbitals are not filled quite regularly. As the 3d orbitals are filled, their energies get closer to that of the 4s orbital and eventually become lower. If the order of filling of electrons on chromium gave the expected configuration, it would be: [Ar] $4s^2 3d^4$. Chemical and spectroscopic evidence indicates, however, that the configuration of Cr has only one electron in the 4s orbital, [Ar] $4s^1 3d^5$. For this element, the 4s and 3d orbitals are nearly equal in energy. Six electrons in these six orbitals of nearly the same energy are more stable with the electrons all unpaired, [Ar] 3*d* ↑ ↑ ↑ ↑ ↑ 4*s* ↑ rather than the predicted order [Ar] 3*d* ↑ ↑ ↑ ↑ _ 4*s* ↑↓.

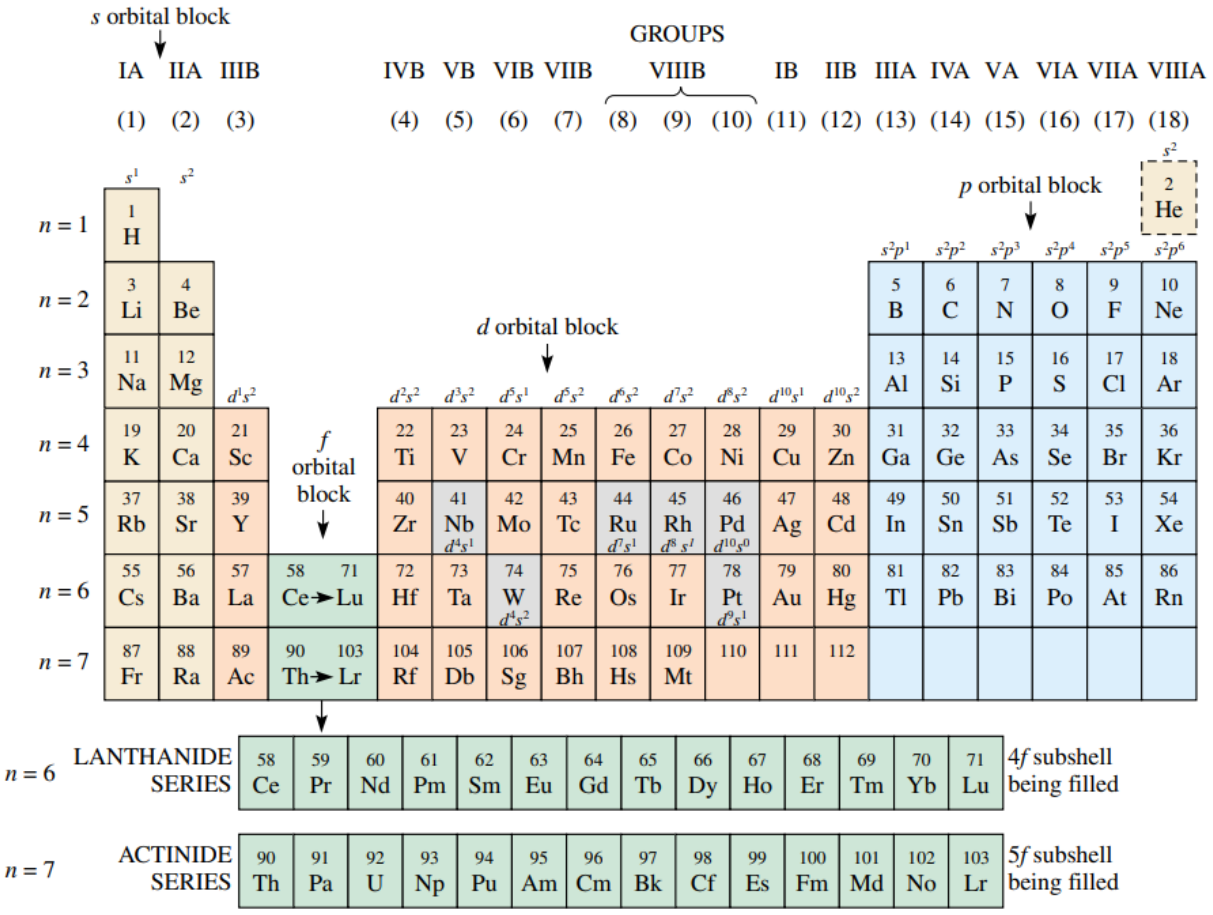
The next elements, Mn to Ni, have configurations as predicted by the Aufbau order, presumably because forming a pair of electrons in the larger 4s orbital is easier than in a smaller, less diffuse, 3d orbital. By the time Cu is reached, the energy of 3d is sufficiently lower than that of 4s, so that the total energy of the configuration [Ar] $4s^1 3d^{10}$ is lower than that of [Ar] $4s^2 3d^9$.

The Periodic Table and Electron Configurations

Periodic table —as a systematic representation of the electron configurations of the elements. The periodic tables in this text are divided into “A” and “B” groups.

- The A groups contain elements in which s and p orbitals are being filled. Elements within any particular A group have similar **electron configurations** and **chemical properties**,
- The B groups are those in which there are one or two electrons in the s orbital of the outermost occupied shell, and the d orbitals, one shell smaller, are being filled.

The electron configurations of the A group elements and the noble gases can be predicted reliably. However, there are some more pronounced irregularities in the B groups below the fourth period.



The d^1s^2, d^2s^2, . . . designations represent known configurations. They refer to (n-1)d and ns orbitals. Several exceptions to the configurations indicated above each group are shown in gray

Electron Configurations of Ions

Ions of the Main-Group Elements

- cations are obtained by removing all the valence electrons from the atoms. Once these atoms have lost their valence electrons, they have stable noble-gas or pseudo-noble-gas configurations
  - ↳ The ion charges equal the group numbers
- anions are obtained by gaining electrons to give noble-gas or pseudo-noble-gas configurations.
  - ↳ The ion charges equal the group numbers minus eight.

Transition-Metal Ions

atoms of transition elements generally lose the ns electrons first; then they may lose one or more (n-1)d electrons. The 2+ ions are common for the transition elements and are obtained by the loss of the highest energy **s** electrons from the atom. Many transition elements also form 3+ ions by losing one (n-1)d electron in addition to the two ns electrons.

Self-Assessment Exercises

1. State the Pauli Exclusion Principle. Would any of the following electron configurations violate this rule: (a) $1s^2$; (b) $1s^2 2p^7$; (c) $1s^3$? Explain.

State Hund's Rule. Would any of the following electron configurations violate this rule: (a) $1s^2$; (b) $1s^2 2s^2 2p_x^2$; (c) $1s^2 2s^2 2p_x^1 2p_y^1$; (d) $1s^2 2s^2 2p_x^1 2p_z^1$; (e) $1s^2 2p_x^2 2p_y^1 2p_z^1$? Explain.

2. . How many magnetic quantum numbers are possible for a 4p subshell? A 3d subshell? How many orbitals are in these subshells?
3. If l = 2 and ml = 2, give all the allowed combinations of the four quantum numbers (n, l,ml, ms) for electrons in the corresponding 3d subshell.
4. Given the following sets of quantum numbers (n, l, ml, ms), identify each principal shell and subshell.

a. 1, 0, 0, ½
b. 2, 1, 0, ½
c. 3, 2, 0, ½
d. 4, 3, 3, ½