UNIT · 01

Atomic Structure



<u>Atomic Structure</u>

The Greek Philosopher Democritus believed that all matter was made up of small indivisible parts, which he called atoms. The word atom comes from the Greek a, meaning not, or without, and tom, meaning to cut. Therefore, the word atom means: not cuttable. He theorised that if one cut a piece of cheese in half, then in half again, and again, and again, et cetera, one would be left with a piece too small to subdivide. This was his single atom.

We now know that an atom is the smallest part of something that retains its identity, although the atom itself can be subdivided. In other words, once we begin to look inside the atom, we can no longer tell which element the atom is. The atom itself comprises a central nucleus, in which most of the mass is concentrated, with electrons orbiting around the outside of this nucleus. This central nucleus consists of protons and neutrons. The properties of these three kinds of particle are given in the following table. In the neutral or elemental atom there are equal numbers of protons and electrons. This causes the atom to have no overall charge.

Particle	Relative Charge	Relative Mass
Proton	+1	1
Neutron	0	1
Electron	-1	o (Negligible, or approximately 1/1836)

	electron	proton	neutron
Symbol of the particle	e	р	n
Mass of the particle / kg	9.107 × 10 ^{•31}	1.6725 × 10 ⁻²⁷	1.6742 × 10 ⁻²⁷
Relative mass of the particle	$\frac{1}{1840}$	1	1
Charge of the particle /C	1.602 × 10 ^{•19}	1.602×10^{-19}	0
Relative charge of the particle	-1	+1	0

Dalton's Atomic Theory

- All matter is made of atoms. Atoms are indivisible and indestructible.
- All atoms of a given element are identical in mass and properties
- Compounds are formed by a combination of two or more different kinds of atoms.
- A chemical reaction is a rearrangement of atoms.

Modern atomic theory is, of course, a little more involved than Dalton's theory but the essence of Dalton's theory remains valid. Today we know that atoms can be destroyed via nuclear reactions but not by chemical reactions. Also, there are different kinds of atoms (differing by their masses) within an element that is known as "isotopes", but isotopes of an element have the same chemical properties.

Many heretofore unexplained chemical phenomena were quickly explained by Dalton with his theory. Dalton's theory quickly became the theoretical foundation in chemistry.

John Dalton



John Dalton FRS was an English chemist, meteorologist and physicist. He is best known for his pioneering work in the development of modern atomic theory, and his research into colour blindness.

Born: September 6, 1766, Cockermouth

Died: July 27, 1844, Manchester

Nationality: English

Awards: Royal Medal

Evidences for the electrical nature of the matter

- Static electricity
- Simple voltic cell
- Electrolysis

Charges are produced by rubbing plastic strips. The interactions of the charges are observed using pith balls, electroscopes, and the strips themselves.

Discharge tube experiments

A Crookes tube is an early experimental electrical discharge tube, invented by English physicist William Crookes and others around 1869-1875, in which cathode rays, streams of electrons, were discovered.

Developed from the earlier Geissler tube, it consists of a partially evacuated glass container of various shapes, with two metal electrodes, one at either end. When a high voltage is applied between the electrodes, cathode rays (electrons) travel in straight lines from the cathode to the anode. It was used by Crookes, Johann Hittorf, Juliusz Plücker, Eugen Goldstein, Heinrich Hertz, Philipp Lenard and others to discover the properties of cathode rays, culminating in J. J. Thomson's 1897 identification of cathode rays as negatively charged particles, which were later named electrons. Crookes tubes are now used only for demonstrating cathode rays.



Discharge tube is also called "CROOCK TUBE". It is made of a glass tube which consists of two metallic plates. One plate is connected to positive terminal of high voltage power supply and the other to negative terminal. The plate connected to the positive terminal is called "ANODE" the other connected to negative terminal is called "CATHODE". The tube is filled with any gas.

4

Cathode rays

In discharge tube experiment, at low pressure and at very high voltage, an electric current is passed. Due to passage of electric current, a stream of rays is passed in the tube originating from cathode. These rays are called "CATHODE RAYS".

Properties of cathode rays

These rays originate from cathode.

When electricity flowed through the Geissler tube, a mysterious greenish glow was produced around the tube. Sir William Crookes gained more knowledge about the mysterious green glow when he created a bent Geissler tube in 1875. He noticed that the glow was the most intense opposite the negative electrode, also called the cathode. Crookes reasoned that rays traveled from the cathode and then hit the end of the tube. Because of this, Crookes named these rays cathode rays.



Cathode rays travel in straight line. •

In later experiments Crookes placed barriers in the path of the cathode rays: Because a shadow was produced behind the barrier, Crookes reasoned that cathode rays:

- Acted like light
- Seemed to travel in straight lines



• Cathode rays carry negative charge.

Jean Perrin constructed an apparatus that had an anode made of a hollow aluminum cylinder that was open at both ends. At the end opposite to the cathode, was a cylinder that was closed at one end.

The closed cylinder collected the cathode rays and was connected to an electroscope, which was used to determine the charge on the cathode rays. The electroscope showed that the cathode rays were negatively charged.



• Cathode rays are deflected by electric field.

Arthur Schuster noticed that the particles were repelled from a negative plate and attracted to a positive plate. This is further proof that cathode rays are negatively charged particles.



• Cathode rays are deflected by magnetic field.

Crookes showed that the rays were deflected by a magnetic field. Crookes noted that charged particles in a magnetic field experience a force. Cathode rays behaved as if they were negatively charged particles.

6



• These rays consist of material particles.

Crookes reported that a paddle wheel placed in the path of the cathode rays turned. This proved that the cathode rays carried energy, and that they might be made of particles. This also indicates that the rays (particles) moved from the cathode to the anode.



- The ratio e / m of these particles was 1.76 x 108 col / gm.
- Cathode rays consist of "electron".
- The rays, upon striking glass or certain other materials, cause them to glow.

Positive rays

Cathode rays consist of negatively charged particles called electrons. These electrons move away from cathode with very high speeds. These fast moving electrons collide with the molecules of the gas in the tube, split the molecule into atoms, and remove one or more electrons from the atoms.

Thus, the atoms get converted into the positive ions due to loss of electrons. These positive ions get attracted by the negative electrode, and pass through the holes in the electrode plate to produce a glow only the glass wall of the discharge tube. A stream of these positively charged particles is called a positive ray (or anode ray).

Properties of positive rays

- Positive rays consist of positively charged particles.
- The nature of these rays depends on the gas used in the discharge tube.
- These rays travel in straight lines. •
- These rays get deflected by an electrical field, and bend towards the negative plate. • Thus the deflection of the positive rays is in a direction opposite to that shown by the cathode rays.
- These rays are also deflected by the magnetic fields in the direction opposite to • that of the cathode rays.
- These rays can produce mechanical as well as chemical effects. •
- The ratio of charge (e) to mass (m), i.e., (e/m) for the particles in the positive rays • is not the same for all gases.
- The ratio e / m for the positive rays is very low as compared to the e / m value for • cathode rays.



Radioactivity

Radioactivity refers to the particles which are emitted from nuclei as a result of nuclear instability. Because the nucleus experiences the intense conflict between the two strongest forces in nature, it should not be surprising that there are many nuclear isotopes which are unstable and emit some kind of radiation. The most common types of radiation are called alpha, beta, and gamma radiation, but there are several other varieties of radioactive decay.

Alpha Radioactivity

Composed of two protons and two neutrons, the alpha particle is a nucleus of the element helium. Because of its very large mass (more than 7000 times the mass of the beta particle) and its charge, it has a very short range. It is not suitable for radiation therapy since its range is less than a tenth of a millimeter inside the body. Its main radiation hazard comes when it is ingested into the body; it has great destructive power within its short range. In contact with fast-growing membranes and living cells, it is positioned for maximum damage.

Alpha particle emission is modeled as a barrier penetration process. The alpha particle is the nucleus of the helium atom and is the nucleus of highest stability.

Beta Radioactivity

Beta particles are just electrons from the nucleus, the term "beta particle" being an historical term used in the early description of radioactivity. The high energy electrons have greater range of penetration than alpha particles, but still much less than gamma rays. The radiation hazard from betas is greatest if they are ingested.

Beta emission is accompanied by the emission of an electron antineutrino which shares the momentum and energy of the decay. The emission of the electron's antiparticle, the positron, is also called beta decay. Beta decay can be seen as the decay of one of the neutrons to a proton via the weak interaction. The use of a weak interaction Feynman diagram can clarify the process.

Gamma Radioactivity

Gamma radioactivity is composed of electromagnetic rays. It is distinguished from x-rays only by the fact that it comes from the nucleus. Most gamma rays are somewhat higher in energy than x-rays and therefore are very penetrating.

It is the most useful type of radiation for medical purposes, but at the same time it is the most dangerous because of its ability to penetrate large thicknesses of material.

Atomic models

Plum pudding model (Thomson model)

The plum pudding model of the atom by J. J. Thomson, who discovered the electron in 1897, was proposed in 1904 before the discovery of the atomic nucleus in order to add the electron to the atomic model. In this model, the atom is composed of electrons (which Thomson still called "corpuscles", though G. J. Stoney had proposed that atoms of electricity be called electrons in 1894[1]) surrounded by a soup of positive charge to balance the electrons' negative charges, like negatively charged "plums" surrounded by positively charged "pudding". The electrons (as we know them today) were thought to be positioned throughout the atom, but with many structures possible for positioning multiple electrons, particularly rotating rings of electrons (see below). Instead of a soup, the atom was also sometimes said to have had a "cloud" of positive charge.



Geiger-Marsden experiment

In 1907 Ernest Rutherford published "Radiation of the α Particle from Radium in passing through Matter." Hans Geiger expanded on this work in a communication to the Royal Society with experiments he and Rutherford had done passing α particles through air, aluminum foil and gold leaf.

More work was published in 1909 by Geiger and Marsden and further greatly expanded work was published in 1910 by Geiger, in 1911-2 Rutherford went before the Royal Society to explain the experiments and propound the new theory of the atomic nucleus as we now understand it.

The key experiment behind this announcement happened in 1910 at the University of Manchester, as Ernest Rutherford's team performed a remarkable experiment in which Hans Geiger and Ernest Marsden under his supervision fired alpha particles (helium nuclei) at a thin film of gold foil. The plum pudding model predicted that the alpha particles should come out of the foil with their trajectories being at most slightly bent. Rutherford had the idea to instruct his team to look for something that shocked him to actually observe: a few particles were scattered through large angles, even completely backwards, in some cases.



He likened it to firing a bullet at tissue paper and having it bounce off. The discovery, beginning with Rutherford's analysis of the data in 1911, eventually led to the Rutherford model of the atom, in which the atom has a very small, very dense nucleus containing most of its mass, and consisting of heavy positively charged particles with embedded electrons in order to balance out the charge (since the neutron was unknown). As an example, in this model (which is not the modern one) nitrogen-14 consisted of a nucleus with 14 protons and 7 electrons (21 total particles), and the nucleus was surrounded by 7 more orbiting electrons.

Atomic Number and Mass Number

There are two useful pieces of information that we can glean from the nucleus of an atom. The first is its atomic number. This allows us to identify which element an atom is. The atomic number, usually denoted by the letter A, is the number of protons in the nucleus of an atom. It is this which places an element in the periodic table.

The second is the mass number. This is equal to the number of protons, plus the number of neutrons (remember that electrons have negligible mass). It is given the symbol Z. The number of neutrons in an atom, therefore, is equal to the mass number (Z), minus the atomic number (A).

<u>Isotopes</u>

Sometimes an atom's proton number will show that it is a particular element, and yet its mass number will be different to other atoms of that element. Atoms which have the same proton number, yet different mass numbers, are referred to as isotopes of the element. The difference in mass number is caused by the presence of extra, or fewer neutrons in the nucleus.

Since the number of protons (and, therefore, of electrons) is the same, the chemical properties of these materials are the same as those of the standard element. The physical properties (melting/boiling point etc.) DO change.

We usually refer to isotopes by the element name, followed by the mass number. For example, a carbon atom with a mass number of 12 (six protons, and six neutrons) is known as carbon-12.

One of the most useful isotopes is carbon-14. It is radioactive, and can be used to determine the age of organic material as old as 60,000 years! Other isotopes are used in medicine as tracers, to determine the location of any blockages in the body.

<u>Relative Masses</u>

The following two definitions are required to be learnt for module one, although they may appear esoteric at first.

Relative Atomic Mass (Ar)

$$A_r = \frac{\text{Mean Mass of One Atom} \times 12}{\text{Mass of One Atom of } {}_6^{12}\!C}$$

This can be calculated from the mass spectrum of a sample by multiplying each peak's m/z value by its relative abundance. This sum is then divided by the total relative abundance. This is shown below for the mass spectrum of boron, in which the two peaks represent ¹⁰B and ¹¹B respectively.

Relative Molecular Mass

This can be calculated from a mass spectrum by taking the m/z value of the peak furthest to the right of the graph, as shown in this example for ammonia.

Mole and Avogadro's number

Dimensions of reciprocal mol and its value is equal to 6.02214129(27) ×1023 mol-1. Changes in the SI units are proposed that will change the constant to exactly 6.02214X×1023 when it is expressed in the unit mol-1 (see New SI definitions, in which an "X" at the end of a number means one or more final digits yet to be agreed upon).

Avogadro's number, a historical term closely related to the Avogadro constant. Revisions in the base set of units of the International System of Units (SI) necessitated redefinitions of the concepts of chemical quantity. Avogadro's number was defined by Perrin as the number of molecules in one gram-molecule of hydrogen. It was later redefined as the number of atoms in 12g of the isotope carbon-12. Thus, Avogadro's number is a dimensionless quantity and has the numerical value of the Avogadro constant given in base units.

Concept of a mole:

Recall that, 1 amu = $1.6605 \times 10^{(-27)}$ kg and

 $1 \text{ mole} = 6.02 \text{ x } 10^{23}$.

Therefore, 1 mole of amus

```
= 1 mole of 1.6605 x 10<sup>(-27)</sup> kg
= 6.02x10<sup>2</sup>3 of 1.6605 x 10<sup>(-27)</sup> kg
= 6.02x10<sup>2</sup>3 x 1.6605 x 10<sup>(-27)</sup> kg ("of" means "x")
= 0.001kg = <u>1g</u>
```

(Please note: Some of the numbers above have been approximated and rounded but for simplicity I've left that stuff out.)

13

The different types of electromagnetic radiation.

The electrons in an atom's "electron shell" all have specific energy levels. If you add energy to an atom, the atom will absorb a specific amount of energy, and the electron will jump up to a higher energy level.

Each different element has its own energy levels, and it can only absorb energy in specific amounts. (When you add a lot of energy to the atom, the atom becomes ionized, as one or more electrons absorb enough energy to break free of the atom completely, leaving the atom with an unbalanced positive electrical charge.)

When those "excited" or jumped-up electrons release the energy, the electron drops back to its previous level, and the atom (or more specifically, the electron) emits a photon, which is a particle of light. Each photon has a frequency or energy that is distinctive to the element and the energy level.

Electrons cannot have intermediate energies; they absorb and release exact "packets" or "quanta" of energy. This is how a mass spectrometer works; the operator ionizes a sample of the material that he wants to analyze, and watches the resulting spectrum. Each wavelength of light emitted by the sample corresponds to one specific element.

A quantum mechanical system or particle that is bound—that is, confined spatially—can only take on certain discrete values of energy. This contrasts with classical particles, which can have any energy. These discrete values are called energy levels. The term is commonly used for the energy levels of electrons in atoms or molecules, which are bound by the electric field of the nucleus, but can also refer to energy levels of nuclei or vibrational or rotational energy levels in molecules.

The energy spectrum of a system with such discrete energy levels is said to be quantized. If the potential energy is set to zero at infinite distance from the atomic nucleus or molecule, the usual convention, then bound electron states have negative potential energy.

If more than one quantum mechanical state is at the same energy, the energy levels are "degenerate". They are then called degenerate energy levels.



Energy Transport and the Amplitude of a Wave

As mentioned earlier, a wave is an energy transport phenomenon that transports energy along a medium without transporting matter. A pulse or a wave is introduced into a slinky when a person holds the first coil and gives it a back-and-forth motion. This creates a disturbance within the medium; this disturbance subsequently travels from coil to coil, transporting energy as it moves. The energy is imparted to the medium by the person as he/she does work upon the first coil to give it kinetic energy. This energy is transferred from coil to coil until it arrives at the end of the slinky. If you were holding the opposite end of the slinky, then you would feel the energy as it reaches your end. In fact, a high energy pulse would likely do some rather noticeable work upon your hand upon reaching the end of the medium; the last coil of the medium would displace you hand in the same direction of motion of the coil. For the same reasons, a high energy ocean wave can do considerable damage to the rocks and piers along the shoreline when it crashes upon it.



The amplitude of a wave is related to the energy which it transports.

V=f λ

Energy of a wave is directly proportional to the frequency.

 $E \; \alpha \; f$

- $E = Constant \times f$
- E = h f- plank equation
- h = plank constant
- $h = 6.624 \times 10^{-34} \text{ Js}^{-1}$
- $V = f \lambda (1)$
- E = h f 2

Therefore

 $E = h v / \lambda$



Electromagnetic spectrum

You actually know more about it than you may think! The electromagnetic (EM) spectrum is just a name that scientists give a bunch of types of radiation when they want to talk about them as a group. Radiation is energy that travels and spreads out as it goes--visible light that comes from a lamp in your house and radio waves that come from a radio station are two types of electromagnetic radiation. Other examples of EM radiation are microwaves, infrared and ultraviolet light, X-rays and gamma-rays. Hotter, more energetic objects and events create higher energy radiation than cool objects.

Only extremely hot objects or particles moving at very high velocities can create highenergy radiation like X-rays and gamma-rays. Here are the different types of radiation in the EM spectrum, in order from lowest energy to highest.



<u>Radio</u>

This is the same kind of energy that radio stations emit into the air for your boom box to capture and turn into your favorite Mozart, Madonna, or Justin Timberlake tunes. But radio waves are also emitted by other things ... such as stars and gases in space. You may not be able to dance to what these objects emit, but you can use it to learn what they are made of.



17

Microwaves

They will cook your popcorn in just a few minutes! Microwaves in space are used by astronomers to learn about the structure of nearby galaxies, and our own Milky Way.



Infrared

Our skin emits infrared light, which is why we can be seen in the dark by someone using night vision goggles. In space, IR light maps the dust between stars.

<u>Visible</u>

This is the part that our eyes see. Visible radiation is emitted by everything from fireflies to light bulbs to stars ... also by fast-moving particles hitting other particles.

<u>Ultraviolet</u>

We know that the Sun is a source of ultraviolet (or UV) radiation, because it is the UV rays that cause our skin to burn! Stars and other "hot" objects in space emit UV radiation.



<u>X-rays</u>

Your doctor uses them to look at your bones and your dentist to look at your teeth. Hot gases in the Universe also emit X-rays.



Gamma-rays

Radioactive materials (some natural and others made by man in things like nuclear power plants) can emit gamma-rays. Big particle accelerators that scientists use to help them understand what matter is made of can sometimes generate gamma-rays. But the biggest gamma-ray generator of all is the Universe! It makes gamma radiation in all kinds of ways.



Different types of spectrum



Continuous Spectrum

We know that blackbodies emit a well understood spectrum. This spectrum is continuous. That is, a blackbody emits at least some radiation at every wavelength. At right, in Part (a) of Figure 5-14, we see a picture of a hot blackbody and its continuous emission spectrum. That is, if you look directly at a blackbody, you will see emission at all wavelengths. "But wait!" you say. "You told me I see everyday objects such as shirts and dogs because of reflected light, NOT emitted light."

This is true. Blue and red shirts both have the same temperature. But both do emit some visible radiation, the key is that they emit only a tiny, tiny amount. Effectively (but not exactly) none. A blackbody emits a continuous spectrum. If you look directly at a blackbody, you will see this continuous spectrum.

Absorption Line Spectrum

If there is an absorbing material (such as a cloud of cooler gas) between you and the blackbody, then you will not see a completely continuous spectrum. Part (b) at right shows a cloud of cool gas between the blackbody and us, and says that we see an "absorption line spectrum," an almost-continuous spectrum, if you will.

Like a gold prospector, panning for gold in a pile of dirt, the cloud of cool gas is "looking" for certain types of light in the "pile of light" (the continuous spectrum) coming from the blackbody. If the prospector finds a nugget, he gets excited and keeps it, but passes along the dirt (who collects dirt?). Similarly, if the gas cloud finds light at a wavelength (color) that excites its atoms, the gas cloud will keep that light. But will transmit the light that is unexciting.

In this way, gas cloud plucks out certain colors from the continuous spectrum before passing the rest on to us, the observers. So what do we see? An absorption line spectrum. An almost-continuous spectrum that has certain colors removed (absorbed).

Clouds of gas absorb certain wavelengths (colors) of light. A continuous spectrum that hits a cloud of cool gas will be partially absorbed. The transmitted spectrum is called an absorption line spectrum (because certain lines are absorbed), and is continuous except for the colors that were absorbed by the gas.

Emission Line Spectrum

The cool gas cloud does not ONLY absorb. In fact, anything that absorbs must also emit. In the context of the picture at right, if we look at only the cloud of gas (i.e. without the blackbody in our line of sight), we will see an emission line spectrum. This is shown in Part (c) at right. The question is, as always, why?. Well, we know that the cloud of gas absorbs certain wavelengths of light from the blackbody. Each absorbed photon excited one atom in the gas. But an excited atom will not stay excited forever.

Eventually, the excited atom will return to its unexcited (or, "ground") state. The ground state has less energy than the excited state, and because we know that energy must be conserved, the atom will emit a photon whose wavelength (color) is exactly the same as the photon it initially absorbed. So a cloud of cool gas that absorbs certain colors of light will also emit those same colors. If we look at the cool gas without the blackbody in the line of sight, we will see an emission line spectrum, and the colors of the lines we see are exactly the same colors that were missing from the absorption line spectrum.

Anything that absorbs also emits. A cloud of cool gas that absorbs certain colors from a blackbody will emit exactly those colors as the gas atoms de-excite. If we look at the cloud without the blackbody in our line of sight, we will see an emission line spectrum. The lines of emission have the same color as the absorption lines in the absorption line spectrum. If you added an emission line spectrum and an absorption line spectrum, you would get a continuous spectrum.

<u>Hydrogen spectrum</u>

The spectrum of hydrogen is particularly important in astronomy because most of the Universe is made of hydrogen. Emission or absorption processes in hydrogen give rise to series, which are sequences of lines corresponding to atomic transitions, each ending or beginning with the same atomic state in hydrogen. Thus, for example, the Balmer Series involves transitions starting (for absorption) or ending (for emission) with the first excited state of hydrogen, while the Lyman Series involves transitions that start or end with the ground state of hydrogen; the adjacent image illustrates the atomic transitions that produce these two series in emission.

The corresponding spectrum may exhibit a continuum, or may have superposed on the continuum bright lines (an emission spectrum) or dark lines (an absorption spectrum)



Hydrogen spectrum series



Lyman Series

When an electron jumps from any of the higher states to the ground state or 1st state (n = 1), the series of spectral lines emitted lies in ultra-violet region and are called as Lyman Series. The wavelength (or wave number) of any line of the series can be given by using the relation:

$$v = RZ_2 (1/12 - 1/n_{22}) n_2 = 2, 3, 4, 5, ...$$

(For H atom Z = 1) Series limit (for H - atom): $\infty \rightarrow 1$ i.e. v = R

 α line: 2 —> 1; also known as first line or first member

 β line: 3 —> 2; also known as second line or second member

 γ line: 4 —> 1; also known as third line or third member

Balmer Series

When an electron jumps from any of the higher states to the state with

n = 2 (IInd state), the series of spectral lines emitted lies in visible region and are called as Balmer Series. The wave number of any spectral line can be given by using the relation:

v = RZ2 (1/22 – 1/n22) n2 = 3, 4, 5, 6, ... Series limit (for H – atom) : ∞ –> 2 i.e. v = R/4 α line : 3 –> 2; β line : 4 –> 2; γ line : 5 –> 2

Paschen Series

When an electron jumps from any of the higher states to the state with

n = 3 (IIIrd state), the series of spectral lines emitted lies in near infra-red region and are called as Paschen Series. The wave number of any spectral line can be given by using the relation:

 $v = RZ_2 (1/32 - 1/n22) n_2 = 4, 5, 6, 7, ...$

Series limit (for H – atom) : $\infty \rightarrow 3$ i.e. v = R/9

α line: 4 -> 3; β line: 5 -> 3; γ line : 6 -> 3

Brackett Series

When an electron jumps from any of the higher states to the state with

n = 4 (IVth state), the series of spectral lines emitted lies in far infra-red region and called as Brackett Series. The wave number of any spectral line can be given by using the relation:

 $v = R Z_2 (1/42 - 1/n22) n_2 = 5, 6, 7, 8,...$

Pfund Series

When an electron jumps from any of the higher states to the state with n = 5 (Vth state), the series of spectral lines emitted lies in far infra-red region and are called as Pfund Series. The wave number of any spectral line can be given by using the relation:

 $v = R Z_2 (1/52 - 1/n22) n_2 = 6, 7, 8, ...$

23

Quantum Numbers

The Bohr model was a one-dimensional model that used one quantum number to describe the distribution of electrons in the atom. The only information that was important was the size of the orbit, which was described by the n quantum number. Schrödinger's model allowed the electron to occupy three-dimensional space. It therefore required three coordinates, or three quantum numbers, to describe the orbitals in which electrons can be found.

The three coordinates that come from Schrödinger's wave equations are the principal (n), azimuthal (l), magnetic (me) and spin (ms) quantum numbers. These quantum numbers describe the size, shape, and orientation in space of the orbitals on an atom.

Principal quantum number (n) •

The principal quantum number (n) describes the size of the orbital. Orbitals for which n = 2 are larger than those for which n = 1, for example. Because they have opposite electrical charges, electrons are attracted to the nucleus of the atom. Energy must therefore be absorbed to excite an electron from an orbital in which the electron is close to the nucleus (n = 1) into an orbital in which it is further from the nucleus (n = 2). The principal quantum number therefore indirectly describes the energy of an orbital.

Azimuthal quantum number (l) •

The Azimuthal (angular) quantum number (l) describes the shape of the orbital. Orbitals have shapes that are best described as spherical (l = 0), polar (l = 1), or cloverleaf (l = 2). They can even take on more complex shapes as the value of the angular quantum number becomes larger. There is only one way in which a sphere (l = o) can be oriented in space. Orbitals that have polar (l = 1) or cloverleaf (l = 2) shapes, however, can point in different directions. Therefore need a third quantum number, known as the magnetic quantum number (m), to describe the orientation in space of a particular orbital.

Magnetic quantum number (m_e) •

It is called the magnetic quantum number because the effect of different orientations of orbitals was first observed in the presence of a magnetic field.

• Spin quantum number (m_s)

The Spin Quantum Number (s) is a value (of 1/2) that describes the angular momentum of an electron. An electron spins around an axis and has both angular momentum and orbital angular momentum. Because angular momentum is a vector, the Spin Quantum Number (s) has both a magnitude (1/2) and direction (+ or -). This vector is called the magnetic spin quantum number (ms)

Rules Governing the Allowed Combinations of Quantum Numbers

- The three quantum numbers (n, l, and m) that describe an orbital are integers: 0, 1, 2, 3, and so on.
- The principal quantum number (n) cannot be zero. The allowed values of n are therefore 1, 2, 3, 4, and so on.
- The angular quantum number (1) can be any integer between 0 and n 1. If n = 3, for example, l can be 0, 1, or 2.
- The magnetic quantum number (m) can be any integer between -1 and +1. If 1 = 2, m can be 2, -1, 0, +1, or +2.

Principles n rules relevant to filling up patterns of electrons

Hund's rule

Every orbital in a subshell is singly occupied with one electron before any one orbital is doubly occupied, and all electrons in singly occupied orbitals have the same spin.

In atomic physics, Hund's rules refer to a set of rules formulated by German physicist Friedrich Hund around 1927, which are used to determine the term symbol that corresponds to the ground state of a multi-electron atom. In chemistry, the first rule is especially important and is often referred to as simply Hund's Rule.

The three rules are:

- For a given electron configuration, the term with maximum multiplicity has the lowest energy. The multiplicity is equal to , where is the total spin angular momentum for all electrons. The term with lowest energy is also the term with maximum.
- For a given multiplicity, the term with the largest value of the total orbital angular momentum quantum number has the lowest energy.

• For a given term, in an atom with outermost subshell half-filled or less, the level with the lowest value of the total angular momentum quantum number (for the operator) lies lowest in energy. If the outermost shell is more than half-filled, the level with the highest value of is lowest in energy.

These rules specify in a simple way how the usual energy interactions dictate the ground state term. The rules assume that the repulsion between the outer electrons is very much greater than the spin-orbit interaction which is in turn stronger than any other remaining interactions.

Pauli Exclusion Principle

The Pauli Exclusion Principle is the quantum mechanical principle that no two identical fermions (particles with half-integer spin) may occupy the same quantum state simultaneously. A more rigorous statement is that the total wave function for two identical fermions is anti-symmetric with respect to exchange of the particles. The principle was formulated by Austrian physicist Wolfgang Pauli in 1925.

For example, no two electrons in a single atom can have the same four quantum numbers; if n, l, and ml are the same, ms must be different such that the electrons have opposite spins, and so on.

Aufbau principle

Aufbau comes from the German word "Aufbauen" which means "to build". In essence when writing electron configurations we are building up electron orbitals as we proceed from atom to atom. As we write the electron configuration for an atom, we will fill the orbitals in order of increasing atomic number. The Aufbua principle originates from the Pauli's exclusion principle which says that no two fermions (e.g., electrons) in an atom can have the same quantum number, hence they have to "pile up" or "build up" to higher energy levels.



Electronic Configuration

At GCSE level, electrons are presented as point like entities that orbit around the nucleus of the atom, with the first orbital being able to hold two electrons, the second eight, and the third eighteen. We now know that this is not strictly accurate, and at A level a more sophisticated model is required.

We think of the electron orbitals as inhabiting a sub-level within a principal level. Each sub-level is capable of containing orbitals of a single shape referenced by the letters s, p, d and f. The sub levels themselves are commonly referred to by the letter of the orbital type which they can contain. Instead of saying the 3rd sub level of principal level 4 you would say the d sub level of level 4.

In the table below you should be able to see that the third sub level (d) of principal level 3 can contain 5 orbitals of type d. As each orbital can contain up to 2 electrons this means that this sub level can contain 10 electrons.

27

Principal Level	Sub-level Electrons	
n=1	\rightarrow 1 type s orbital	2
Maximum Electrons in level		2
n=2	\rightarrow 1 type s orbital	2
	\rightarrow 3 type p orbitals	6
Maximum Electrons in level		8
n=3	\rightarrow 1 type s orbital	2
	\rightarrow 3 type p orbitals	6
	\rightarrow 5 type d orbitals	10
Maximum Electrons in level		18
n=4	\rightarrow 1 type s orbital	2
	\rightarrow 3 type p orbitals	6
	\rightarrow 5 typed orbitals	10
	\rightarrow 7 type f orbitals	14
Maximum Electrons in level		32

As shown in the table, the maximum number of orbitals in each type of sub level is related to its type. An 's' sub level can contain only one orbital (2 electrons), a 'p' sub level con contain a maximum of 3 orbitals (6 electrons) ; a 'd' a maximum of 5 orbitals (10 electrons); and an 'f' a maximum of 7 (14 electrons).

The capacity of each principal level is the sum of the capacities of its sub levels. You should be able to see that the capacities of the principal levels equate to the simpler GCSE model of electron shells.

There are certain rules that it is necessary to know about the filling of these orbitals.

The orbitals are filled in the order of the table, from top to bottom. This is in ascending order of energy; that is to say, each successive energy level (lower down the table) has higher energy than the previous level.

Each orbital must be filled before electrons are put into the next orbital. An atom, for example, must always have two electrons in its 1s sub-energy level before any are placed into the 2s orbital.

Ionization energy

The ionization energy, or ionization potential, is the energy required to completely remove an electron from a gaseous atom or ion. The closer and more tightly bound an electron is to the nucleus, the more difficult it will be to remove, and the higher its ionization energy

Ionization energy is measured in electronvolts (eV). Sometimes the molar ionization energy is expressed, in J/mol.

<u>First Ionization Energy (ΔH IE I)</u>

The first ionization energy is the energy required to remove one electron from the parent atom. The second ionization energy is the energy required to remove a second valence electron from the univalent ion to form the divalent ion, and so on. Successive ionization energies increase. The second ionization energy is always greater than the first ionization energy.

Second, Third, Fourth, and Higher Ionization Energies

By now you know that sodium forms Na+ ions, magnesium forms Mg2+ ions, and aluminum forms Al3+ ions. But have you ever wondered why sodium doesn't form Na2+ ions, or even Na3+ ions? The answer can be obtained from data for the second, third, and higher ionization energies of the element.

The first ionization energy of sodium, for example, is the energy it takes to remove one electron from a neutral atom.

$$Na(g) + energy Na+(g) + e$$
-

The second ionization energy is the energy it takes to remove another electron to form an Na2+ ion in the gas phase.

$$Na+(g) + energy Na_2+(g) + e$$
-

The third ionization energy can be represented by the following equation.

The energy required to form a Na₃+ ion in the gas phase is the sum of the first, second, and third ionization energies of the element.

First, Second, Third, and Fourth Ionization Energies of Sodium, Magnesium, and Aluminum (kJ/mol)

Na	<u>1st IE</u> 495.8	<u>2nd IE</u> 4562.4	<u>3rd IE</u> 6912	<u>4th IE</u> 9543
Mg	737.7	1450.6	7732.6	10,540
A1	577.6	1816.6	2744.7	11,577

It doesn't take much energy to remove one electron from a sodium atom to form an Na+ ion with a filled-shell electron configuration. Once this is done, however, it takes almost 10 times as much energy to break into this filled-shell configuration to remove a second electron. Because it takes more energy to remove the second electron than is given off in any chemical reaction, sodium can react with other elements to form compounds that contain Na+ ions but not Na2+ or Na3+ ions. A similar pattern is observed when the ionization energies of magnesium are analyzed. The first ionization energy of magnesium is larger than sodium because magnesium has one more proton in its nucleus to hold on to the electrons in the 3s orbital.

Mg: [Ne] 3s2

The second ionization energy of Mg is larger than the first because it always takes more energy to remove an electron from a positively charged ion than from a neutral atom. The third ionization energy of magnesium is enormous, however, because the Mg2+ ion has a filled-shell electron configuration. The same pattern can be seen in the ionization energies of aluminum. The first ionization energy of aluminum is smaller than magnesium. The second ionization energy of aluminum is larger than the first, and the third ionization energy is even larger. Although it takes a considerable amount of energy to remove three electrons from an aluminum atom to form an Al₃+ ion, the energy needed to break into the filled-shell configuration of the Al₃+ ion is astronomical. Thus, it would be a mistake to look for an Al₄+ ion as the product of a chemical reaction.

Ionization Energy Trends in the Periodic Table

Ionization energies increase moving from left to right across a period (decreasing atomic radius). Ionization energy decreases moving down a group (increasing atomic radius). Group I elements have low ionization energies because the loss of an electron forms a stable octet. It becomes harder to remove an electron as the atomic radius decreases because the electrons are generally closer to the nucleus, which is also more positively charged.

Periodic table

A periodic table is a tabular display of the chemical elements, organized on the basis of their atomic numbers, electron configurations, and recurring chemical properties. Elements are presented in order of increasing atomic number (number of protons). The standard form of table comprises an 18×7 grid or main body of elements, positioned above a smaller double row of elements.



The table can also be deconstructed into four rectangular blocks: the s-block to the left, the p-block to the right, the d-block in the middle, and the f-block below that. The rows of the table are called periods; the columns of the s-, d-, and p-blocks are called groups, with some of these having names such as the halogens or the noble gases. Since, by definition, a periodic table incorporates recurring trends, any such table can be used to derive relationships between the properties of the elements and predict the properties of new, yet to be discovered or synthesized, elements. As a result, a periodic table—whether in the standard form or some other variant—provides a useful framework for analyzing chemical behavior, and such tables are widely used in chemistry and other sciences.

Although precursors exist, Dmitri Mendeleev is generally credited with the publication, in 1869, of the first widely recognized periodic table. He developed his table to illustrate periodic trends in the properties of the then-known elements. Mendeleev also predicted some properties of then-unknown elements that would be expected to fill gaps in this table. Most of his predictions were proved correct when the elements in question were subsequently discovered. Mendeleev's periodic table has since been expanded and refined with the discovery or synthesis of further new elements and the development of new theoretical models to explain chemical behavior.

All elements from atomic numbers 1 (hydrogen) to 118 (ununoctium) have been discovered or synthesized. Of these, all up to and including californium exist naturally; the rest have only been synthesized in laboratories. Production of elements beyond ununoctium is being pursued, with the question of how the periodic table may need to be modified to accommodate any such additions being a matter of ongoing debate. Numerous synthetic radionuclides of naturally occurring elements have also been produced in laboratories.

<u>Blocks</u>

Because of the importance of the outermost electron shell, the different regions of the periodic table are sometimes referred to as blocks, named according to the subshell in which the "last" electron resides.

- The s-block comprises the first two groups (alkali metals and alkaline earth metals) as well as hydrogen and helium.
- The p-block comprises the last six groups which are groups 13 to 18 in IUPAC (3A to 8A in American) and contains, among other elements, all of the metalloids.
- The d-block comprises groups 3 to 12 in IUPAC (or 3B to 2B in American group numbering) and contains all of the transition metals.

32

• The f-block, usually offset below the rest of the periodic table, comprises the lanthanides and actinides.

<u>Periods</u>

A period is a horizontal row in the periodic table. Although groups generally have more significant periodic trends, there are regions where horizontal trends are more significant than vertical group trends, such as the f-block, where the lanthanides and actinides form two substantial horizontal series of elements.

- The first period contains fewer elements than any other, with only two, hydrogen and helium. They therefore do not follow the octet rule. Chemically, helium behaves as a noble gas, and thus is taken to be part of the group 18 elements. However, in terms of its nuclear structure it belongs to the s block, and is therefore sometimes classified as a group 2 element, or simultaneously both 2 and 18. Hydrogen readily loses and gains an electron, and so behaves chemically as both a group 1 and a group 17 element.
- A period 2 element is one of the chemical elements in the second row (or period) of the periodic table. The periodic table is laid out in rows to illustrate recurring (periodic) trends in the chemical behavior of the elements as their atomic number increases; a new row is started when chemical behavior begins to repeat, creating columns of elements with similar properties. The second period contains the elements lithium, beryllium, boron, carbon, nitrogen, oxygen, fluorine, and neon. This situation can be explained by modern theories of atomic structure. In a quantum mechanical description of atomic structure, this period corresponds to the filling of the 2s and 2p orbitals. Period 2 elements obey the octet rule in that they need eight electrons to complete their valence shell. The maximum number of electrons that these elements can accommodate is ten, two in the 1s orbital, two in the 2s orbital and six in the 2p orbital. All of the elements in the period can form diatomic molecules except beryllium and neon.
- A period 3 element is one of the chemical elements in the third row (or period) of the periodic table of the chemical elements. The periodic table is laid out in rows to illustrate recurring (periodic) trends in the chemical behaviour of the elements as their atomic number increases: a new row is begun when chemical behaviour begins to repeat, meaning that elements with similar behavior fall into the same vertical columns. The third period contains eight elements: sodium, magnesium, aluminium, silicon, phosphorus, sulfur, chlorine, and argon.

The first two, sodium and magnesium, are members of the s-block of the periodic table, while the others are members of the p-block. Note that there is a 3d orbital, but it is not filled until Period 4, such giving the period table its characteristic shape of "two rows at a time". All of the period 3 elements occur in nature and have at least one stable isotope.

- Period 4 includes the biologically essential elements potassium and calcium, and is the first period in the d-block with the lighter transition metals. These include iron, the heaviest element forged in main-sequence stars and a principal component of the earth, as well as other important metals such as cobalt, nickel, copper, and zinc. Almost all have biological roles.
- Period 5 contains the heaviest few elements that have biological roles, molybdenum and iodine. (Tungsten, a period 6 element, is the only heavier element that has a biological role.) It includes technetium, the lightest exclusively radioactive element.
- Period 6 is the first period to include the f-block, with the lanthanides (also known as the rare earth elements), and includes the heaviest stable elements. Many of these heavy metals are toxic and some are radioactive, but platinum and gold are largely inert.
- All elements of period 7 are radioactive. This period contains the heaviest element which occurs naturally on earth, californium. All of the subsequent elements in the period have been synthesized artificially. Whilst one of these (einsteinium) is now available in macroscopic quantities, most are extremely rare, having only been prepared in microgram amounts or less. Some of the later elements have only ever been identified in laboratories in quantities of a few atoms at a time.
- Although the rarity of many of these elements means that experimental results are not very extensive, periodic and group trends in behaviour appear to be less well defined for period 7 than for other periods. Whilst francium and radium do show typical properties of Groups 1 and 2 respectively, the actinides display a much greater variety of behaviour and oxidation states than the lanthanides.

Initial studies suggest Group 14 element flerovium appears to be a noble gas instead of a poor metal, and group 18 element ununoctium probably is not a noble gas. These peculiarities of period 7 may be due to a variety of factors, including a large degree of spin-orbit coupling and relativistic effects, ultimately caused by the very high positive electrical charge from their massive atomic nuclei.

• No element of the eighth period has yet been synthesized. A g-block is predicted. It is not clear if all elements predicted for the eighth period are in fact physically possible. There may therefore be no ninth period.

<u>Groups</u>

A group or family is a vertical column in the periodic table. Groups usually have more significant periodic trends than periods and blocks, explained below. Modern quantum mechanical theories of atomic structure explain group trends by proposing that elements within the same group generally have the same electron configurations in their valence shell.

Consequently, elements in the same group tend to have a shared chemistry and exhibit a clear trend in properties with increasing atomic number. However in some parts of the periodic table, such as the d-block and the f-block, horizontal similarities can be as important as, or more pronounced than, vertical similarities.

1st Group

The first column of the periodic table is the group of elements known as the Group 1 or alkali metals. This group includes lithium, sodium, potassium, rubidium, cesium, and francium. By definition, a metal is an element that loses one or more electrons to create a positively charged ion known as a cation (pronounced "cat"- "ion"). The alkali metals have only one electron in their outermost energy level.

All elements would like to have complete s and p orbitals in their outermost energy levels, an arrangement of eight electrons called an octet. The rule of thumb for creating any type of ion is called the Octet Rule. The Octet Rule says that elements lose, gain, or share electrons to form the required octet in their highest remaining energy level.

2nd Group

The second column of elements from the left of the periodic table is known as the Group 2 or alkaline earth metals. It consists of beryllium, magnesium, calcium, strontium, barium, and radium.

Originally the term "alkaline earths" referred only to the oxides of calcium, strontium, and barium. The definition was later broadened to include the entire Group 2 family of elements. This group commonly loses the two s orbital electrons found in their outermost energy level. The remaining ion then has the desired complete octet of s and p orbital electrons in its outermost energy level.

<u>3rd Group – 12th Group</u>

The remaining elements of the periodic table can be lumped into two major divisions, the transition metals (Groups 3-12) and the rare earths (which can be further broken down into the actinides and lanthanides). Each group in the transition metals has complete s and p orbitals with incomplete d orbitals. The elements tend to want the most stable configuration; for example, one electron in each orbital instead of a complete s orbital and four d orbitals with one electron each. This leads to some unique characteristics.

13th Group

The last of the p block families we will be looking at is the boron family -- Group 13. This group includes the elements boron, aluminum, gallium, indium, and thallium. All five have three electrons in their outer energy level. Only one member of this family is a metalloid -- boron. The others are classified as metals, forming positive ions by giving up their three outermost electrons.

14th Group

Group 14 is the carbon family. The five members are carbon, silicon, germanium, tin, and lead. All of these elements have four electrons in their outermost energy level. Of the Group 14 elements, only carbon and silicon form bonds as nonmetals (sharing electrons covalently). Silicon and germanium are semimetals (metalloids), existing in compounds with either +4 or -4 charges. Tin and lead are definitely metals. They always lose electrons due to the distance of their outer shells from the nucleus. They usually form compounds as cations with a +4 charge. All of the elements of this family can form four bonds, the most of any family.

15th Group

The Group 15 elements are generally known as the Pnitrogens (nitrogen family). All of the elements of this family have five electrons in their outermost energy level. This group is divided into nonmetals, semimetals, and metals by characteristic. The top two elements, nitrogen and phosphorus, are very definitely nonmetals, forming -3 charge anions. Nitrogen is a diatomic gas and phosphorus is a solid.

The elements arsenic, antimony, and bismuth all have some characteristics of semimetals such as brittleness as a free element. Arsenic is the only true semimetal of the three, existing in compounds with both -3 or + 5 charges. Antimony and bismuth can exist with a -3 charge in compound but are more commonly found as metals with a +5 charge because of their size.

The pull of the positive protons found in their nucleus is so far from the outer shell (highest energy level) that the outer energy level electrons are more easily stripped off than they are able to attract three more electrons to complete the octet. In fact, bismuth is generally classified as a metal.

16th Group

Group 16 is the chalcogens (oxygen family). It consists of the elements oxygen, sulfur, selenium, tellurium, and polonium. Each has six of the desired eight electrons required for the octet in its highest energy level. This means that it takes or accepts two electrons from atoms of other elements to form anions or shares two electrons to form covalent bonds.

17th Group

Group 17 is a family of elements known as the halogens. The word "halogen" means "salt-former." The halogens form salts when they react with a metal. Halogens exist in a variety of states at room temperature.

Fluorine and chlorine are gases, bromine is a liquid, and iodine and astatine are solids. All of these elements exist as diatomic molecules in their gaseous state. This means that two atoms bond together to form a molecule of the gas.

18th Group

Let's look at the other side of the periodic table now. The group of elements at the far right of the table (Group 18) is known commonly as the noble gases. They are generally chemically inert. This means that they do not react with other elements because they already have the desired eight total s and p electrons in their outermost (highest) energy level.

The elements in this group are helium, neon, argon, krypton, xenon, and radon. They are monatomic gases. These gases were not discovered until the last five years of the 1800s. They are extremely rare in nature, and none was known until helium was discovered to exist on the sun. In fact, the name of the element helium was derived from the Greek word Helios, used to refer to the sun.

Trends shown by s and p block elements across the period and down the group

Electronegativity

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. The Pauling scale is the most commonly used. Fluorine (the most electronegative element) is assigned a value of 4.0, and values range down to cesium and francium which are the least electronegative at 0.7.

Consider a bond between two atoms, A and B. Each atom may be forming other bonds as well as the one shown - but these are irrelevant to the argument.

If the atoms are equally electronegative, both have the same tendency to attract the bonding pair of electrons, and so it will be found on average half way between the two atoms. To get a bond like this, A and B would usually have to be the same atom. You will find this sort of bond in, for example, H₂ or Cl₂ molecules.