Applied Chemistry

Atomic Structure

1. Rutherford Model of the Atom

Ernest Rutherford proposed his atomic model on the basis of his famous alpha-particle scattering experiment, in which a thin gold foil was bombarded with a beam of fast-moving, positively charged alpha particles, and the scattering pattern of these particles was observed on a surrounding fluorescent screen.

The key observations made during this experiment, and the conclusions drawn from them, are summarised below:

Observation from Alpha-Scattering Experiment	**Conclusion Drawn**
Most alpha particles passed straight through the gold foil undeflected	Most of the atom is empty space
A small fraction of alpha particles were deflected through small angles	There is a concentration of positive charge within the atom that repels the positively charged alpha particles
A very small number of alpha particles bounced back at large angles (nearly 180°)	The entire positive charge and almost the whole mass of the atom are concentrated in a very small, dense central region, called the nucleus

On the basis of these observations, Rutherford proposed the following model of the atom:

- The entire positive charge and almost the whole mass of an atom is concentrated in an extremely small central region called the nucleus.
- Electrons, which are negatively charged, revolve around the nucleus in circular paths (orbits) at relatively large distances from it, much like planets revolving around the Sun.
- The size of the nucleus is very small compared to the overall size of the atom, and most of the volume of the atom is essentially empty space.
- The number of orbiting electrons is such that their total negative charge exactly balances the total positive charge of the nucleus, making the atom as a whole electrically neutral.

Although Rutherford's model successfully explained the existence of the nucleus, it had a major limitation: according to classical electromagnetic theory, an electron revolving in a circular orbit is continuously accelerating and should therefore continuously radiate energy, causing it to spiral inward and eventually collapse into the nucleus. This would make atoms inherently unstable, which contradicts the well-established stability of matter observed in nature. Rutherford's model was also unable to explain the line (discrete) spectrum observed for atoms such as hydrogen. These shortcomings were addressed by Bohr's theory.

2. Bohr's Theory of the Atom

Niels Bohr modified Rutherford's model by incorporating ideas from the emerging quantum theory, in order to overcome its shortcomings regarding atomic stability and the observed line spectra of atoms. Bohr's theory is based on the following postulates (expressions for the energy and radius of an orbit are not required at this level):

1. Electrons revolve around the nucleus only in certain specific, permitted circular orbits, called stationary orbits or energy levels, without radiating any energy while in these orbits, despite their circular (accelerated) motion.
2. Each stationary orbit is associated with a fixed amount of energy, and the orbits are arranged in order of increasing energy as their distance from the nucleus increases; these orbits are numbered n = 1, 2, 3, and so on, called the principal quantum number.
3. An electron can move from a lower energy orbit to a higher energy orbit only by absorbing a definite (quantised) amount of energy, and can move from a higher energy orbit to a lower energy orbit only by emitting a definite (quantised) amount of energy, equal to the difference in energy between the two orbits.
4. The energy absorbed or emitted during such a transition is released or absorbed in the form of a photon (a quantum of electromagnetic radiation), whose frequency is directly related to the energy difference between the two orbits involved.
5. The angular momentum of an electron revolving in a permitted orbit is an integral multiple of $h/2\pi$ (where h is Planck's constant), meaning that only certain specific orbits, with specific angular momenta, are allowed.

Bohr's theory successfully explained the stability of the atom (since electrons in permitted stationary orbits do not radiate energy) and, importantly, provided a satisfactory explanation for the line spectrum of the hydrogen atom, as discussed below.

3. Explanation of the Hydrogen Spectrum Based on Bohr's Model

When hydrogen gas is subjected to an electric discharge, its atoms absorb energy and their electrons are excited from the ground state (n = 1) to higher energy orbits. Since these excited states are unstable, the electrons quickly fall back to lower energy orbits, releasing the absorbed energy in the form of photons of specific, well-defined frequencies.

Because only certain specific orbits (energy levels) are permitted according to Bohr's theory, an electron can only make transitions between these specific energy levels, and each such transition releases a photon of a specific, fixed energy (and therefore a specific frequency and wavelength). This explains why the hydrogen spectrum consists of a series of sharp, discrete lines, rather than a continuous band of colours — each line in the spectrum corresponds to an electron transition between two specific, permitted orbits.

Depending on the particular lower energy level (n_1) to which the electron falls, the emission lines of hydrogen are grouped into several distinct series, each lying in a different region of the electromagnetic spectrum:

Spectral Series	**Transition ($n_2 \rightarrow n_1$)**	**Spectral Region**
Lyman series	$n_2 = 2, 3, 4, \ldots \rightarrow n_1 = 1$	Ultraviolet
Balmer series	$n_2 = 3, 4, 5, \ldots \rightarrow n_1 = 2$	Visible
Paschen series	$n_2 = 4, 5, 6, \ldots \rightarrow n_1 = 3$	Infrared
Brackett series	$n_2 = 5, 6, 7, \ldots \rightarrow n_1 = 4$	Infrared
Pfund series	$n_2 = 6, 7, 8, \ldots \rightarrow n_1 = 5$	Infrared

This successful explanation of the hydrogen spectrum, based on transitions between quantised (permitted) energy levels, was one of the greatest triumphs of Bohr's theory, providing strong experimental support for the concept of quantised electron orbits.

4. Heisenberg Uncertainty Principle

Although Bohr's theory successfully explained the hydrogen spectrum, it treated electrons as particles moving in well-defined circular orbits, with both a precisely known position and a precisely known momentum at every instant. This assumption was later shown to be fundamentally inconsistent with the wave-like nature of very small particles such as electrons, as expressed by the Heisenberg uncertainty principle.

The Heisenberg uncertainty principle states that it is impossible to determine, simultaneously and with absolute precision, both the exact position and the exact momentum (or velocity) of a microscopic particle, such as an electron. If Δx represents the uncertainty in position and Δp represents the uncertainty in momentum, the principle is expressed as:

- $\Delta x \times \Delta p \geq h / 4\pi$

where h is Planck's constant. This relation shows that the more precisely the position of an electron is known, the less precisely its momentum can be known, and vice versa; both quantities cannot be determined exactly at the same time.

The Heisenberg uncertainty principle has a major conceptual consequence: it rules out the idea of an electron moving in a fixed, well-defined orbit around the nucleus (as proposed by Bohr), since this would require knowing both its exact position and its exact velocity simultaneously. This led to the replacement of the concept of definite electron "orbits" with the modern concept of "orbitals", which describe only the probability of finding an electron within a given region of space around the nucleus.

5. Quantum Numbers and the Orbital Concept

An orbital is defined as a three-dimensional region of space around the nucleus of an atom within which there is a high probability of finding an electron. Unlike the fixed, well-defined orbits of Bohr's theory, an orbital represents a probability distribution, consistent with the wave nature of the electron and the Heisenberg uncertainty principle.

The complete description of the state of an electron in an atom, including the size, shape, orientation, and spin associated with its orbital, requires four quantum numbers, summarised below:

Quantum Number	Symbol	Physical Significance	Possible Values
Principal Quantum Number	n	Determines the main energy level (shell) and the approximate size and energy of the orbital	n = 1, 2, 3, … (positive integers)
Azimuthal (Angular Momentum) Quantum Number	l	Determines the shape of the orbital (sub-shell) within a given shell	l = 0, 1, 2, …, (n − 1)
Magnetic Quantum Number	m_l	Determines the orientation of the orbital in space	m_l = −l, …, 0, …, +l

Spin Quantum Number	m_s	Determines the spin (intrinsic angular momentum) direction of the electron	m_s = +½ or −½

The azimuthal quantum number l is associated with different types of sub-shells, conventionally labelled using letters: l = 0 corresponds to an s sub-shell, l = 1 corresponds to a p sub-shell, l = 2 corresponds to a d sub-shell, and l = 3 corresponds to an f sub-shell. Together, these four quantum numbers uniquely specify the state of every electron in an atom.

6. Shapes of s, p, and d Orbitals

6.1 Shape of s-Orbitals

An s-orbital (l = 0) has a spherical shape, with the probability of finding the electron being the same in all directions at a given distance from the nucleus. The size of an s-orbital increases with an increase in the principal quantum number n (that is, a 2s orbital is larger than a 1s orbital), but the spherical symmetry is maintained in every case.

6.2 Shape of p-Orbitals

A p-orbital (l = 1) has a dumbbell (or double-lobed) shape, consisting of two lobes on either side of the nucleus, separated by a plane (called a nodal plane) passing through the nucleus, where the probability of finding the electron is zero. There are three p-orbitals in any given sub-shell, designated p_x, p_y, and pz, each oriented along one of the three mutually perpendicular axes (x, y, and z), corresponding to the three possible values of the magnetic quantum number when l = 1.

6.3 Shape of d-Orbitals

A d-orbital (l = 2) generally has a more complex shape than s- and p-orbitals, most commonly consisting of four lobes arranged in a double-dumbbell (cloverleaf) pattern, although one of the five d-orbitals (dz^2) has a somewhat different shape, consisting of two lobes along the z-axis together with a ring (or “doughnut”) of electron density around the centre. There are five d-orbitals in any given sub-shell, corresponding to the five possible values of the magnetic quantum number when l = 2, designated d_{xy}, d_yz, d_xz, $d_{x^2-y^2}$, and dz^2.

7. Pauli's Exclusion Principle

Pauli's exclusion principle states that no two electrons in the same atom can have the same set of all four quantum numbers; in other words, at least one of the four quantum numbers (n, l, m_l, m_s) must be different for any two electrons within the same atom.

A direct and important consequence of this principle is that a single orbital, which is defined by a fixed set of n, l, and m_l values, can accommodate a maximum of only two electrons, and these two electrons must necessarily have opposite spins (one with $m_s = +½$ and the other with $m_s = −½$), so that their complete sets of four quantum numbers remain different from each other.

8. Hund's Rule of Maximum Multiplicity

Hund's rule of maximum multiplicity states that, when electrons are to be filled into a set of orbitals of equal energy (called degenerate orbitals, such as the three p-orbitals or the five d-orbitals within the same sub-shell), electrons first occupy each of these orbitals singly, with parallel (unpaired) spins, before any orbital receives a second electron (which would require pairing, with opposite spin).

This rule reflects the fact that electrons, being negatively charged, repel one another, and this mutual repulsion is minimised when electrons occupy separate orbitals rather than being forced to pair up within the same orbital. For example, in the case of nitrogen (atomic number 7), with three electrons to be distributed among the three 2p orbitals, each of the three orbitals receives one electron with parallel spin, rather than two of the orbitals being doubly and singly occupied while the third remains empty.

9. Aufbau Principle

The Aufbau principle (from the German word “aufbau”, meaning “building up”) states that, in the ground state of an atom, electrons are filled into the available orbitals in order of their increasing energy, with orbitals of lower energy being filled completely before electrons begin to occupy orbitals of higher energy.

The relative order in which orbitals are filled, according to the Aufbau principle, generally follows the sequence: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, and so on. This particular filling order can be conveniently remembered using the diagonal rule, in which orbitals are arranged in increasing order of the sum of their principal and azimuthal quantum numbers ($n + l$); where two orbitals have the same ($n + l$) value, the orbital with the lower value of n is filled first.

10. Electronic Configuration

The electronic configuration of an atom is a systematic representation showing the distribution of its electrons among the various shells, sub-shells, and orbitals, written in accordance with the Aufbau principle, Pauli's exclusion principle, and Hund's rule together. It is generally written in the form (principal quantum number)(sub-shell letter)^(number of electrons in that sub-shell), such as $1s^2\ 2s^2\ 2p^6$.

For example, the electronic configurations of a few elements, determined by applying these three principles together, are as follows:

- Hydrogen (Z = 1): $1s^1$
- Carbon (Z = 6): $1s^2\ 2s^2\ 2p^2$
- Nitrogen (Z = 7): $1s^2\ 2s^2\ 2p^3$ (each of the three 2p orbitals singly occupied, in accordance with Hund's rule)
- Neon (Z = 10): $1s^2\ 2s^2\ 2p^6$
- Sodium (Z = 11): $1s^2\ 2s^2\ 2p^6\ 3s^1$

Writing the correct electronic configuration of an element is essential for understanding and predicting its chemical behaviour, including its valency, reactivity, and position in the periodic table, since chemical bonding is governed primarily by the arrangement of electrons in the outermost (valence) shell of an atom.

11. Multiple Choice Questions (MCQs)

Answer the following questions by selecting the most appropriate option.

1. Rutherford's alpha-particle scattering experiment led to the discovery of:

A) The electron
B) The nucleus of the atom
C) The neutron
D) Isotopes

2. According to Rutherford's model, most of the mass and positive charge of an atom is concentrated in:

A) The electron cloud
B) The nucleus
C) Empty space
D) The outermost shell

3. The main drawback of Rutherford's atomic model was that it could not explain:

A) The existence of the nucleus
B) The stability of the atom and the line spectrum of hydrogen
C) The presence of protons

D) The size of the nucleus

4. According to Bohr's theory, an electron does not radiate energy while moving in:

A) Any random path
B) A stationary (permitted) orbit
C) A straight line
D) An unstable orbit

5. According to Bohr's theory, an electron emits energy in the form of radiation when it:

A) Remains in the same orbit
B) Jumps from a higher energy orbit to a lower energy orbit
C) Jumps from a lower energy orbit to a higher energy orbit
D) Leaves the atom entirely

6. The Balmer series of the hydrogen spectrum lies in the:

A) Ultraviolet region
B) Visible region
C) Infrared region
D) X-ray region

7. The Lyman series of the hydrogen spectrum arises from transitions to which energy level?

A) n = 1
B) n = 2
C) n = 3
D) n = 4

8. The Heisenberg uncertainty principle states that it is impossible to simultaneously determine, with absolute precision:

A) The mass and charge of an electron
B) The position and momentum of a particle such as an electron
C) The number of protons and neutrons in a nucleus
D) The energy and mass of a photon

9. The principal quantum number (n) determines:

A) The shape of the orbital
B) The orientation of the orbital
C) The main energy level (shell) and approximate size of the orbital
D) The spin of the electron

10. The azimuthal quantum number (l) determines:

A) The size of the orbital
B) The shape of the orbital (sub-shell)
C) The spin of the electron
D) The total number of electrons in an atom

11. The shape of an s-orbital is:

A) Dumbbell-shaped
B) Spherical
C) Double dumbbell-shaped
D) Cubic

12. The shape of a p-orbital is:

A) Spherical
B) Dumbbell-shaped
C) Ring-shaped
D) Flat and circular

13. Pauli's exclusion principle states that no two electrons in an atom can have:

A) The same principal quantum number
B) The same set of all four quantum numbers
C) Different spin quantum numbers
D) The same azimuthal quantum number only

14. Hund's rule of maximum multiplicity states that electrons are distributed among orbitals of equal energy so as to:

A) Pair up as early as possible
B) Keep their spins paired at all times
C) First singly occupy each orbital with parallel spins before pairing occurs
D) Occupy only the lowest energy orbital

15. According to the Aufbau principle, electrons are filled into orbitals:

A) In random order
B) In order of increasing energy of the orbitals
C) In order of decreasing energy of the orbitals
D) Only into the outermost shell first

Answer Key

1. B) The nucleus of the atom | 2. B) The nucleus | 3. B) The stability of the atom and the line spectrum of hydrogen | 4. B) A stationary (permitted) orbit | 5. B) Jumps from a higher energy orbit to a lower energy orbit | 6. B) Visible region | 7. A) n = 1 | 8. B) The position and momentum of a particle such as an electron | 9. C) The main energy level (shell) and approximate size of the orbital | 10. B) The shape of the orbital (sub-shell) | 11. B) Spherical | 12. B) Dumbbell-shaped | 13. B) The same set of all four quantum numbers | 14. C) First singly occupy each orbital with parallel spins before pairing occurs | 15. B) In order of increasing energy of the orbitals

12. Broad / Long Answer Questions

1. Describe Rutherford's alpha-particle scattering experiment and explain the conclusions drawn from its observations regarding the structure of the atom.

2. State the postulates of Bohr's theory of the hydrogen atom (expressions for energy and radius not required).

3. Explain, on the basis of Bohr's model of the atom, how the line spectrum of hydrogen is produced.

4. Describe the different series observed in the hydrogen spectrum, mentioning the transitions involved and the spectral region in which each series lies.

5. State the Heisenberg uncertainty principle, and explain its significance in the context of the wave nature of electrons.

6. Explain the four quantum numbers used to describe the state of an electron in an atom, along with the physical significance of each.

7. Describe the shapes of s, p, and d orbitals with reference to their spatial orientation.

8. State Pauli's exclusion principle and explain its significance in determining the maximum number of electrons that can occupy a given orbital.

9. State Hund's rule of maximum multiplicity and illustrate it with the electronic configuration of nitrogen (atomic number 7).

10. State the Aufbau principle, and use it to write the electronic configuration of an element with atomic number 20 (calcium).