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PREFACE

This course provides a comprehensive exploration of fundamental concepts in chemistry, covering a wide range of topics from the quantum model of atoms to the structure and bonding of molecules. The content is organized into ten distinct chapters, each dedicated to a specific area of study.

Chapter I delves into the quantum model of atoms, examining the various quantum numbers, shapes of atomic orbitals, and the principles governing electron configuration and electronic behavior. This lays the groundwork for understanding the periodic table and the properties of elements.

Chapter II focuses on the organization of the modern periodic table, exploring the concepts of groups, blocks, and the periodicity of properties such as ionization energy, electron affinity, electronegativity, and atomic radius.

Chapter III explores the structure and bonding of molecules, including the Lewis structures, the octet rule, and the different types of chemical bonding, including covalent, ionic, metallic, hydrogen, and van der Waals bonds. The chapter also covers bond polarization, electric dipole moments, and the VSEPR model.

Subsequent chapters dive into the study of individual elements and their groups, starting with hydrogen, oxygen, and sulfur in Chapter IV, followed by the halogens and pnictogens in Chapters VI and VII, respectively. The unique properties and applications of these elements are thoroughly examined.

Chapter VIII focuses on the group 14 (VIA) elements, with a detailed exploration of carbon and silicon, their forms, and their various uses.

Chapter IX examines the alkali metals, alkaline earth metals, and transition metals, discussing their physical and chemical properties, reactivity, and industrial applications.

Finally, Chapter X introduces the concept of coordination compounds, delving into the role of ligands, bonding theories, magnetic susceptibility, and the colors of transition metal complexes.

Throughout the course, a wealth of exercises and worked examples are provided to reinforce the understanding of the material. The goal of this course is to equip students with a solid foundation in chemistry, enabling them to appreciate the fundamental principles that govern the behavior of matter and their applications in various scientific and technological fields.

CHAPTER I

A Review of the Quantum Model

A Review of the Quantum Model

The quantum model of atomic structure originates from the work of Louis de Broglie. De Broglie demonstrated that just as electromagnetic waves could be treated as streams of particles (photons), moving particles could exhibit wave-like properties. Thus, it was also valid to represent electrons either as particles or as waves. Utilizing this wave-particle duality, Erwin Schrödinger developed a partial differential equation to represent the behavior of an electron around an atomic nucleus.

Quantum Numbers

There are multiple solutions to a wave equation, each corresponding to a distinct orbital and representing a different probability distribution for an electron within that orbital. These orbitals are uniquely characterized by a set of three integers: n, l, m et m_s.

The possible values of the quantum numbers are defined as follows:

n, the principal quantum number, can have all positive integer values from 1 to ∞

l, the angular momentum quantum number, can have all integer values from (n - 1) to 0.

m, the magnetic quantum number, can have all integer values from + l through 0 to - l.

m_s, the spin quantum number, can have values of $+\frac{1}{2}$ and $-\frac{1}{2}$

Values of Quantum Numbers

To identify the electron orbital corresponding to each set of quantum numbers, we use the value of the principal quantum number n, followed by a letter for the angular momentum quantum number l. Thus, when $n = 1$, there is only the $1s$ orbital. When $n = 2$, there is a $2s$ orbital and three $2p$ orbitals (corresponding to the m values of +1, 0, and -1). The letters s, p, d, and f are derived from the categories of spectral lines: sharp, principal, diffuse, and fundamental.

l Value	Orbital designation
0	s
1	p
2	d
3	f

Shapes of the Atomic Orbitals

We decompose the wave equation into two parts: a radial part and an angular part. Each of the three quantum numbers derived from the wave equation represents a different aspect of the orbital:

- The principal quantum number $\boldsymbol{n}$ indicates the size of the orbital.

- The angular momentum quantum number $\boldsymbol{l}$ represents the shape of the orbital.

- The magnetic quantum number $\boldsymbol{m}$ represents the spatial orientation of the orbital.

The spin quantum number $\boldsymbol{m_s}$ has little physical significance; it simply allows two electrons to occupy the same orbital. The energy of the electron is determined primarily by the principal quantum number and, to a lesser extent, by the angular momentum quantum number. Although the electron does not literally spin, it behaves as if it does, and it possesses the magnetic properties expected of a rotating particle.

The s Orbitals

s orbitals are spherical in shape and centered around the atomic nucleus. As the principal quantum number increases, the probability of finding the electron further from the nucleus increases. A region where an electron is most likely to be found is referred to as a high electron density area. Conversely, regions with a low probability of finding an electron are called low electron density areas (Figure I.1).

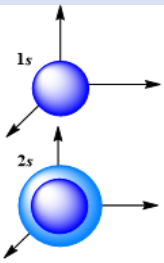


Figure I.1 Comparative shapes and sizes of the 1s and 2s orbitals

The p Orbitals

p orbitals consist of two separate regions of space (lobes) with the nucleus located between them. Since there are three p orbitals, each one is assigned a direction according to Cartesian coordinates: p_x, p_y and p_z **Figure I.2** shows the representations of the three 2p orbitals. Perpendicular to the axis of higher probability, there is a nodal plane passing through the nucleus. For example, the $2p_z$ orbital has a nodal plane in the xy plane. In terms of wave function signs, one lobe is positive and the other is negative.

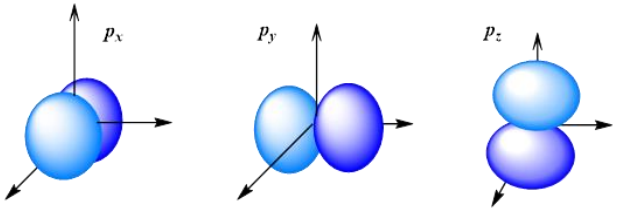


Figure I.2 Representations of the shapes of the $\boldsymbol{2p_x}$, $\boldsymbol{2p_y}$, and $\boldsymbol{2p_z}$ orbitals

The d Orbitals

The five d orbitals have intricate shapes. Three of them are positioned between the Cartesian axes, while the other two align along the axes. The nucleus is located at the point where the axes intersect. Three of these orbitals each feature four lobes situated between pairs of axes (**Figure I.3**) and are labeled d_{xy}, d_{xz} and d_{yz}. The $d_{x^2-y^2}$orbital is similar to the d_{xy} orbital but is rotated by 45°.

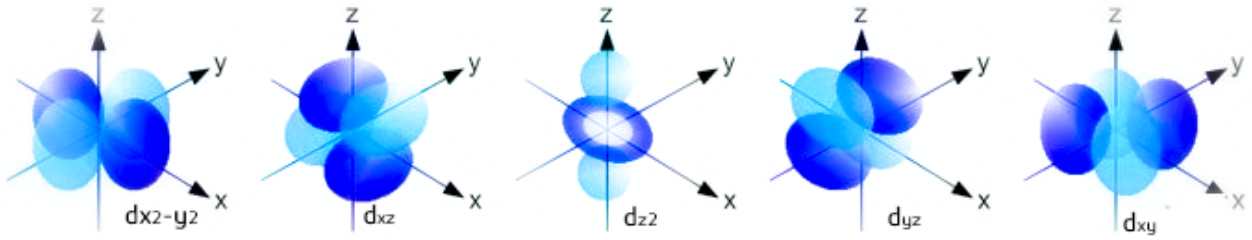


Figure I.3 Representations of the shapes of the 3d orbitals

The *f* Orbitals

The f orbitals exhibit greater complexity compared to the *d* orbitals. There is a total of seven f orbitals, with four featuring eight lobes each. The remaining three orbitals resemble the d_{z^2} orbital but with the addition of two torus-shaped rings (**Figure I.4**). Due to their limited involvement in bonding, these orbitals do not require detailed consideration.



Figure I.4 Representations of the shapes of the 4f orbitals

Electron Configuration

Pauli's Exclusion Principle

According to this rule, two electrons in an atom cannot possess identical sets of the four quantum numbers. Thus, there can be only one orbital for each set of three quantum numbers per atom, and each orbital can contain only two electrons, one with $m_s = +\frac{1}{2}$ and the other with $m_s = -\frac{1}{2}$.

Hund's Rule

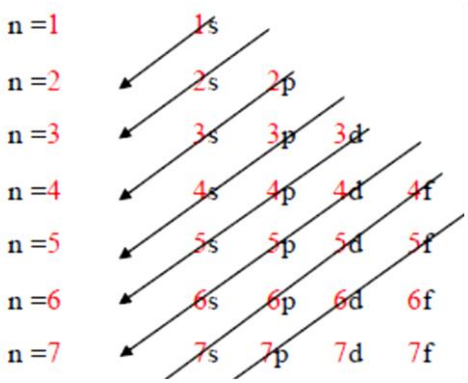
When filling a set of degenerate orbitals, the number of unpaired electrons will be maximized, and these electrons will have parallel spins.

Klechkowski's Rule

Klechkowski's rule indicates that the filling of electron subshells in electrically neutral atoms in their ground state, arranged by increasing atomic number, proceeds as follows:

- In ascending order of the values of $n + l$ defines the electron subshells.

- In ascending order of the values of n when multiple subshells have equal $n + l$ values.



The order of filling electron subshells in electrically neutral atoms in their ground state, arranged by increasing atomic number

Exceptions

A half-filled subshell leads to a configuration of maximum spin, which provides it with some stability under Hund's rule. For example, chromium (atomic number 24) has an electron configuration of *[Ar]* $3d^5 4s^1$, rather than *[Ar]* $3d^4 4s^2$. Similarly, copper (atomic number 29) has an electron configuration of *[Ar]* $3d^{10} 4s^1$, instead of *[Ar]* $3d^9 4s^2$, allowing the *3d* subshell to be fully filled and the *4s* subshell to be half-filled.

Generally, exceptions occur when electron configurations are of the form:

$(n\text{-}1)\ d^4\ ns^2$ is replaced by $(n\text{-}1)\ d^5\ ns^1$

$(n\text{-}1)\ d^9\ ns^2$ is replaced by $(n\text{-}1)\ d^{10}\ ns^1$

EXERCISES

1. Determine the electronic configuration of the following elements:

a) Oxygen (Z = 8)

b) Calcium (Z = 20)

c) Nitrogen (Z = 7)

d) Silver (Z = 47)

e) Chlorine (Z = 17)

2. Write the abbreviated electron configuration (using noble gas notation) for the following elements:

a) Aluminum (Z = 13)

b) Bromine (Z = 35)

c) Potassium (Z = 19)

d) Iron (Z = 26)

e) Xenon (Z = 54)

3. Determine the number of unpaired electrons in the ground-state electron configuration of the following elements:

a) Carbon (Z = 6)

b) Chromium (Z = 24)

c) Oxygen (Z = 8)

d) Vanadium (Z = 23)

e) Nickel (Z = 28)

4. Identify the element based on its electron configuration:

a) [He] $2s^2$ $2p^4$

b) [Ne] $3s^2$ $3p^6$

c) [Ar] $4s^2$ $3d^{10}$ $4p^4$

d) [Kr] $5s^2$ $4d^{10}$ $5p^2$

e) [Xe] $6s^2$ $4f^{14}$ $5d^{10}$ $6p^4$

CHAPTER II

Organization of the Modern Periodic Table

Organization of the Modern Periodic Table

In the modern periodic table, elements are arranged in order of increasing atomic number (the number of protons). The periodic table of elements is a "representation of all chemical elements ordered by their increasing atomic number Z." It is organized into:

• Horizontal rows called **periods**

• Columns called **groups**

• **Blocks**

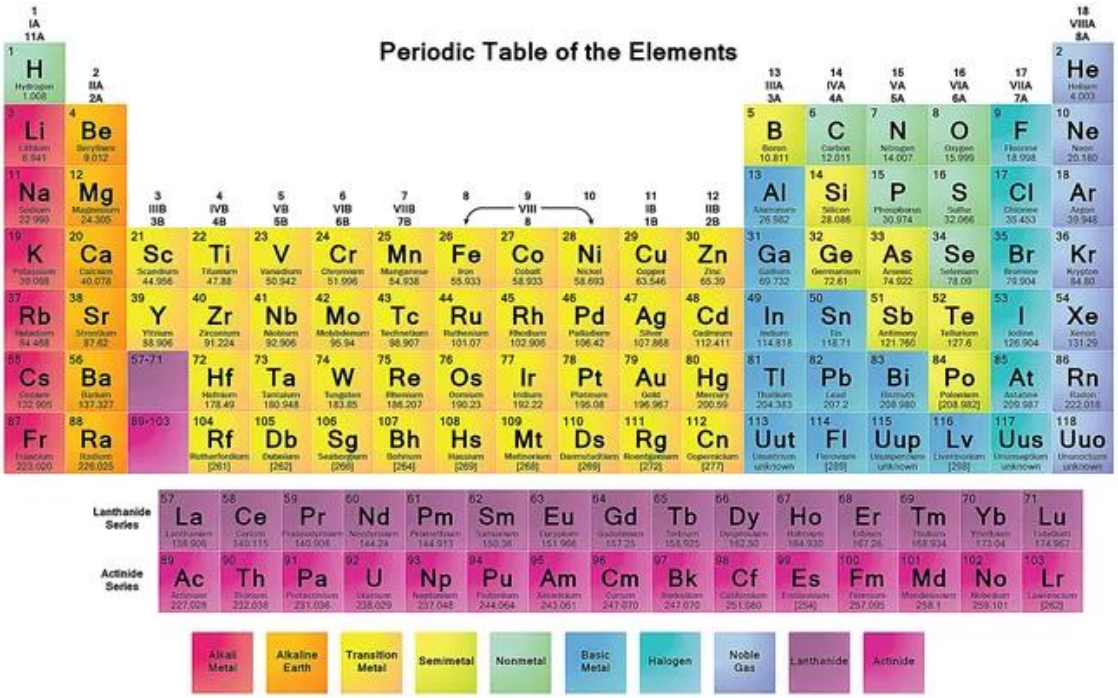


Figure II.1 Periodic Table of Elements

Periods

A period is defined by the progressive filling of electronic orbitals (subshells) as one moves to the right of the table.

The filling of subshells follows the Klechkowski's rule.

There are 7 periods, each corresponding to the complete filling of an electronic shell.

Along a period, the properties of the elements vary significantly. However, there are some similarities between elements in the same period, notably among transition metals, elements of the 6th period (lanthanides), and the 7th period (actinides).

Groups

The periodic table comprises 18 groups numbered either from 1 to 18 or in Roman numerals (in order: IA, IIA, IIIB, IVB, VB, VIB, VIIB, VIIIB, IB, IIB, IIIA, IVA, VA, VIA, VIIA, VIIIA).

Each group consists of a set of elements whose properties are relatively homogeneous and distinct from elements of other groups.

Elements in the same group have "the same electronic configuration" of valence shells, giving them similar physical and chemical properties.

Homogeneity within a group is particularly evident in the groups at the edges of the periodic table (s and p blocks), with some groups forming entire chemical series.

Blocks

Depending on the type (s, p, d, or f) of the highest energy orbital, called the valence shell, the periodic table is subdivided into 4 blocks: s block, p block, d block, and f block.

- The s block: consists of elements whose peripheral orbitals are of type s. These are the elements of the first two groups of the periodic table (hydrogen, alkali metals, and alkaline earth metals).

- The p block: consists of elements whose peripheral orbitals are of type p. These are the elements of groups 13 to 18, except for helium (He) (group 18), whose outermost orbital is of type s, but it is classified among the noble gases due to its chemistry.

- The d block: consists of elements whose peripheral orbitals are of type d. These are the elements of columns 3 to 12 (mainly transition metals).

- The f block: consists of elements whose peripheral orbitals are of type f. These are the lanthanide and actinide series.

Periodicity of Properties

Ionization Energy

In general, ionization energy can be defined as the energy required to remove an electron from a gaseous atom. For hydrogen, there is only one ionization potential as the atom has only one electron. Atoms with more than one electron have an ionization potential for each electron, and these often differ considerably. The series of ionization energies (I) for a given atom increases as follows:

$$I_1 < I_2 < I_3 < \cdots I_n$$

Tableau II.2 The different families of chemical elements and their respective groups

Column	Group	Family	Bloc
1	*IA*	Alkali metals (except for hydrogen)	*s*
2	*IIA*	Alkaline earth metals	*s*
14	*IVA*	Crystallogens	*p*
15	*VA*	Pnictogens	*p*
16	*VIA*	Chalcogens	*p*
17	*VIIA*	Halogens	*p*
18	*VIIIA*	Noble gases	*p*
3-12	*IIIB-IIB*	Transition metals	*d*

Electron Affinity

Many atoms have a tendency to gain one or more electrons when forming compounds, which is generally an energetically favorable process. A crucial step in the formation of an ionic bond involves the addition of an electron to a neutral gaseous atom, resulting in the formation of a negative ion. This process can be represented by the following equation:

$$X_{(g)} + \acute{e}_{(g)} \rightarrow X^-_{(g)}$$

The energy change associated with this process is known as the electron addition enthalpy. Conversely, the energy required to remove an electron from a negatively charged ion (an atom that has already gained an electron) is referred to as the electron affinity:

$$X^-_{(g)} \rightarrow X_{(g)} + \acute{e}_{(g)}$$

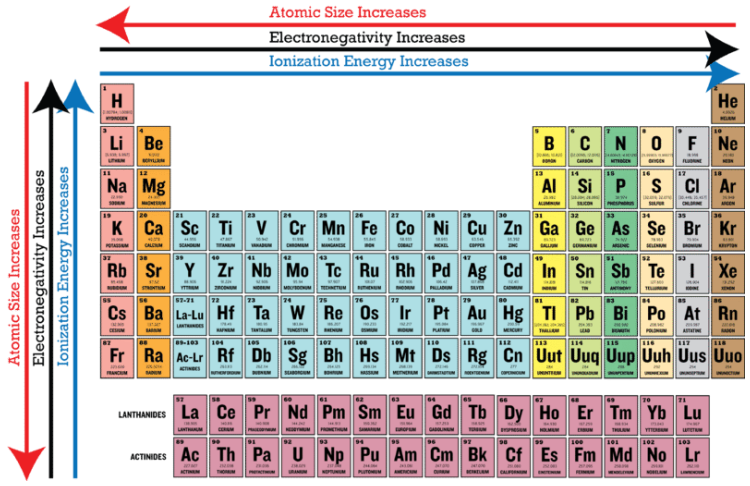


Figure II.2 Trend of ionization energy, atomic radius, electron affinity, and electronegativity in the periodic table.

Electronegativity

When two atoms form a covalent bond, they do not share electrons equally unless the atoms are identical. Linus Pauling introduced the concept of electronegativity to explain the tendency of an atom in a molecule to attract electrons.

Pauling's numerical scale for electronegativity is based on the observation that polar covalent bonds between atoms with different electronegativities are more stable than purely covalent bonds. The stabilization of the bond, Δ_{AB}, in a diatomic molecule AB due to this effect can be expressed as:

$$\Delta_{AB} = D_{AB} - (1/2)[D_{AA} + D_{BB}]$$

Where D_{AA}andD_{BB} represent the bond energies in the diatomic species $A_2$and B_2, respectively, and D_{AB} is the bond energy of the molecule AB. Thus, the term Δ_{AB} represents the additional contribution to the bond strength of AB due to the different electronegativities of the atoms. The extent of stabilization can also be expressed in terms of the difference in electronegativity between the atoms using the equation:

$$\Delta_{AB}(KJ.mo^{-1}) = 96.48|\chi_A - \chi_B|^2$$

where $\chi_A$and χ_B are the electronegativities of atoms A and B, respectively. Therefore, it is the difference in electronegativities that relates to the additional stabilization of the bond. However, a value for the electronegativity of at least one atom must be specified. Assigning a value to one atom leads to a relative value for every other atom. Pauling's electronegativity scale was established with a value of 4.0 for fluorine, and other atoms were then given values between 0 and 4. Pauling's electronegativity scale is not the only one of its kind; the electronegativity of an atom A was defined by Mulliken as:

$$\chi_A = (1/2)[I + E]$$

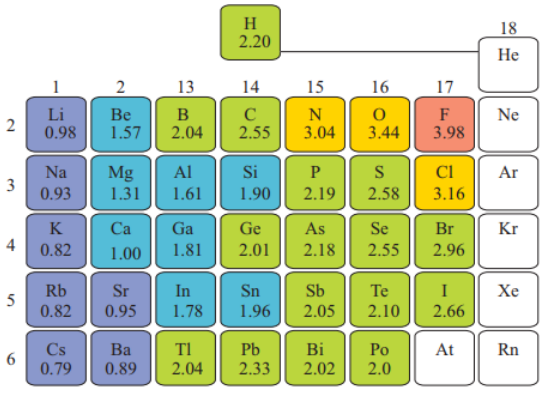


Figure II.3 Values of electronegativity of some elements in the periodic table

Where I and E are the ionization potential and the electron affinity of the atom, respectively.

Atomic Radius

The radius of an atom can only be defined when the atom is part of a molecule. It varies depending on the nature of the bonds and the surrounding atoms. The atomic radius r_a is defined as half the distance between the nuclei of two atoms in a single covalent bond.

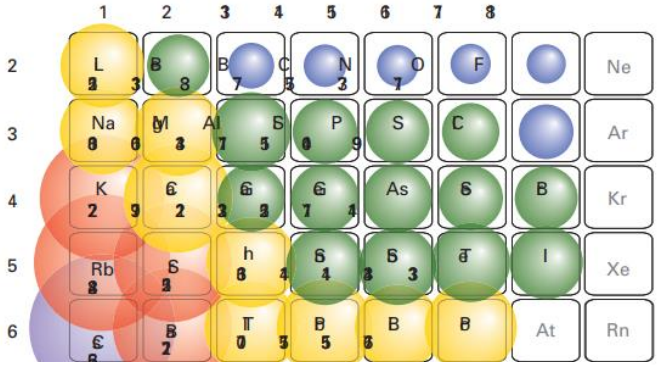


Figure II.3 Atomic radii of some elements in the periodic table

When moving across a period in the periodic table, the atomic radius decreases as the atomic number Z increases. This is because the number of electrons in the same shell increases, which raises the effective nuclear charge Z^*. Since the screening effect of electrons within the same period is minimal, this results in stronger electrostatic interactions between the nucleus and the outer electrons. Consequently, the atomic orbitals contract, leading to a reduction in the atomic radius.

In contrast, when moving down a group in the periodic table, the atomic radius increases. This phenomenon can be explained by two opposing factors:

- The effective nuclear charge Z^* increases due to the significant screening effect of electrons in lower shells, which tends to decrease the atomic radius through Coulombic attractions.

- At the same time, the transition to higher principal quantum number shells increases the spatial extension of the orbitals of the outer electrons, resulting in an overall increase in the atomic radius.

EXERCISES

- Rank the following elements in order of increasing atomic radius: Na, Mg, Al, Si.
- Explain the trend in atomic radius across a period and down a group.
- Which element has a higher ionization energy: Li or Be? Explain your answer.
- Describe the general trend in ionization energy across a period and down a group.
- Rank the following elements in order of increasing electronegativity: F, O, N, C.
- Explain the concept of electronegativity and its relationship to chemical bonding.
- Compare the metallic character of sodium (Na) and chlorine (Cl).
- Describe the general trend in metallic character across a period and down a group.
- List the elements in Group 17 (halogens) and describe their common properties.
- Explain why elements in the same group have similar chemical properties.

- Describe the changes in physical properties (e.g., state, density) as you move across Period 3 from sodium to argon.
- Explain why there is a general increase in atomic size from left to right across a period.

CHAPTER III

Molecular structure and bonding

Molecular structure and bonding

Chemical bonding is essential for understanding how atoms combine to form molecules and compounds, influencing their properties and behaviors. Bonds arise from electron interactions, leading to stable atom arrangements. The main bond types are: Covalent Bonds, Ionic Bonds, and Metallic Bonds.

Advanced theories like valence bond theory and molecular orbital theory provide deeper insights into bonding. Understanding chemical bonds is crucial for predicting compound behaviors and designing new materials, bridging microscopic interactions and macroscopic properties.

Lewis structures

Lewis proposed that a covalent bond forms when two adjacent atoms share a pair of electrons. This single bond, represented as a shared electron pair (A:B), is denoted as A–B. Similarly, a double bond, involving two shared pairs of electrons (A::B), is denoted as A=B, and a triple bond, with three shared electron pairs (A:::B), is represented as A≡B. An unshared pair of valence electrons on an atom (A:) is known as a lone pair. While lone pairs do not participate directly in bonding, they significantly influence the molecule's shape and properties.

The octet rule

Lewis proposed the octet rule to explain the formation of a wide range of molecules. According to this rule, each atom shares electrons with neighboring atoms to achieve a total of eight valence electrons, forming an "octet." This configuration mimics the stable, closed-shell configuration of noble gases, where eight electrons fill the s and p subshells of the valence shell. The exception is hydrogen, which only needs two electrons to fill its 1s orbital, forming a "duplet."

The octet rule is useful for constructing Lewis structures, which visually represent the arrangement of bonds and lone pairs in a molecule. Constructing a Lewis structure typically involves three steps:

1. **Count the Valence Electrons:** Determine the total number of valence electrons in the molecule by adding the valence electrons of all atoms. For example, hydrogen contributes one electron, while oxygen, with the configuration $[He]2s^2 2p^4$, contributes six electrons. Adjust for any ionic charges: add electrons for negative charges and subtract electrons for positive charges.

2. Arrange the Atoms: Write the chemical symbols of the atoms in a way that shows which atoms are bonded together. Typically, the less electronegative element is the central atom (e.g., CO_2, SO_4^{2-}), though there are exceptions like H_2O and NH_3.

3. Distribute the Electrons: Place pairs of electrons between bonded atoms to form single bonds. Then, allocate remaining electron pairs to give each atom an octet, forming lone pairs or multiple bonds as needed. Each bonding pair of electrons is represented by a single line (–). For polyatomic ions, the net charge is considered to belong to the ion as a whole, rather than to any individual atom.

Chemical Bonding

There are three main types of strong chemical bonds:

Covalent Bonding

Covalent bonds, also known as homopolar bonds, form between non-ionized atoms with similar electronegativities. These bonds can only be understood through quantum mechanics: valence electrons (those in the outermost sublayers) are shared between atoms, forming one or more bonding pairs of electrons.

In a molecule, the external electrons of the atoms are arranged in pairs (with opposite spins): some pairs form bonds (σ and π bonds), while others do not participate in bonding and are called lone pairs. These pairs of electrons are also referred to as electron pairs. Covalent bonds, made up of bonding pairs, are directional. For instance, in methane (CH_4), the four C-H bonds form angles of 109°28' with each other. A single covalent bond is called a "σ bond" and is always a strong bond. When there is a double bond (e.g., O_2) or a triple bond (e.g., N_2), the σ bond is accompanied by one or two π bonds, which are weaker than σ bonds but still considered strong bonds.

Ionic Bonding

Ionic bonds, also known as heteropolar bonds, form between oppositely charged ions (e.g., Na^+ and Cl^-). These bonds involve classical electrostatic forces. Ionic bonds typically form between atoms that readily produce positive ions (low ionization energy) and negative ions (high electron affinity).

Pure ionic bonds are mainly found in solids formed from elements on opposite sides of the periodic table, such as alkali halides (NaCl) or alkaline earth halides ($CaCl_2$). Due to the strength of ionic bonds, significant energy is required to break them (transforming a solid or liquid into a gas) or even to weaken them enough to melt the solid. Consequently, ionic compounds, like alkali halides, have high melting and boiling points (801°C and 1439°C for NaCl, respectively).

Metallic Bonding

Metallic bonds form between atoms with low electronegativities (around 1 on the Pauling scale) and few outer electrons, but only if there are enough such atoms. This type of bonding is primarily observed in certain solids or liquids. Like ionic bonds, metallic bonds are non-directional.

Elements to the left of the B/Si/As diagonal in the periodic table bond through metallic bonds. Groups IA (alkali metals) and IIA (alkaline earth metals) produce soft metals with low melting points, which are highly oxidizable and sensitive to moisture. Transition metals are harder (indicating stronger bonds) but remain pliable, making them useful construction materials due to their malleability.

Hydrogen Bonding

Hydrogen bonding occurs between a hydrogen atom already bonded to a highly electronegative atom and another highly electronegative atom also engaged in a molecule. In practice, only F, O, N, and Cl atoms can participate in hydrogen bonding. These atoms, although already bonded, attract hydrogen from neighboring molecules if it is bonded to another electronegative atom.

Thus, hydrogen tends to share between the two molecules, forming a hydrogen bond. It is said that the two electronegative atoms (e.g., O, F) are connected by a hydrogen bridge: F-H···F, O-H···O, O-H···N, N-H···N, etc. Exceptionally, a hydrogen bond can be so strong that the proton is equidistant from the atoms of the molecules to which it is bonded, as in the ion $(F\text{-}H\text{-}F)^-$. In all cases, hydrogen bonds are directional, like covalent bonds, unlike ionic, metallic, and van der Waals bonds.

Van der Waals Bonds

Van der Waals bonds are generally very weak (e.g., in liquid or solid He, Ne, Ar) but can sometimes be stronger (e.g., solid iodine, I_2). These bonds cause the condensation of all molecules or atoms into liquids or solids at low temperatures when no stronger bonds are present. Besides inert gases, H_2, O_2, N_2, F_2, Cl_2, etc., condense due to van der Waals forces between molecules.

Van der Waals bonds arise from the attraction between permanent electric dipoles (in polar molecules) or induced dipoles in atoms or molecules.

Bond Polarization

When a bond forms between two different atoms, it is always partially ionic to some extent. Typical examples are H_2O and HCl. In an H_2O molecule, due to the high electronegativity of oxygen, the electrons in the O-H bonds are attracted towards the oxygen atom. Consequently, these covalent bonds become polarized (partially ionic), resulting in a small positive charge (δ^+) on the hydrogen atoms and a small negative charge (δ^-) on the oxygen atom, where $\delta < 1$.

Electric Dipole Moment

The polarization of the two bonds in the water molecule leads to a situation where the center of negative charge does not coincide with the center of positive charge (which lies along the symmetry axis between the two hydrogens). This results in the molecule having a permanent electric dipole moment $\overrightarrow{\mu_e}$.

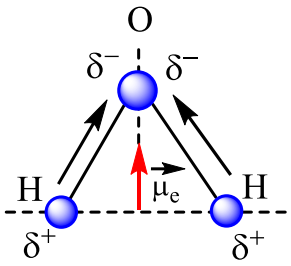


Figure III.1 Electric dipole moment of H_2O

In general, a molecule possesses an electric dipole moment $\overrightarrow{\mu_e}$ whenever the centers of positive and negative charges do not coincide. This misalignment depends on the polarization of the bonds (hence the electronegativity of the atoms) and the molecule's geometric shape.

Definition: Let q be the positive charge. If d is the distance between the two charge centers, the electric dipole moment is a vector whose magnitude is defined as:

$$\mu_e = q.d$$

The SI unit is the coulomb-meter (C·m). However, the debye (D) is more commonly used, based on the older electrostatic unit of charge (ues):

$$1\ debye\ (D) = 10^{-18}\ ues \cdot cm = \ 3{,}3 \cdot 10^{-30}\ C \cdot m$$

Chemists orient the vector $\overrightarrow{\mu_e}$ from positive to negative (physicists generally use the opposite convention). It is usually impossible (or very difficult) to calculate the exact value of μ_e, so it is determined experimentally.

Percentage of Ionicity

In a polarized A-B bond, such as in a heteronuclear diatomic molecule AB, there exists a dipole moment μ_e. If the bond were perfectly ionic, i.e., A^+B^-, the dipole moment could be easily calculated as the product of the elementary charge e and the equilibrium bond distance R_0. However, most bonds are only partially ionic: instead of A^+B^-, we have $A^{\delta+}B^{\delta-}$, where δ is the percentage of ionicity (ranging from 0 to 100% or 0 to 1).

We can determine δ from the experimentally measured dipole moment μ_e of the A-B bond. Let μ_{ion} (ionic dipole moment) be the dipole moment calculated assuming a completely ionic bond, which involves two-point charges +e and -e separated by the equilibrium distance R_0:

$$\mu_{ion} = e \cdot R_0$$

For a partially ionic bond, the charges are only $+\delta e$ and $-\delta e$. Therefore:

$$\mu_e = \delta e \cdot R_0$$

Thus:

$$\frac{\mu_e}{\mu_{ion}} = \frac{\delta e \cdot R_0}{e \cdot R_0} = \delta$$

This gives us the percentage of ionicity.

The VSEPR model

Predicting the numerical value of bond angles in simple molecules is generally challenging, except when the shape is dictated by symmetry. However, the Valence Shell Electron Pair Repulsion (VSEPR) model, which relies on basic principles of electrostatic repulsion and the presence or absence of lone pairs, offers a surprisingly effective approach to determining molecular shapes.

In the VSEPR model, the arrangement of atoms around a central atom A is based on distributing the valence electron pairs to minimize electrostatic repulsion. This concept is encapsulated in Gillespie's rules.

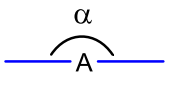
A: The central atom.

X_n: The bonding pairs of electrons, where n is the number of bonds (counting multiple bonds as one).

E_m: The lone pairs of electrons, where m is the number of non-bonding pairs.

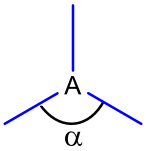
The molecular shape is determined by the sum of n and m. For instance, if $n + m$ equals 2, the molecule is linear; if $n + m$ equals 3, it forms an equilateral triangle; if $n + m$ equals 4, the shape is tetrahedral, and so on.

AX_2: linear shape



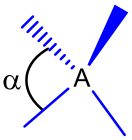
$\alpha = 180^0$

AX_3, AX_2E : Triangular shape



$\alpha = 120^0$

AX_4, AX_3E, AX_2E_2 : Tetrahedral shape



$\alpha = 109^028'$

Molecules with an atom having more than 4 bonds are rare, but they do exist.

AX_5, AX_4E, AX_3E_2 , etc.: shape of a trigonal bipyramid (as shown). There are two values for the angles: $\alpha = 120^0$ (angle between the 3 bonds in the horizontal equilateral triangle) and $\beta = 90^0$ (angle of the 2 vertical bonds with the 3 horizontal bonds).

AX_6, AX_5E, AX_4E_2 , AX_3E_3 Octahedral shape $\alpha = 90^0$

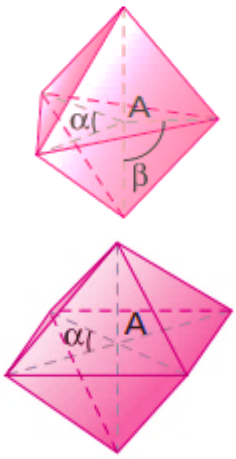


Figure III.2 Trigonal bipyramid and Octahedral shapes

Modifications of valence angles:

Influence of the number n of lone pairs.

In the series AX_4; AX_3E_1; AX_2E_2, there is a decrease in the XAX angle when moving from n = 0 to n = 2.

CH_4: HCH = 109.5°

NH_3: HNH = 107.3°

H_2O: HOH = 104.5°

This regular decrease is due to the repulsion of the lone pairs, which occupy a larger volume around the atom A than the bonded pairs, which are mainly confined between A and X.

Influence of the electronegativity of the central atom:

In the series AX_3E_1: NH_3, PH_3, AsH_3; SbH_3, experimentally determined:

HNH = 107.3°; HPH = 93.3°; HAsH = 91.8°, HSbH = 91.3°

In group VA, electronegativity decreases from nitrogen to antimony; the bonded pairs are more attracted towards the nitrogen atom in NH_3 than towards the antimony atom in SbH_3, thus their repulsion is stronger and the valence angle is higher.

Influence of the electronegativity of X:

When the electronegativity χ of atom X increases, with A remaining the same, the bonded pairs are more attracted towards X and the valence angle decreases:

Table III.1 Different electronegativity values and bond angles in some phosphorus halides.

	PCl_3	PBr_3	PI_3
χ (X)	3.3	3.0	2.8
Angle AXA	100.3°	101.5°	102°

Figure III.3 illustrate the Shape of Molecules and ions with different geometries

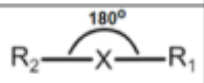
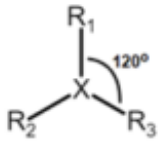
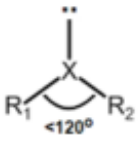
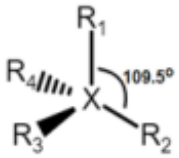
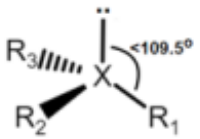
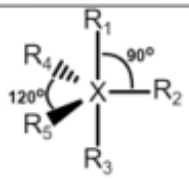
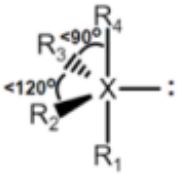
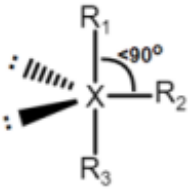
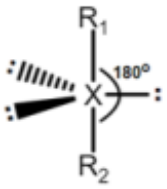
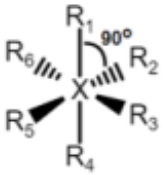
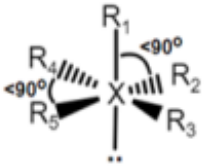
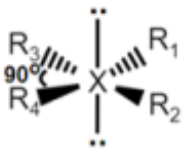
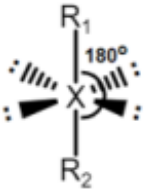
Steric No.	Electron Domain Geometry	Molecular Geometry				
		No Lone Pairs	1 Lone Pair	2 Lone Pair	3 Lone Pair	4 Lone pair
2	Linear	 Linear				
3	Trigonal Planar	 Trigonal planar	 Bent			
4	Tetrahedral	 Tetrahedral	 Trigonal pyramidal	 Bent		
5	Trigonal Bipyramidal	 Trigonal Bipyramidal	 Sawhorse	 T-shaped	 Linear	
6	Octahedral	 Octahedral	 Square pyramidal	 Square planar	 T-shaped	 Linear

Figure III. 3 The Shape of Molecules and ions with different geometries

Orbital Hybridization

The concept of orbital hybridization states that the wave functions of electrons in the atomic orbitals of an atom (usually the central atom of a molecule) can mix during bond formation to occupy hybrid atomic orbitals. If the wave functions of an s orbital and one or more p orbitals are combined, the possible hybrid orbitals produced are all similar to those represented in Figure III.4. These hybrid orbitals are labeled as sp, sp^2, and sp^3 depending on whether the wave functions of one, two, or three p orbitals are "mixed" with the s orbital wave function. The number of hybrid orbitals formed equals the sum of the number of atomic orbitals involved in mixing the wave functions. Like s and p orbitals, d orbitals can also be mixed. The number of atomic orbitals used, the symbol of the hybrid orbital, and the geometry of the resulting molecule are all listed in Table III.2.

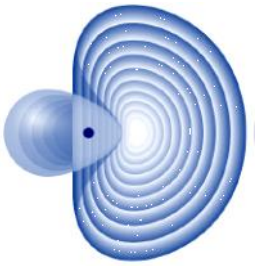


Figure III.4 The 90% probability surface of a hybrid orbital involving combinations of s and p orbitals. The black dot in the small lobe identifies the location of the nucleus.

Table III.2 Number of hybrid orbitals and type of hybridization for various molecular geometries.

Orbitals			Hybridization	Number of hybrid orbitals	Geometry
s	p	d			
1	1	0	sp	2	Linear
1	2	0	sp^2	3	Trigonal planar:
1	3	0	sp^3	4	Tetrahedral
1	3	1	sp^3d	5	Trigonal bipyramidal
1	3	2	sp^3d^2	6	Octahedral

Molecular Orbital Energy Diagram

Simplified Application of Linear Combination of Atomic Orbitals (LCAO)

Each molecular orbital Ψ_i is obtained by a Linear Combination of Atomic Orbitals (LCAO). For a diatomic molecule A-B, if $\varphi_\mu(A)$ and $\varphi_\mu(B)$ are the atomic orbitals (AO) of atoms A and B respectively, we can express the following development based on the complete series of AOs of both atoms:

$$\Psi_i = \sum_{\mu=1} c_{i\mu}\varphi_\mu + \sum_{\nu=1} c_{i\nu}\varphi_\nu$$

where $c_{i\mu}$ and $c_{i\nu}$ are numerical coefficients.

Combination Criteria

- AOs of complete inner subshells do not, or minimally, participate in MO formation; they are non-bonding.

- AOs with energies that interact most have energies of similar values. These are the AOs of similar energy that are most important to combine. Therefore, only the valence subshell AOs of each atom, whether filled or not, are involved in the combination.

- After choosing the AOs to combine, the combinations are carried out respecting the following two criteria:

- **Energy Criterion:** In practice, only AOs whose energies differ by approximately less than 10 eV are combined.

- **Symmetry Criterion (Orthogonality Theorem):** The overlap integral S is zero between AOs of different "symmetry types" because they are orthogonal. Hence, their combination will not result in any bonding regardless of the distance R between them.

It can be stated that the symmetry criterion dictates that the overlap will be rigorously zero between:

- An s orbital of one atom and a p_x or p_y orbital of the other atom.
- A p_x orbital of one atom and a p_y or p_z orbital of the other atom.
- A p_y orbital of one atom and a p_z orbital of the other atom.

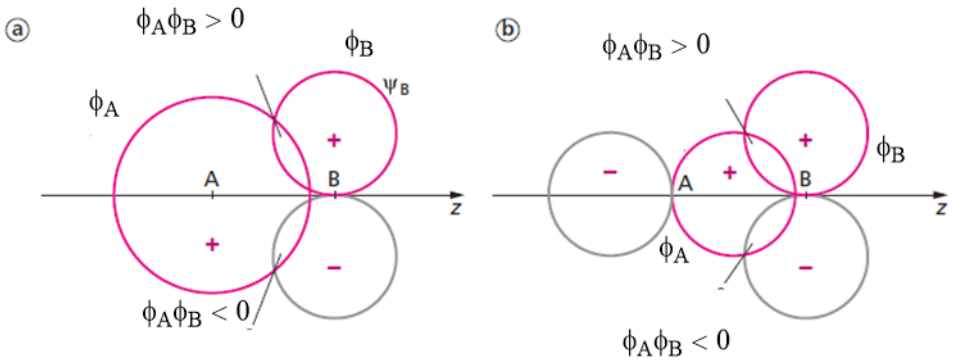


Figure III.5 a). Zero overlap between an s and a p_x orbital. b). Zero overlap between a p_z and a p_x orbital.

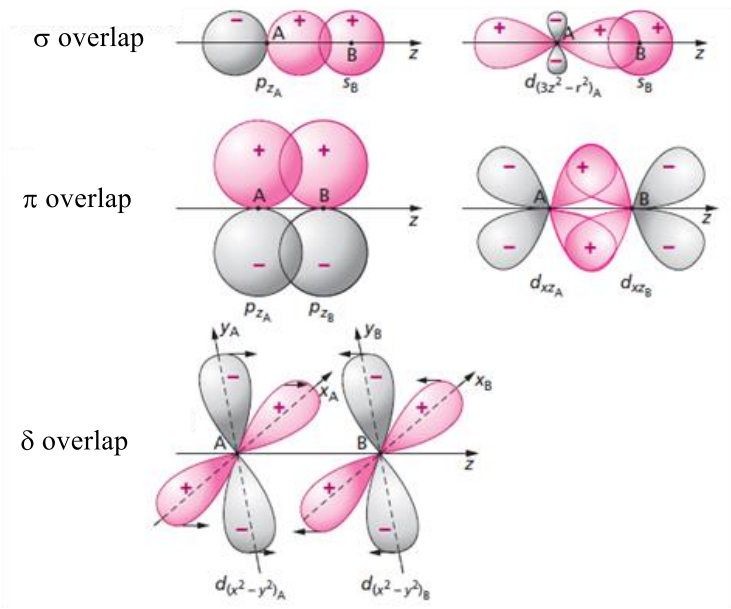


Figure III.6 Various non-zero overlaps between atomic orbitals

Study of Some Homonuclear Diatomic Molecules

Molecular Ion H_2^+

- Energy diagram

The lowest energy molecular orbital (MO) of H_2^+ is constructed similarly to H_2, starting from the 1s atomic orbitals (AOs) of each atom. The only difference from H_2 is that there is only one electron involved in bonding. Electron configuration: $(\sigma_s)^1$.

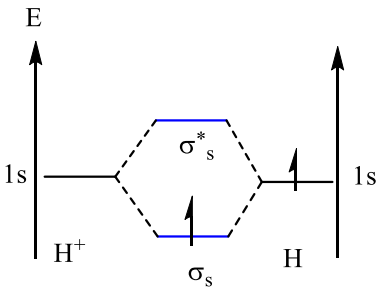


Figure III.7 Energy diagram of the H_2 molecule.

- Bond order

Represents the number of bonds or bond order defined by:

$$BO = \frac{(number\ of\ bonding\ electrons - number\ of\ antibonding\ electrons)}{2}$$

Thus: $BO = \frac{1-0}{2} = \frac{1}{2}$ Indeed, bonding is carried out by a single electron instead of a pair.

Oxygen Molecule O_2

- Energy diagram

Only the valence AOs of both atoms are combined: 2s and 2p. In this case, the energy gap between the 2s level (at -28.5 eV) and the 2p level (at -13.6 eV) is greater than 10 eV, indicating weak interaction between 2s and 2p (energy criterion). Therefore, they are treated separately.

- Bond order

$BO = \frac{8-4}{2} = 2$, corresponding to the formula: O=O

The electron configuration is written as:

$$(\sigma_s)^2(\sigma_s^*)^2(\sigma_z)^2(\pi_x,\pi_y)^2(\pi_x^*,\pi_x^*)^1$$

- Magnetic properties

Any molecule (or atom) with one or more unpaired electrons is magnetic: it is paramagnetic. Paramagnetism arises from unpaired electrons, as the total angular momentum (orbital and spin) of paired electrons in complete subshells is zero. Therefore, dioxygen O_2 is paramagnetic. Molecules and atoms with no unpaired electrons are not magnetic: they are diamagnetic.

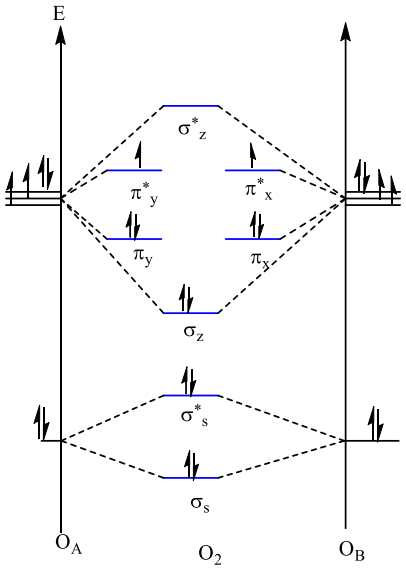


Figure III.8 Energy diagram of the O_2 molecule.

Nitrogen Molecule N_2

- Energy diagram

For N_2, only the valence AOs of both atoms are combined: 2s (at -20.3 eV) and 2p (all three at -14.5 eV). The symmetry criterion requires separate consideration of $2p_x$ and $2p_y$. Here, we cannot neglect the interaction between 2s and $2p_z$.

- Bond order

$BO = \frac{8-2}{2} = 3$, corresponding to the formula: N≡N

The electron configuration is:

$$(\sigma_s)^2(\sigma_s^*)^2(\pi_x,\pi_y)^2(\sigma_z)^2$$

- Magnetic properties

The molecule N_2 is **diamagnetic**.

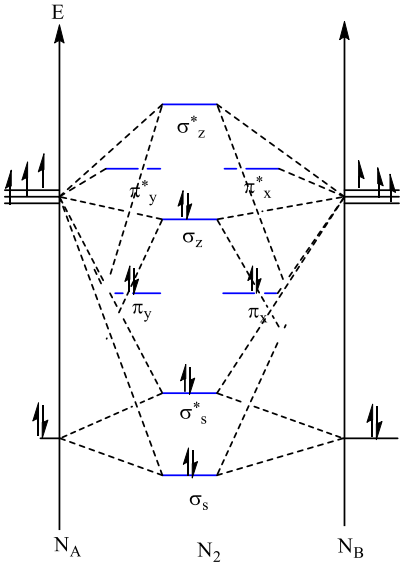


Figure III.9 Energy diagram of the N_2 molecule.

EXERCISES

Exercise 1:

Determine the molecular geometry of the following molecules using the VSEPR theory:

a) H_2O

b) CH_4

c) NH_3

d) SF_6

Exercise 2:

Draw the Lewis dot structures for the following molecules:

a) CO_2

b) SO_3

c) NO_2

d) ClF_3

Exercise 3:

Identify the type of bond (ionic, covalent, or coordinate covalent) in the following compounds:

a) NaCl

b) H_2O

c) NH_4^+

d) BF_3

CHAPTER IV

HYDROGEN

Hydrogen



Hydrogen gas is trapped inside this glass sphere, and gives off a purple glow when electrified

Despite being the simplest atom, hydrogen's chemistry is remarkably extensive. This is partly because the hydrogen atom shares similarities with elements from two different groups. With its electron configuration of $1s^1$, hydrogen somewhat resembles the alkali metals in Group IA, which have configurations of ns^1. However, the ionization energy of hydrogen is about 1314 kJ mol^{-1}, and the H-H bond strength in the diatomic molecule is around 435 kJ mol^{-1}. As a result, forming a simple H^+ species requires considerable energy. In fact, so much energy is needed for the formation of H^+ that compounds with a single proton as a cation are unlikely to form. In contrast, the alkali metals have ionization energies ranging from approximately 377 kJ mol^{-1} for Cs to about 519 kJ mol^{-1} for Li, making many of their compounds essentially ionic and containing singly charged ions. However, there are some solid compounds containing ions like $H_5O_2^+$ or $H_9O_4^+$, which are solvated protons with two and four water molecules of hydration, respectively. These ions exist due to the high heat of hydration of H^+ (approximately -1100 kJ mol^{-1}), a consequence of its small size and high charge-to-size ratio. The heat of hydration for H_3O^+ is estimated to be around -390 kJ mol^{-1}.

Hydrogen was discovered by Cavendish in 1781, who prepared a gas that produced water upon combustion. Soon after, the gas was named hydrogen. Most simple hydrogen compounds are covalent, as the hydrogen atom shares an electron pair. With its singly occupied 1s level, the hydrogen atom also resembles the halogens, which need a single electron to complete their valence shell. Consequently, hydrogen forms numerous compounds where it gains an electron to become a hydride ion. Thus, although hydrogen is the simplest atom, its chemistry is indeed varied and includes a wide range of compounds and reactions.

The abundance

Hydrogen holds the distinction of being the first element in the periodic table due to its having the simplest atoms of all elements, each comprising just one proton and one electron. In its pure form, hydrogen appears as a transparent gas. In the vast expanse of planets like Jupiter, hydrogen dominates as a major component, along with gases like helium and methane. On Earth, hydrogen is notably abundant in water. While relatively scarce in Earth's atmosphere, hydrogen reigns as the most



This gaseous stellar nursery is giving birth to thousands of stars



Three quarters of this planet is made up of layers of gaseous and

abundant element in the universe. Stars, including our Sun, contain significant quantities of hydrogen, where at their cores, hydrogen atoms undergo fusion, releasing immense heat and light. New stars take shape within nebulae, such as the Orion Nebula, which are clouds of hydrogen gas gradually collapsing under their own gravity.



The Sun is four-fifths hydrogen

Isotopes of Hydrogen

The isotopes of hydrogen are particularly significant in chemistry due to their substantial differences in physical properties and, to a lesser extent, in chemical behavior. Natural hydrogen contains three isotopes: protium, or "common" hydrogen, which has zero neutrons (abundance 99.985%); deuterium, which has one neutron (abundance 0.015%); and radioactive tritium, which has two neutrons (abundance 10^{-15} %). In fact, this is the only set of isotopes for which special symbols are used: H for protium, D for deuterium, and T for tritium.

The covalent bonds of deuterium (and tritium) with other elements are stronger than those of common hydrogen. For example, when water is electrolyzed to produce gaseous hydrogen and oxygen, the O-H covalent bonds break more easily than the O-D bonds. As a result, the remaining liquid contains an increasing proportion of "heavy" water, or deuterium oxide (D_2O).

Normal water and heavy water (D_2O) differ in all their physical properties. For example, deuterium oxide melts at 3.8°C and boils at 101.4°C. The density of deuterium oxide is about 10% higher than that of protium oxide at all temperatures. Consequently, heavy water ice will sink in "light" water at 0°C.

Tritium is a radioactive isotope with a half-life of about 12 years. Tritium is formed through the interaction of cosmic rays with atoms in the upper atmosphere. One production pathway involves the impact of a neutron on a nitrogen atom:

$$^{14}_{7}N + ^{1}_{0}n \rightarrow ^{12}_{6}C + ^{3}_{1}T$$

The isotope decays to produce the rare isotope of helium, $^{3}_{2}He$e:

$$^{3}_{1}T \rightarrow ^{3}_{2}He + ^{0}_{-1}e$$

A simpler synthesis method involves bombarding $^{6}_{3}Li$ with neutrons in a nuclear reactor:

$$^{6}_{3}Li + ^{1}_{0}n \rightarrow ^{4}_{2}He + ^{3}_{1}T$$

Properties of Hydrogen



Atomic structure

A hydrogen (H) atom has one electron moving around a nucleus consisting of a single proton



Physical properties

Hydrogen gas is the lightest material in the Universe. Pure hydrogen is rare on Earth, as it escapes quickly from the atmosphere into space



Chemical properties

Hydrogen is highly flammable. It forms compounds with both metals and non-metals



Compounds

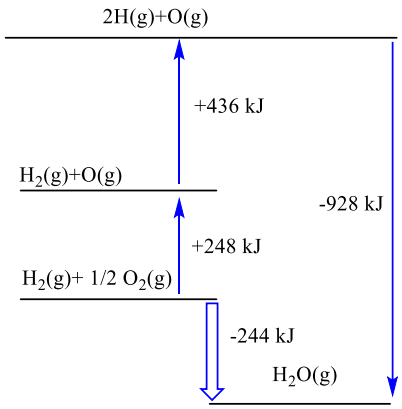
The most common hydrogen compound is water. Acids are compounds that contain hydrogen.

Reactions of Hydrogen Gas

Dihydrogen is a colorless and odorless gas that liquefies at -253°C and solidifies at -259°C. Hydrogen gas is relatively unreactive, partly due to the strong H-H covalent bond energy (436 kJ/mol). Dihydrogen reacts with dioxygen as follows:

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$$

This reaction must be controlled by enthalpy because there is a decrease in entropy resulting from the 3 moles of gaseous reactants to 2 moles of gaseous products. When bond energies summed, the strong O-H bond (464 kJ/mol) makes the reaction thermodynamically feasible (Scheme IV.1).



Scheme IV.1. Theoretical Enthalpy Cycle for the Formation of Water

Dihydrogen reacts with halogens, with the reaction rate decreasing down the group. It reacts violently with fluorine to give hydrogen fluoride:

$$H_2(g)\ F_2(g) \rightarrow 2\,HF(g)$$

The reaction of dihydrogen with dinitrogen is very slow in the absence of a catalyst:

$$3H_2(g) + N_2(g) \rightleftharpoons 2\,NH_3(g)$$

At high temperatures, dihydrogen reduces many metal oxides to the metallic element. For example, copper (II) oxide is reduced to metallic copper:

$$CuO(s) + H_2(g) \xrightarrow{\Delta} Cu(s) + H_2O(g)$$

In the presence of a catalyst (usually powdered palladium or platinum), dihydrogen will reduce carbon-carbon double and triple bonds to single bonds. For example, ethene, C_2H_4, is reduced to ethane, C_2H_6:

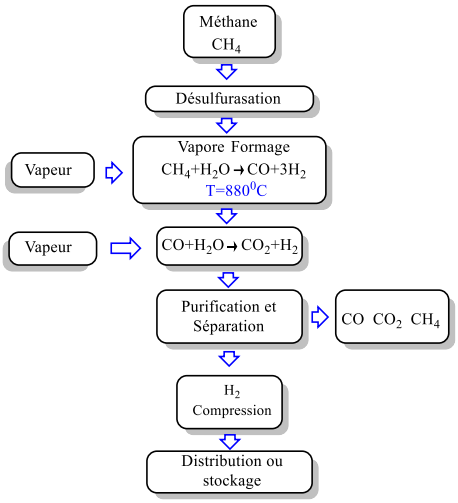
$$H_2C = CH_2(g) + H_2(g) \rightarrow H_3C - CH_3(g)$$

Hydrogen Gas Synthesis

In the laboratory, hydrogen gas can be generated by the action of dilute acids on many metals. A particularly convenient reaction is between zinc and dilute hydrochloric acid:

$$Zn(s) + 2\,HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$$

There are several different industrial synthesis pathways, one of which is the steam reforming process (Scheme IV.2). In the first step of this process, the endothermic reaction of natural gas (methane) with high-temperature steam produces carbon monoxide and hydrogen gas. It is difficult to separate the two products because the mixture must be cooled below -205°C before the carbon monoxide condenses. To overcome this problem and increase the yield of hydrogen gas, the mixture is cooled, additional steam is injected, and the combination is passed over a different catalytic system. Under these conditions, carbon monoxide is oxidized in an exothermic reaction to carbon dioxide, and the added water is reduced to hydrogen:



Scheme IV.2. The Steam Reforming Process

$$CH_4(g) + H_2O(g) \xrightarrow[500]{Ni}{}^{\circ}C\ CO(g) + 3\,H_2(g)$$

$$CO(g) + H_2O(g) \xrightarrow{\Delta} CO_2(g) + H_2(g)$$

Carbon dioxide can be separated from hydrogen gas in several ways. One method is to cool the products below the condensation temperature of carbon dioxide (-78°C), which is higher than that of dihydrogen (-253°C). However, this process still requires large-scale refrigeration systems.

Hydrides

Hydrogen forms ionic compounds with highly electropositive metals and covalent compounds with nonmetals. Additionally, it forms metallic hydrides with certain transition metals. The distribution of the three main types of hydrides is represented in Table IV.1.

Table IV.1 Three common types of hydrides: ionic, covalent, and metallic

Ionic Metallic Covalent

H																	He
Li	Be											B	C	N	O	F	NE
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Ti	Pb	Bi	Po	At	Rn
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Uuq	Uup	Uuh	Uus	Uuo

Ionic hydrides are white solids with high melting points, and all alkali metal hydrides have the crystal structure of sodium chloride. Because they resemble the salts of alkali and alkaline earth metals, ionic hydrides are often called saline or saline hydrides.

Uses:



This liquid is used as a cleaner



Hydrogen bomb explosion

This powerful explosion was created by fusing hydrogen atoms



This balloon can rise high into the atmosphere where sensors gather information about atmospheric pressure, temperature, and wind speed

Margarine is made of vegetable oils thickened by adding hydrogen





This powerful rocket uses 45,460 litres (12,000 gal) of liquid hydrogen as fuel.

EXERCISES

Exercise 1:

Explain the following properties of hydrogen:

a) Hydrogen is the lightest element.

b) Hydrogen has the highest reduction potential among all elements.

c) Hydrogen has a low boiling point.

Exercise 2:

Describe two methods for the commercial production of hydrogen gas. Explain the key steps involved in each method.

Exercise 3:

Explain three major applications of hydrogen gas.

CHAPTER V

OXYGEN & SULFUR

Oxygen

The Oxygen Group does not include any natural metals. The first two members, oxygen (O) and sulfur (S), are non-metals widespread in nature. The remaining three natural elements are semi-metals. Only the artificial member, livermorium (Lv), is thought to be a metal, but chemists don't really know for sure.



This glass sphere traps pure oxygen, which produces a silver-blue glow when electrified

Numerous oxygen compounds occur naturally, and the earth's crust is rich in oxygen-containing compounds. For instance, the atmosphere consists of 21% oxygen by volume or 23.3% by weight. Water, which covers about two-thirds of the earth's surface, is composed of 89% oxygen. Oxygen is essential for the life processes of all known animal forms. Many solid rocks and minerals are complex oxygen-containing compounds such as silicates, phosphates, and carbonates.

Oxygen and its compounds are also crucial in commerce and industry. Many of the most widely used compounds contain oxygen. These chemicals are not merely laboratory curiosities but are essential raw materials in numerous manufacturing processes that produce everyday necessities. Consequently, understanding the chemistry of oxygen is fundamental to understanding our environment.

The sheer volume of oxygen and its compounds used is almost beyond comprehension. Sulfuric acid, containing over 65% oxygen, is the leading chemical in terms of production. It is integral to many manufacturing processes in both heavy industry and specialized preparations. The production and use of sulfuric acid are so extensive that it serves as a "barometer" for gauging the state of the economy. In the following sections, we will delve into some of the chemistry of this crucial element, oxygen.

OZONE O_3

In addition to the usual form of oxygen, there exists a second allotrope, ozone, O_3. This is a high energy form of the element having a heat of formation of +143 kJ mol^{-1}.

$$\frac{3}{2}\,O_2(g) \rightarrow O_3(g) \qquad \Delta H_f^0 = +143\ Kj.\ mol^{-1}$$

Liquid ozone is a blue, diamagnetic substance that becomes explosive when mixed with oxygen at high concentrations. The explosive nature of O_3/O_2 mixtures increases under high pressure, requiring the mixture to be kept below 20°C. In its solid state, ozone is black, with a melting point of -193°C and a boiling point of -112°C. Ozone is somewhat more soluble in water compared to O_2, with a given volume of water dissolving about half its volume of O_3 at 0°C, while only about 0.049 volumes of O_2

will dissolve. The ozone molecule can be represented by two principal resonance structures (Figure V.1)

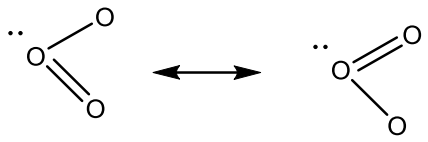


Figure V.2 Ozone structure

Properties of elements of the Oxygen Group



Atomic structure

All members have six electrons in the outer shell of each atom. This electron structure makes these elements highly reactive



Physical properties

The members of this group are solids, except oxygen (O), which is a gas at room temperature. The density of the elements increases down the group



Chemical properties

The reactivity of these elements decrease down the group. Oxygen is always involved in the process of combustion.



Compounds

These elements can form compounds with each other. They all react with carbon (C) to form compounds, some with strong smells.

Reactions of Oxygen

The gas combines with most other elements to form oxides. In these, oxygen atoms are almost always bivalent. For example, it combines with hydrogen to form water (H−O−H):

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(g)$$

There are a great many organic compounds containing oxygen atoms. They burn in air or oxygen to form carbon dioxide and water. The reaction is more vigorous in oxygen and can be dangerous (oxygen will reignite a glowing splint). Controlled oxidation of carbohydrates takes place in the body:

$$C_xH_{2y}O_y + xO_2 \rightarrow xCO_2 + yH_2O$$

Sodium burns in an excess of oxygen to give a pale-yellow solid which, when added to an acid, gives a solution of hydrogen *peroxide* (H-O-O-H). (The solid is mainly sodium peroxide, $(Na^+)_2[O_2]^{2-}$, the yellow colour coming from a trace of *superoxide*, $(Na^+)[O_2]^-$.)

$$2\,Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2{}^{\uparrow}$$

$$Na_2O_2 + 2H^+{}_{(aq)} \rightarrow 2Na^+{}_{(aq)} + H_2O_{2(aq)}$$

The solution has strong oxidizing properties. It is used as a bleach and in the treatment of wastes. Pure hydrogen peroxide can be obtained by fractional distillation under reduced pressure, but the process is hazardous. The substance is made industrially by the oxidation of a quinol.

Preparation of oxygen

Because the atmosphere is about 21% oxygen, it serves as the primary source for large-scale oxygen production. Liquid air is distilled, and since oxygen has a boiling point of -183°C, nitrogen, with a boiling point of -196°C, evaporates first. Smaller amounts of oxygen are obtained from the electrolysis of water, which is primarily done to produce high-purity hydrogen. In the laboratory, O_2 can be prepared by decomposing certain oxygen-containing compounds. Heavy metal oxides, like HgO, are thermally unstable and decompose relatively easily.

$$2\,HgO \xrightarrow{\Delta} 2Hg + O_2$$

Peroxides can also be decomposed: $2\,BaO_2 \xrightarrow{\Delta} 2BaO + O_2$

Finally, the usual general chemistry experiment for the preparation of oxygen involves the decomposition of $KClO_3$. $2\,KClO_3 \xrightarrow[\Delta]{MnO_2} 2KCl + 3O_2$

Electrolysis of aqueous solutions of many compounds leads to the preparation of oxygen because OH is more easily oxidized than are many other anions. For example,

$$4OH^- \xrightarrow{electricity} 2H_2O + O_2 + 4e^-$$

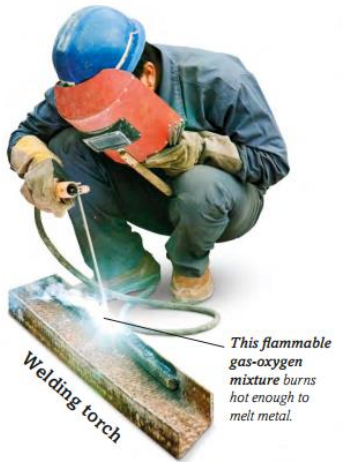
The oxygen is, of course, liberated at the anode as a result of the process being an oxidation reaction

Uses:

The oxygen in this cylinder can last for up to 30 minutes



Scuba diver



This rocket carries liquid oxygen that mixes with the fuel to produce hot gases, which help the rocket lift of



This liquid contains an oxygen Compound that prevents water from freezing in an engine.



The oxygen in this cylinder is given to patients in controlled amounts.



Sulfur

Sulfur-containing compounds and materials are quite common in volcanic regions of the Earth, including Italy, Sicily, Greece, the Middle East (such as Palestine and Iran), as well as Mexico, Chile, Peru, Japan, and the United States. These areas have experienced volcanic activity. Additionally, several important metal ores contain metals in the form of sulfides, such as *galena* (PbS), *zinc blende* (ZnS), *cinnabar* (HgS), *iron pyrites* (FeS_2), *gypsum* ($CaSO_4$), and *chalcopyrite* (CuS_2). The presence of sulfur in volcanic regions may result from the reaction between *sulfur dioxide* (SO_2) and *hydrogen sulfide* (H_2S), both of which are found in volcanic emissions. One such reaction can be represented by the equation:



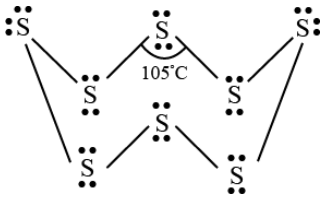


Natural Sulfur



$$2\,H_2S + SO_2 \rightarrow 3S + 2\,H_2O$$

Although elemental sulfur exists primarily as S_8 rings, for convenience it will be represented simply as S in most equations. **Sulfur dioxide** may be produced by burning sulfur: $S + O_2 \rightarrow SO_2$



or the roasting of metal sulfides: $2\,FeS + 3O_2 \xrightarrow{\Delta} 2FeO + 2SO_2$

Hydrogen sulfide is produced by the action of acids on sulfide minerals. For example, the reaction of galena with an acid to produce hydrogen sulfide can be represented as:

$$PbS + 2H^+ \rightarrow Pb^{2+} + H_2S$$

Reactions of Sulfur

Sulfur burns in air to sulfur dioxide: $S + O_2 \rightarrow SO_2$

This is a colourless gas with a choking smell. It dissolves in water to give a weakly acidic solution:

$SO_2 + H_2O \rightarrow H^+_{(aq)} + HSO_3{}^-_{(aq)}$

Reactions with alkalis give salts of SO_3^{-2} and HSO_3^- ions:

$$S_2O + 2OH^-{}_{(aq)} \rightarrow SO_3^{-2}{}_{(aq)} + H_2O$$

$$SO_3^{-2}{}_{(aq)} + SO_2 + H_2O \rightarrow 2HSO_3^-{}_{(aq)}$$

These are called respectively ***sulfites*** and ***bisulfites*** (hydrogensulphites). They are colourless (unless the cation is coloured) and are useful reducing agents, being readily oxidized.

Sulfur dioxide combines further with oxygen in the presence of a catalyst to give sulfur trioxide:

$$2SO_2 + O_2 \rightarrow 2SO_3$$

This is a colourless gas which condenses to a white solid containing $(SO_3)_3$ molecules. It reacts vigorously with a stoicheiometric quantity of water to give hydrogen sulfate or *concentrated sulfuric acid* (*oil of vitriol*):

$SO_3 + H_2O \rightarrow H_2SO_4$

This is a colourless, oily liquid. It is very corrosive and burns the skin. It reacts vigorously with more water to form *sulfuric acid*: $H_2SO_4{}_{(aq)} \leftrightarrow 2H^+_{(aq)} + SO_4{}^-_{(aq)}$

This is a strong acid and widely used. Sulfates are colourless (unless the cation is coloured).

Some occur naturally, e.g. $CaSO_4{\cdot}2H_2O$ (gypsum).

Uses:





Creams that contain sulfur compounds can disinfect skin weatherproof



Some antibiotics contain sulfur compounds that kill harmful bacteria.





Some dried fruits are preserved using powder containing a sulfur compound rubber – is

EXERCISES

Exercise 1:

Explain the following properties of oxygen:

a) Oxygen is a highly reactive element.

b) Oxygen has a high electronegativity.

c) Oxygen has a low boiling point.

Exercise 2:

Describe three major applications of oxygen gas.

Exercise 3:

Explain the following properties of sulfur:

a) Sulfur is a nonmetal with a low melting point.

b) Sulfur exhibits allotropism.

c) Sulfur has a high boiling point compared to other nonmetals.

Exercise 4:

Describe three major applications of sulfur.

CHAPTER VI

HALOGENS

Halogens

One of the most reactive groups in the periodic table, this set includes non-metals. The name "halogen" means "salt former", which refers to the way that elements in this group react with metals to form salts, such as sodium chloride, widely known as common salt. Scientists don't know much about tennessine (Ts), an artificial halogen.

Occurrence

Fluorine is found in nature as the minerals fluorite (CaF_2), cryolite (Na_3AlF_6), and fluoroapatite ($Ca_5(PO_4)_3F$). One commercial source of natural cryolite is Greenland. Fluorite and fluoroapatite are widespread, though fluoroapatite is primarily used for fertilizer production rather than as a fluorine source. Extensive deposits of fluorite are found in southeastern Illinois and northwestern Kentucky. From a utilization standpoint, both cryolite and fluorite are crucial minerals. Cryolite serves as the electrolyte in the electrochemical production of aluminum from bauxite, and fluorite is used as a flux in steelmaking. Today, most cryolite is synthetic rather than naturally occurring.

Chlorine is abundantly available in NaCl and salt water, making the quantity of chlorine in these natural sources enormous. The Great Salt Lake contains 23% salt, and the Dead Sea contains about 30%. While chlorine does occur in a few minerals, the abundance of natural salt water makes these sources relatively unimportant.

Bromine is found as bromide salts of Group IA and Group IIA metals, often alongside chlorides. Both bromine and iodine are present in compounds found in brines and seawater. A few minerals, such as lautarite ($Ca(IO_3)_2$), contain iodine, which is also found in various sea plants and animals.

Properties of elements of the Halogen Group



Atomic structure

All members have seven electrons in the outer shell of each atom. There is space for one more electron in each outer shell.



Physical properties

Bromine (Br) is the only halogen that is liquid. Fluorine (F) and chlorine (Cl) are gases, while iodine and astatine (At) are solids.



Chemical properties

Every halogen atom receives one electron from other atoms to form a compound. Reactivity decreases down the group.



Compounds

The halogens react with hydrogen (H) to form acidic compounds. Halogen compounds are used in products such as bleach.

Physical properties

Table VI.1 summarizes some physical properties of the halogens. These properties evolve continuously along the 17th column of the periodic table. Thus, their polarizability increases with atomic number, which concurrently increases the London forces in the elemental forms. Consequently, their melting and boiling temperatures increase from −220°C and −188°C for fluorine to 113.7°C and 184.3°C for iodine. Conversely, their ionization energy and electronegativity decrease from 1681 kJ·mol^{-1} and 3.98 for fluorine to 1008 kJ·mol^{-1} and 2.66 for iodine.

Table VI.1 Some physical properties of the halogens

Element	Fluorine	Chlorine	Bromine	Iodine
Atomic mass	18,99	35,45	79,90	126,90
Melting point	−219,67 °C	−101,5 °C	−7,2 °C	113,7 °C
Boiling point	−188,11 °C	−34,04 °C	58,8 °C	184,3 °C
Density	1,696 g·l^{-1}	3,2 g·l^{-1}	3,1028 g·cm^{-3}	4,933 g·cm^{-3}
Covalent radius	64 pm	102±4 pm	120±3 pm	139±3 pm
Ionization energy	1 681 kJ·mol^{-1}	1 251,2 kJ·mol^{-1}	1 139,9 kJ·mol^{-1}	1 008,4 kJ·mol^{-1}
Electronegativity (Pauling)	3,98	3,16	2,96	2,66

Chemical properties

The chemical reactivity of halogens makes them dangerous or even lethal to living organisms when present in significant quantities. This high reactivity stems from their elevated electronegativity, which is a result of their high effective nuclear charge. Fluorine is one of the most reactive chemical elements, capable of forming compounds with a wide range of generally inert substances, as well as with all other known chemical elements except for helium and neon. It exists as a corrosive and highly toxic gas. Its reactivity is such that it attacks glass in the presence of even trace amounts of moisture to form silicon tetrafluoride, SiF_4. This is why fluorine must be handled using glassware free of any moisture, polytetrafluoroethylene (PTFE), or metals such as copper and steel, which form a passivation layer of fluoride on their surface.

Hydrogen Halides

All halogens react with hydrogen to form hydrogen halides. The reaction is of the form:

$$[\, H_2 + X_2 \rightarrow 2\, HX \,]$$

where HX represents hydrogen fluoride (HF), hydrogen chloride (HCl), hydrogen bromide (HBr), and hydrogen iodide (HI). Astatine behaves similarly to a halogen and forms astatine hydride (AtH) by the same reaction. Hydrogen fluoride is the only one of the five to form hydrogen bonds.

The reaction between hydrogen and halogens slows down as we consider heavier halogens. It is immediately explosive with fluorine even in the dark at low temperatures, while it is explosive with chlorine only in the presence of light and at high temperatures, and explosive with bromine only in the presence of a flame. With iodine and astatine, the reaction is incomplete.

All hydrogen halides are gases at room temperature, soluble in water to form hydrohalic acids: hydrofluoric acid, hydrochloric acid, hydrobromic acid, hydroiodic acid, and astatohydric acid. Hydrofluoric acid is a weak acid, while the other four are strong acids, with astatohydric acid being the strongest; however, it tends to decompose into astatine and hydrogen.

Hydrogen halides are all irritating and toxic compounds. Hydrogen fluoride and hydrochloric acid are very acidic. Hydrogen fluoride is used in industry and is highly toxic, capable of causing pulmonary edema and cellular damage. Hydrogen chloride is lethal at concentrations above 50 ppm in the atmosphere.

Metal Halides

All halogens react with sodium, forming sodium fluoride (NaF), sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI), and sodium astatide (NaAt). These reactions produce light orange flames.

Iron reacts with fluorine, chlorine, and bromine to form iron (III) halides through reactions of the type:

$$[\,2\,Fe\ +\ 3\,X_2 \rightarrow 2\,FeX_3]$$

With iodine, however, it forms iron (II) iodide (FeI_2).

Iron wool can react quickly with fluorine, even at low temperatures, to form white iron (III) fluoride (FeF_3). Iron reacts hot with chlorine to give anhydrous iron (III) chloride ($FeCl_3$), which is black when dry but reddish-brown in the presence of moisture. Iron can also react with bromine, though less vigorously than with fluorine and chlorine, to produce anhydrous iron (III) bromide ($FeBr_3$), which is reddish-brown under anhydrous conditions. With iodine, iron forms iron (II) iodide (FeI_2), probably gray, though it is difficult to be certain due to contamination of the product by excess iodine.

Interhalogens

Interhalogens have the form XY_n, where X and Y are halogens and *n* is 1, 3, 5, or 7. They consist of at most two different halogens. Large interhalogen molecules, such as chlorine trifluoride (ClF_3), are produced by reacting a pure halogen with a smaller interhalogen like chlorine monofluoride (ClF). All,

except iodine heptafluoride (IF_7), can also be produced by combining pure halogens under various conditions.

Table VI.2 Some Interhalogens

	F	**Cl**	**Br**	I	**At**
F	F_2				
Cl	ClF, ClF_3, ClF_5	Cl_2			
Br	BrF, BrF_3, BrF_5	BrCl	Br_2		
I	IF, IF_3, IF_5, IF_7	ICl, $(ICl_3)_2$	IBr	I_2	
At	—	AtCl	AtBr	AtI	?

Interhalogens are generally more reactive than pure halogens, except for the molecule difluorine F_2, because interhalogen bonds are weaker than those in homonuclear halogen molecules. However, their general properties are overall similar to those of pure halogens. Many interhalogens consist of one or more fluorine atoms bonded to a heavier halogen: up to five fluorine atoms can bond to a chlorine or bromine atom, and up to seven to an iodine atom. Most of them are gases under normal conditions of temperature and pressure, but some are liquids, such as bromine trifluoride BrF_3, and many iodine interhalogens are solids, like iodine monobromide IBr.

Reactions

Halogens react at room temperature (and vigorously when heated) with nearly all metals to form ionic compounds such as sodium chloride NaCl, iron (III) chloride $FeCl_3$, and uranium (III) iodide UI_3. They also react with most non-metals such as carbon, hydrogen, and silicon to form covalent halides. With hydrocarbons, they form halogenated hydrocarbons, which are an important class of industrial materials, such as chloroform (trichloromethane $CHCl_3$), chlorofluorocarbons (CFCs), and perfluorocarbons (PFCs).

With water H_2O, they produce a series of oxoacids in which the halogen exhibits varying oxidation states.

Fluorine

This highly reactive element is extremely dangerous in its pure form; even a small amount in the air can be lethal. Fluorine, a pale-yellow gas, reacts aggressively with materials like brick, glass, and steel, burning holes through them. Due to its dangerous nature, pure fluorine is typically stored in nickel containers, which are resistant to its corrosive effects. Minerals such as **cryolite** and **fluorite** contain fluorine. Both the gas and its less harmful compounds have many uses. Hydrofluoric acid, a toxic liquid, is used to etch patterns on glass, such as those seen in some glass vases.



Fluorite

Fluorite (calcium fluoride, CaF_2). When treated with sulfuric acid, it produces hydrogen fluoride:

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF^{\uparrow}$$

This colorless gas condenses into a colorless liquid at 19°C and is stored in steel cylinders. Due to its corrosiveness towards glass and potential to cause severe burns, it must be handled with protective clothing in metal or polyfluorocarbon equipment. The liquid also serves as an excellent solvent.

Hydrogen fluoride easily dissolves in water to form hydrofluoric acid, which can be handled in polyethylene containers. When it reacts with glass, it produces $[SiF_6]^{2-}$ ions.

$$SiO_2 + 6HF_{(aq)} \rightarrow 2H^+_{(aq)} + [SiF_6]^{2-}{}_{,aq)} + 2H_2O$$



Hydrofluoric acid in polythene bottle

Hydrofluoric acid is a weak acid:

$$HF_{(aq)} \leftrightarrow H^+_{(aq)} + F^-_{(aq)}$$

$$F^-_{(aq)} + HF_{(aq)} \leftrightarrow HF_2{}^-_{(aq)}$$

For elements with multiple valencies, fluorine tends to bring out the highest valency. For instance, sulfur burns in fluorine to produce sulfur hexafluoride (SF_6).

$$S + 3F_2 \rightarrow SF_6$$

Uses:

Some ceramic glazes contain fluorine minerals. When heated, these glazes release fluorine, which hardens the ceramic beneath. Polytetrafluoroethylene (PTFE), another fluorine compound, is widely used to make non-stick pans because it is slippery and prevents burned food from sticking. PTFE is also used to make lightweight, waterproof clothing. Additionally, one of the most common uses of fluorine compounds is in toothpaste, where they strengthen teeth against decay.

Upon injection, this fluorinerich liquid heals damaged tissues by carrying oxygen to them.



Oxycyte



Fluorine-rich plastic clothing repels water



Non-stick pan

This pan has a PTFE coating that resists heat.



Chlorine

Chlorine gets its name from the Greek word "chlóros," meaning "pale green," which describes the color of this gaseous element. Chlorine is highly reactive and forms various compounds; it does not exist in a pure form in nature. The most common chlorine compound is sodium chloride, also known as the mineral halite. Chlorine compounds are vital for the body, playing a role in muscle and nerve function, and are also present in sweat.



Chlorine

Chlorine (Cl_2) is made by electrolysis of aqueous sodium chloride (NaCl).

Sodium chloride occurs naturally as *rock salt*. The gas is stored in metal cylinders.

Hydrogen burns in chlorine to form hydrogen chloride:

$$Cl_2 + H_2 \rightarrow 2HCl$$

This is a colourless gas with a sharp, irritating smell. It fumes in moist air and dissolves very readily in water to give hydrochloric acid ($H^+_{(aq)}, Cl^-_{(aq)}$).

Chlorine combines with other elements to form chlorides. These can also be made using hydrogen chloride or hydrochloric acid. For example, iron reacts with hydrogen chloride to give its lower chloride ($FeCl_2$), while chlorine gives the higher chloride ($FeCl_3$):

$$Fe + 2HCl \rightarrow FeCl_2 + H_2^{\uparrow}$$

$$2Fe + 3Cl_2 \rightarrow 2FeCl_3$$

Chlorine partially dissolves in water and is used to kill bacteria in water supplies. The gas dissolves in aqueous sodium hydroxide to give a solution used as a bleach. This contains hypochlorite ions (ClO^-, chlorate(I)); $Cl_2 + 2OH^-_{(aq)} \rightarrow ClO^-_{(aq)} + Cl^-_{(aq)} + H_2O$

Chlorine can be produced in a laboratory through various methods, with one straightforward approach involving the reaction of hydrochloric acid with bleaching powder:

$$\left(Ca(OCl)_2, CaCl_2, 2H_2O\right) + 4H^+_{(aq)} \rightarrow 2Ca^{2+}_{(aq)} + 2Cl_2^{\uparrow} + 4H_2O$$

Another method involves the reaction of concentrated sulfuric acid with sodium chloride to produce hydrogen chloride:

$$NaCl + H_2SO_4 \rightarrow HCl^{\uparrow} + NaHSO_4$$

Uses:

Chlorine gas, known for its toxicity in its pure state, was deployed as a weapon during World War I, necessitating soldiers to wear protective masks. The distinctive orange color in this context originates from the presence of hematite mineral. The vivid red hue, on the other hand, results from impurities. The skin of a particular tree frog contains a chlorine compound. Halite forms cube-shaped crystals, while carnallite is associated with the red-eyed tree frog. A glass sphere holds pure chlorine, which is denser than air.



The soles of some running shoes contain chlorine compounds

In contemporary applications, chlorine finds extensive use across various industries. Its compounds are ubiquitous, found in everyday items ranging from athletic shoes to chloroform. Chlorine reacts with hydrogen to produce hydrochloric acid, a potent industrial cleaner that corrodes most metals, releasing hydrogen gas in the process. Diluted chlorine acids are employed for water treatment in swimming pools, while household bleach and other cleaning products utilize chlorine compounds to eliminate germs. Polyvinyl chloride (PVC), among the most widely used plastics, incorporates chlorine, making it a durable material used in manufacturing numerous rigid objects.



Breathing in this chlorine-infused liquid makes people fall



This bleach cleaner contains a compound called sodium hypochlorite





Bromine

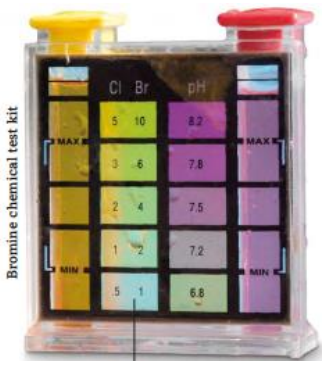
Bromine stands as the sole non-metal that remains in liquid form at typical room temperatures. Inhalation of the dense vapor emitted by this liquid poses significant hazards. Pure bromine does not occur naturally. Its compounds readily dissolve in water and are commonly found dissolved in seawater and highly saline lakes like the Dead Sea in the Middle East. As water evaporates, solid bromine salts, such as potassium bromide, accumulate and form deposits of white crystalline crusts. Bromine can subsequently be extracted from these solid salts.



Bromine

Uses:

Bromine, derived from the Greek word for "stench" due to its strong odor, is commonly sealed in glass containers to prevent its vapors from escaping. It appears as a red-brown liquid. One prevalent use of bromine is as a disinfectant for water purification, particularly in applications like hot tubs where it outperforms chlorine, which easily dissipates in warm water. Swimming pools maintain bromine levels using chemical test kits. Bromine compounds find application in photography, aiding in the development of images from negatives. Presently, bromine is primarily employed in fire-resistant materials such as firefighter gear and furnishings, as it exhibits low flammability.



The colours on this test kit show how much bromine is in the water



The fabric used to make this suit contains bromine compounds that make it fireproof



This fire extinguisher uses a non-flammable, bromine-rich gas to extinguish fires

Iodine

Iodine is the sole halogen that remains solid at room temperature. When heated, it transforms into a purple gas and derives its name from the Greek word "iodes," meaning "violet." Initially discovered in seaweed, iodine is abundant in many marine plants and animals. Seafood, such as crabs and fish, is a significant dietary source of iodine. The human body requires small quantities of iodine to produce thyroxine, a crucial hormone for growth. Additionally, iodine finds application in the production of printing ink, red and brown food coloring, and disinfectants.



Iodine

Uses:

These lenses contain iodine, which filters out bright, reflected light





This disinfectant is applied to wounds to stop the spread of infection



The bright red colour of these cherries is due to an iodine dye



Astatine

Atoms of astatine are inherently unstable and typically decay into lighter elements like bismuth within a few hours. This radioactive element itself is produced when atoms of a heavier element, francium, undergo decay. Small quantities of this rare element can be found in uranium ores such as uraninite. Emilio Segrè, an Italian physicist, was among the first scientists to isolate a pure sample of astatine. He achieved this using a particle accelerator, a device that collides atoms together to observe the outcomes.

Tennessine

Tennessine is the newest addition to the periodic table, synthesized in 2011 in the Russian city of Dubna. It was named after the US state of Tennessee, where the Oak

Ridge National Laboratory is located, known for housing one of the earliest large-scale nuclear reactors. Despite only a few atoms of this halogen element being produced, scientists have hypothesized it to be a semi-metal, which distinguishes it from the non-metallic nature of all other halogens.

EXERCISES

1. List two uses of bromine in industry.
2. Discuss the role of iodine in human health and its importance in diet.

Essay Question

Discuss the chemical properties, industrial production methods, and practical applications of chlorine. Include in your answer:

- The reactivity and physical state of chlorine.
- The electrolysis process used to produce chlorine on an industrial scale.
- At least three major uses of chlorine in everyday life or industry.

CHAPTER VII

PNICTOGENS

Pnictogens

This group comprises various natural elements, including non-metals, semi-metals, and dense metals, along with the synthetic element moscovium (Mc). The group is also referred to as "pnictogens," a term derived from the Greek word "pnígein," meaning "to choke," alluding to the potential toxicity of nitrogen (N) in certain forms.

The first two elements in group 15, nitrogen and phosphorus, are non-metals, while the remaining three, arsenic, antimony, and bismuth, display certain metallic properties.

Nitrogen and phosphorus are both nonconductors of electricity and form acidic oxides, clearly classifying them as nonmetals. The ambiguity begins with arsenic. Despite the common allotrope of arsenic appearing metallic, sublimation and recondensation of the solid produce a yellow powder, a second allotrope. Due to having both metallic-looking and nonmetallic allotropes and forming amphoteric oxides, arsenic can be classified as a metalloid. However, much of its chemistry is similar to phosphorus, making a strong case for considering it a nonmetal.

Antimony and bismuth are nearly as ambiguous as arsenic. Their electrical resistivities are much higher than a "true" metal like aluminum (2.8 mΩ·cm) and even higher than a "weak" metal like lead (22 mΩ·cm). Generally, though, these two elements are categorized as metals. All three of these borderline elements predominantly form covalent compounds.

To determine the vague border between metals and metalloids, melting and boiling points are useful indicators. In Group 15, these parameters increase down the group, except for a decrease in melting point from antimony to bismuth (Table VII.1). As noted for alkali metals, the melting points of main group metals tend to decrease down a group, whereas those of nonmetals tend to increase. This increase-decrease pattern indicates that the lighter members of Group 15 follow the typical nonmetal trend, with the shift to the metallic decreasing trend starting at bismuth.

Table VII.1 Melting and Boiling Points of Group 15 Elements

Element	Melting Point (°C)	Boiling Point (°C)
N_2	-210	-196
P_4	44	281
As	Sublimes at 615	
Sb	631	1387
Bi	271	1564

Properties of elements of the Pnictogens



Atomic structure

Members of this group have atoms with five electrons in the outer shell. These atoms can form up to three bonds at the same time.



Physical properties

All the members are solids, except nitrogen (N). The density of elements increases down the group: bismuth (Bi) is 8,000 times denser than nitrogen.



Chemical properties

Phosphorus (P), which exists in two main forms, is reactive, but the others in this group are fairly stable.



Compounds

When reacting with three hydrogen (H) atoms, all members of the group form reactive gaseous compounds called hydrides

Nitrogen

Nitrogen is a plentiful element, making up 78% of the atmosphere by volume. Discovered independently by various researchers in 1772, nitrogen is found in many important natural compounds, especially nitrates like KNO_3 and $NaNO_3$. Nitrogen is vital for life as it is a key component of amino acids found in all living protoplasm.



Nitrogen

Nitrogen molecules are very small, with a bond length of just 1.10 Å (110 pm), due to the strong triple bond between the atoms. This bond has a high force constant of 22.4 mdynes $Å^{-1}$.

Industrially, nitrogen is obtained by distilling liquid air, since oxygen boils at -183°C and liquid nitrogen at -195.8°C. This process requires a lot of oxygen, making it the primary industrial source of nitrogen. In the lab, small amounts of nitrogen can be produced by decomposing sodium azide, NaN_3:

$$2\mathrm{NaN_3} \xrightarrow{\Delta} 2Na + 3N_2$$

Nitrides

Like hydrides, borides, and carbides, different types of nitrides can form depending on the metal involved. Nitrides are classified as ionic, covalent, or interstitial.

Nitrogen can form binary compounds with most elements, although many aren't produced by direct combination. For instance, the reaction with sodium can be shown as:

$$6Na + N_2 \rightarrow 2Na_3N$$

Hydrogen Compounds

Ammonia, NH_3

Liquid ammonia is a widely used non-aqueous solvent. Around 22 billion pounds of NH_3 are used annually, mainly as fertilizer or to produce nitric acid. The Haber process synthesizes NH_3 from its elements:

$$3H_2 + N_2 \xrightarrow{300\ atm\ ;\ 450\ C\ /Catalyseur} 2NH_3$$

The conditions used are a balance since higher temperatures speed up the reaction, but NH_3 becomes less stable as its formation enthalpy is -46 kJ/mol.

Hydrazine, N_2H_4

Hydrazine, with the structure $H2N - NH2$, is similar to hydrogen peroxide ($HO - OH$). Both are thermodynamically unstable, with hydrazine having a formation enthalpy of 50 kJ/mol. Hydrazine is a weak base with $K_{b1} = 8.5 \times 10^{-7}\ and, K_{b2} = 8.9 \times 10^{-16}$ It is a strong reducing agent that reacts vigorously with powerful oxidizers and burns easily. For example, the reaction:

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

is highly exothermic.

Diimine, N_2H_2

Diimine, or $HN = NH$, is unstable but can exist as an intermediate in some processes. It decomposes to N_2 and H_2:

$$N_2H_2 \rightarrow N_2 + H_2$$

Hydrogen Azide, HN_3

Hydrogen azide (or hydrazoic acid) is a volatile, weak acid with $K_a = 1.8 \times 10^{-5}$ It is a hazardous explosive (98% nitrogen) and highly toxic.

Nitrogen Oxides

There are several nitrogen oxides, which are detailed in Table VII.2.

Table VII.2 Oxides of Nitrogen

Formula	Name	Characteristics
N_2O	Nitrous oxide	Colorless gas, weak oxidizing agent
NO	Nitric oxide	Colorless gas, paramagnetic
N_2O_3	Dinitrogen trioxide	Blue solid, dissociates in gas
NO_2	Nitrogen dioxide	Brown gas, equilibrium mixture
N_2O_4	Dinitrogen tetroxide	Colorless gas
N_2O_5	Dinitrogen pentoxide	Solid is $NO_2^+NO_3^-$, gas unstable

Uses:

Certain nitrogen compounds are produced through industrial processes and have various applications. Some of these compounds are used in explosives, such as TNT and nitroglycerine, which detonate because the nitrogen bonds break rapidly.

Nitrogen fuels like nitromethane provide significantly more power in drag bikes compared to traditional carbon-and-hydrogen fuels like gasoline. The compound hydrazine is utilized in spacecraft thrusters, such as those on the Phoenix Mars Lander. Additionally, nitrogen compounds are found in dyes and adhesives.

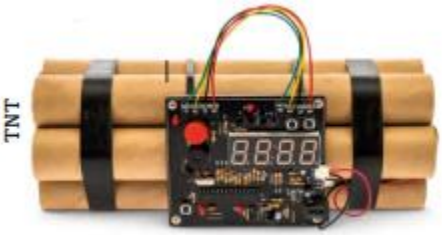
The Haber process is an industrial method that converts nitrogen and hydrogen gas into ammonia, a liquid extensively used to manufacture nitrogen fertilizers. These fertilizers, when mixed with soil, enhance plant growth.



Nitroglycerine can be used to treat heart conditions



Superstrong glues contain small nitrogen compounds that link together



Trinitrotoluene (TNT) does not explode below 240°C (464°F).



The fertilizers contain compounds called ammonium nitrates that promote growth in plants

Motorcycles use nitromethane to fuel their powerful engines

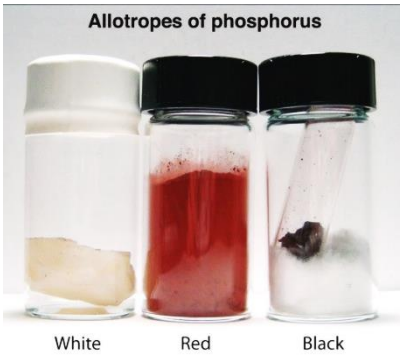


Phosphorus

Phosphorus is commercially extracted from rocks containing phosphate minerals. The process involves treating crushed phosphate rock with carbon and silica in an electric furnace at 1200-1400°C, which allows phosphorus to be distilled:

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \xrightarrow{1200-1400°C} 6CaSiO_3 + 10CO + P_4$$

To collect the gaseous tetraphosphorus, it is pumped into a tower and sprayed with water, causing it to liquefy and accumulate at the bottom of the tower, where it is then drained into storage tanks.



Below 800°C, elemental phosphorus exists as P_4 molecules with a tetrahedral structure. At higher preparation temperatures, some P_4 molecules dissociate into P_2. Phosphorus has several allotropes, **with** the common ones being white (or yellow) phosphorus and **red** phosphorus. The most stable form, **black** phosphorus, is the hardest to produce and requires heating white phosphorus under high pressure (about 1.2 GPa).

Phosphine, PH_3

Phosphine (PH_3), the analog of ammonia, is a highly toxic colorless gas. The $P-H$ bond in phosphine is much less polar than the $N-H$ bond in ammonia, making phosphine a very weak base that does not form hydrogen bonds. Consequently, the phosphonium ion (PH_4^+), similar to the ammonium ion, is difficult to create. Phosphine can be prepared by reacting a phosphide of a highly electropositive metal with water:

$$Ca_3P_2 + 6H_2O \rightarrow 3Ca(OH)_2 + 2PH_3$$

Phosphorus Oxides

Phosphorus forms two oxides: tetraphosphorus hexoxide, P_4O_6, and tetraphosphorus decoxide, P_4O_{10}. Both are white solids at room temperature. Tetraphosphorus hexoxide forms when white phosphorus burns in an oxygen-deficient environment:

$$P_4 + 3O_2 \rightarrow P_4O_6$$

Conversely, tetraphosphorus decoxide, the more common and important oxide, forms when white phosphorus burns in the presence of excess oxygen:

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

Phosphoric Acid

Pure (ortho) phosphoric acid is a colorless solid melting at 428°C. A concentrated aqueous solution of phosphoric acid (85% by mass and having a concentration of 14.7 $mol \cdot l^{-1}$) is called "syrupy" phosphoric acid, its viscous nature caused by extensive hydrogen bonding. Phosphoric acid is a weak acid, undergoing three stages of ionization:

$$H_3PO_4(aq) + H_2O(l) \overset{\Delta}{\rightarrow} H_3O^+(aq) + H_2PO_4^-(aq)$$

$$H_2PO_4^-(aq) + H_2O(l) \overset{\Delta}{\rightarrow} H_3O^+(aq) + HPO_4^{2-}(aq)$$

$$HPO_4^{2-}(aq) + H_2O(l) \overset{\Delta}{\rightarrow} H_3O^+(aq) + PO_4^{3-}(aq)$$

Pure phosphoric acid is prepared by burning white phosphorus to produce tetraphosphorus decoxide, and then treating the oxide with water:

$$P_4(s) + 5O_2(g) \rightarrow P_4O_{10}(s)$$
$$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4\,H_3PO_4(l)$$

Uses:

China tea set
This light, strong china contains calcium phosphate

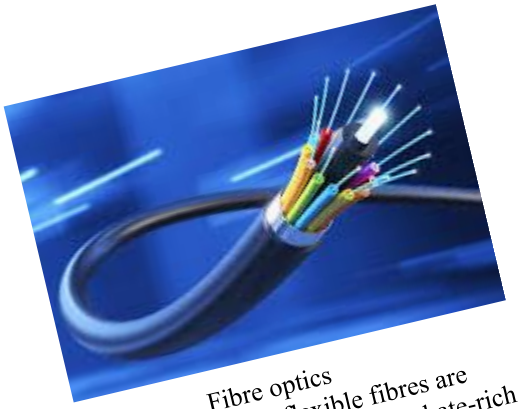




Spraying crops with phosphates kills pests, such as insects



The striking surface on the sides of the box contains phosphorus, which ignites the match upon contact



Fibre optics
These flexible fibres are composed of phosphate-rich glass

This fertilizer contains ammonium phosphate to boost plant growth.



Arsenic

Arsenic is frequently referred to as the "king of poisons" due to its toxic nature in every form, whether pure or in compounds, affecting animals. It has historically been used as a poison for centuries. This semi-metal is present in various minerals, such as orpiment, known for their vivid colors. Naturally occurring arsenic appears shiny and grey.







Uses:

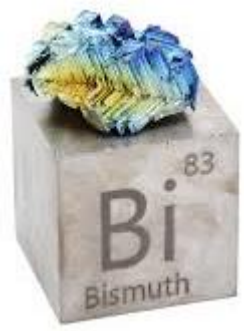
Arsenic compounds are employed in the production of certain rodent poisons. A primary contemporary application of arsenic involves its use in strengthening lead. This is achieved by blending arsenic with lead to form a robust alloy commonly utilized in car batteries.





Bismuth

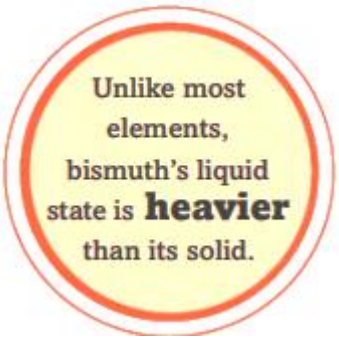
Bismuth, despite being radioactive, has atoms that are relatively stable and can persist for millions of years. It has been recognized for centuries: the Incas in South America incorporated it into bronze weapons to enhance their durability, and ancient Egyptians used a bismuth mineral to add sparkle to their cosmetics. When exposed to air, pure bismuth develops an oxide that crystallizes into colorful structures known as hopper crystals.



Uses:

Bismuth, in its pure elemental form, is very brittle and has limited applications. It is naturally abundant in Earth's crust, approximately twice as much as gold. When exposed to oxygen, the surface of bismuth develops rainbow colors, a phenomenon seen in laboratory-produced bismuth crystals known as hopper crystals. Bismuthinite is the primary mineral source of pure bismuth.

In various industries, bismuth pigments find use in paints and cosmetics, while different bismuth compounds serve medicinal purposes. Additionally, an alloy of bismuth and tin is utilized in fire sprinkler systems.



This nail polish gives a pearly effect because of bismuth compounds.



Yellow cosmetics



This cold box uses a compound called bismuth telluride, which becomes cold when electrified, and keeps items cool.

Antimony

Antimony derives its name from the Greek word "anti-monos," which means "not alone." This likely refers to the fact that antimony is never found in its pure form in nature but is always found combined with heavier metals like lead. Its chemical symbol, Sb, originates from "stibium," the Latin word for kohl, a type of eye make-up. The mineral ore stibnite serves as the primary source of pure antimony.



Stibnite



Jasimonite



Pure Antimony

Uses:

Pure antimony is primarily utilized in creating durable alloys, such as those found in metal types used by certain printers. In ancient Egypt, powdered stibnite was used to make **kohl**.



EXERCISES

- List two industrial uses of antimony.
- Discuss the role of phosphorus in biological systems and its importance in agriculture.

Essay Question

Discuss the chemical properties, industrial production methods, and practical applications of phosphorus. Include in your answer:

- The reactivity and allotropes of phosphorus.
- The production methods of phosphorus, focusing on the extraction from phosphate rock.
- At least three major uses of phosphorus in industry or agriculture.

CHAPTER VIII

CARBON & SILICON

Group 14 (VIA)

The elements of Group 14, including carbon, silicon, germanium, tin, and lead, exhibit considerable diversity in their chemical and physical properties. Carbon, a nonmetal, is fundamental to life and central to organic chemistry, but in this section, we focuse on its inorganic chemistry. Silicon, widely distributed in the natural environment, is a metalloid known for its intriguing chemistry due to the variety of oxoanions it forms, many of which are found in minerals. Germanium is also a metalloid, while tin and lead are metals with weak electropositivity, presenting a stark contrast to the highly electropositive alkali metals. Tin and lead find widespread applications in industry and manufacturing.

A notable trend in Group 14 is the increase in metallic properties as we move down the group, from nonmetals carbon and silicon to metalloid germanium, and finally to metals tin and lead. This trend is explained by the increasing atomic radius and the associated decrease in ionization energy down the group. Consequently, the ionization energies of the heavier elements are lower, making it easier for these metals to form cations. The valence configuration (ns^2np^2) suggests that the +4 oxidation state is dominant for these elements, with the major exception of lead. For lead, the most common oxidation state is +2, which is two less than the group maximum, illustrating the inert-pair effect—a significant characteristic of the heaviest p-block elements.

Table V.1: Selected properties of the Group 14 elements

	C	Si	Ge	Sn	Pb
Melting point/C°	3730 (graphite sublimes)	1410	937	232	327
Atomic radius/pm	77	117	122	140	154
First ionization energy, I/(kJ /mol)	1090	786	762	707	716
Pauling electronegativity	2.5	1.9	2.0	1.9	2.3

Carbon

Carbon and its compounds are widely distributed, making it the 14th most abundant element. The most common naturally occurring carbon compounds include CO_2, those in living organisms, coal, natural gas, and petroleum, while relatively small amounts of carbon are found in graphite and diamond forms. Carbon exists primarily as the isotopes (^{12}C) (98.89%) and (^{13}C) (1.11%). The interaction of cosmic ray-produced neutrons with (^{14}N) in the atmosphere generates (^{14}C) and protons via the reaction ($^{14}N + n \rightarrow (^{14}C + p$).

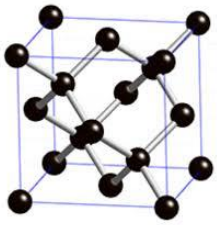
The ^{14}C isotope has a half-life of 5,570 years, resulting in a relatively constant amount of ^{14}C in all carbon-containing materials. When a living organism dies, ^{14}C is no longer replenished, allowing the determination of the material's age by measuring the remaining ^{14}C. This principle forms the basis of radiocarbon dating.

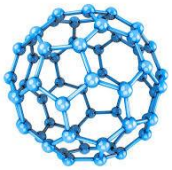
Forms

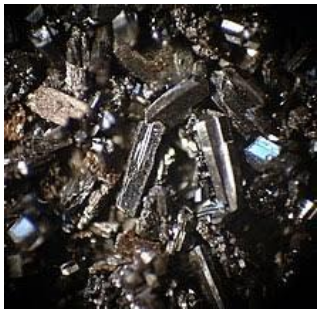
Carbon boasts the most compounds of any element, with over nine million identified. It is the fourth most common element in the Universe. Each carbon atom can bond with four other atoms, enabling the formation of chains and rings. On Earth, pure carbon is found in three forms: graphite, diamond, and **buckminsterfullerene** (a structure composed of 60 interlinked carbon atoms). Among these, diamond is the hardest naturally occurring substance.



Diamond



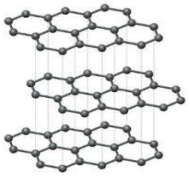




Buckminsterfullerene



Graphite



Carbon dioxide is a colorless, odorless gas commonly used in carbonated beverages. It is denser than air and does not support combustion, making it effective in fire extinguishers. When frozen, carbon dioxide condenses into a white solid known as dry ice at atmospheric pressure, and into a colorless liquid under higher pressure, both of which serve as refrigerants.

Additionally, carbon dioxide dissolves in water to form weakly acidic solutions.

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$

It reacts with alkalis to give salts of CO_3^{2-} and HCO_3^- ions:

$$CO_2 + OH^-_{(aq)} \rightarrow CO^{2-}_{3\,(aq)} + H_2O$$

$$CO_{3\,(aq)}^{2-} + CO_2 + H_2O \rightarrow 2HCO_{3\,(aq)}^{-}$$

These compounds are carbonates and bicarbonates (hydrogencarbonates), which are colorless unless the cation imparts color. Calcium carbonate, found in nature as limestone, is a common example. In the laboratory, carbon dioxide can be produced by reacting an acid with a carbonate.

Carbon monoxide is a colourless, odourless, very poisonous gas. It reacts with some metals to give carbonyls, from which useful derivatives can be made:

$$xM + yCO \rightarrow M_x(CO)_y$$

Metal carbonyls are very toxic.

Uses:

Diamond is the hardest natural substance and is often used in jewelry. The blades of some saws are coated with diamonds, which can cut into any material; only another diamond can cut a diamond. Graphite, on the other hand, is much softer and is used in pencil "leads" and some batteries. Coal is a major fuel source for electricity generation, though its emissions have harmful environmental and health effects. Crude oil, natural gas, and coal are hydrocarbons that naturally occur and can be used as fuels and materials for producing plastics.

This wheel is composed of carbon fibre and some other materials, which make it rigid.





This sharp blade is coated with tiny diamonds.

This battery has a graphite core that carries electric current



Silicon

About 90 per cent of the minerals that make up Earth's rocks contain silicon, a common element in our planet's crust. Nearly all silicon minerals are compounds of silicon and oxygen, known as **silicates**. The most common silicate is **quartz**, the mineral form of silicon dioxide, or **silica**. It is also the most common substance in sand. **Amethyst** is a type of quartz. Quartz deposits are widely found in rocks

such as granite and sandstone. A valuable type of silica is **opal**, which is used as a gemstone. The clays used to make pottery and ceramics are also silicates.



Quartz

Annually, around 500,000 tons of silicon are used for producing metal alloys. While alloy production is the primary use, silicon's role as a semiconductor is crucial for electronic devices, including computers. The silicon used in the electronics industry must be of exceptionally high purity. For example, the presence of just 1 ppb of phosphorus can drastically reduce silicon's specific resistance from 150 to 0.1 kΩ.cm. Due to the expensive purification process, ultrapure electronic-grade silicon is significantly more expensive than 98% pure metallurgical-grade silicon.



Amethyst



Opal

Preparation

Silicon is produced by heating silicon dioxide (quartz) with coke at temperatures exceeding 2000°C in an electric furnace similar to the Acheson process for making calcium carbide. The molten silicon, which has a melting point of 1400°C, is extracted from the furnace:

$$SiO_2(s) + 2C(s) \xrightarrow{\Delta} Si(l) + 2CO(g)$$

To produce ultrapure silicon, the raw silicon is heated to 300°C in a stream of gaseous hydrogen chloride. The resulting trichlorosilane $SiHCl_3$ can be distilled multiple times to achieve impurity levels below parts per billion:

$$Si(s) + 3HCl(g) \xrightarrow{\Delta} SiHCl_3(g) + H_2(g)$$

The reverse reaction occurs spontaneously at 1000°C, depositing ultrapure silicon. The hydrogen chloride can be recycled in the initial part of the process:

$$SiHCl_3(g) + H_2(g) \xrightarrow{\Delta} Si(s) + 3HCl(g)$$

Silicon Dioxide

Silicon dioxide SiO_2, commonly known as silica, is most often found in its crystalline form as quartz. Most sands are composed of silica particles, typically with impurities such as iron oxides. Silicon dioxide is notably unreactive, though it reacts with molten sodium hydroxide to form sodium silicate:



Natural Silica

$$SiO_2(s) + 2NaOH(l) \xrightarrow{\Delta} Na_2SiO_3(s) + H_2O(g)$$

Silicon dioxide is primarily used as an optical material due to its hardness, strength, and transparency to visible and ultraviolet light. Its very low coefficient of expansion means lenses made from it do not distort with temperature changes.

Silica Gel

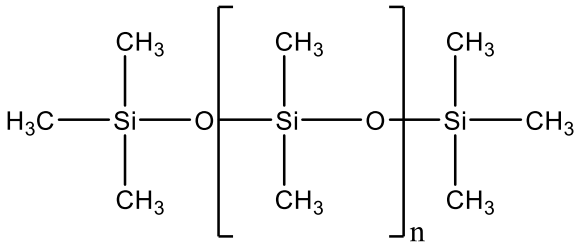
Silica gel, a hydrated form of silicon dioxide $SiO_2.xH_2O$, is widely used as a desiccant to keep environments dry in laboratories, electronics, and pharmaceuticals. These packets or bottles of silica gel maintain dryness even in humid climates.



Silica gel

Silicones

Silicones, or polysiloxanes, are a large family of polymers composed of alternating silicon and oxygen atoms. These chains have organic groups, such as methyl, attached to the silicon atoms.



Uses:

One of the most significant applications of silicon is in the field of electronics. Silicon wafers, which are thin slices of silicon, are essential for driving electronic circuits. This versatile element also plays a crucial role in converting sunlight into electricity in solar panels. Additionally, artificial silica is used to manufacture aerogel, a lightweight yet durable material that has poor thermal conductivity. Aerogel

is utilized in firefighting suits to protect firefighters from flames. Another important silicon compound is silicone, a moldable material used in a variety of products, including baking molds and watches.



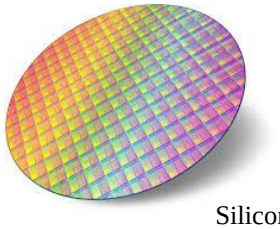
Opal is a jewel containing both silicon oxide and water molecules



Ceramic is made of a silicon-based clay that has been shaped and permanently hardened by heat.



Silicone baking moulds



Silicon wafers

EXERCISES

Exercise 1:

Explain the following properties of carbon:

a) Carbon can form a large number of compounds.

b) Carbon can exist in different allotropic forms.

c) Carbon has a high melting and boiling point.

Exercise 2:

Describe three major applications of carbon.

Exercise 3:

Explain the following properties of silicon:

a) Silicon is a metalloid with a semiconductor behavior.

b) Silicon can form covalent bonds with other elements.

c) Silicon has a high melting and boiling point.

Exercise 4:

Describe three major applications of silicon.

Exercise 5:

a) Compare and contrast the physical and chemical properties of carbon and silicon.
b) Explain the difference between allotropes and isotopes. Give examples of allotropes for both carbon and silicon.
c) Discuss the structure and properties of diamond and graphite, highlighting their differences and similarities.

CHAPTER IX

METALS

Introduction

Materials that are effective conductors of electricity are typically classified as metals. A significant application of metals is their use in electrical circuits. On Earth, all metallic elements are located in the crust, mantle, or core, and many metals discussed in this book also exist as dissolved salts in seawater. Scientists categorize chemical elements into metals, nonmetals, and metalloids based primarily on their electrical conductivity at standard temperatures and pressures. However, additional factors are considered when classifying elements in the periodic table.

As an important introduction, Students should be aware of the general properties of metals:

- Metal atoms are typically larger than those of nonmetals, which influences several of their properties.
- Metals exhibit high electrical conductivity, a key characteristic that sets them apart from nonmetals.
- Metals have low electronegativities and are electropositive, meaning they tend to lose electrons and form positively charged ions, contributing to their electrical conductivity.
- Metals have low electron affinities, making it energetically unfavorable for them to gain additional electrons. They prefer to lose electrons rather than gain them.
- With the exception of mercury, all metals are solid at room temperature under normal conditions, whereas many nonmetals are gases, one is a liquid, and only a few are solids.

Alkali metals



Alkali metals

All of the alkali metals are shiny and silver-colored, exhibiting high electrical and thermal conductivities like other metals. However, they differ significantly in other aspects. For instance, alkali metals are very soft, becoming progressively softer down the group: lithium can be cut with a knife, while potassium can be squashed like soft butter.

Physical Properties

most metals have high melting points, but the alkali metals have very low melting points that decrease down Group 1, with cesium melting just above room temperature. This unique combination of high thermal conductivity and low melting point makes sodium useful as a heat transfer material in some

nuclear reactors. The softness and low melting points of alkali metals are due to their very weak metallic bonding. Typically, metals have an enthalpy of atomization ranging from 400 to 600 kJ/mol, but for alkali metals, these values are much lower.

Additionally, the densities of alkali metals are quite atypical. While most metals have densities between 5 and 15 g/cm³, alkali metals have much lower densities. Remarkably, lithium has a density that is half that of water.

Table IX.2 Melting points and densities of the alkali metals

Element	Melting point (C°)	Density (g/cm^{-3})
Li	180	0.53
Na	98	0.97
K	64	0.86
Rb	39	1.53
Cs	29	1.87

Chemical Reactivity

Due to their low density, lithium could theoretically be ideal for making unsinkable (albeit soft) ships. However, the high chemical reactivity of alkali metals makes this impractical. These metals are typically stored under oil because they rapidly form a thick coating of oxidation products when exposed to air. For example, lithium quickly oxidizes to lithium oxide, which then reacts with carbon dioxide to form lithium carbonate:

$$4Li_{(s)} + O_{2\,(g)} \rightarrow 2Li_2O_{(s)}$$

$$Li_2O_{(s)} + CO_{2\,(g)} \rightarrow Li_2CO_{3(s)}$$

Alkali metals react with most nonmetals. For instance, all molten alkali metals burn in chlorine gas, producing a white smoke of the metal chloride. The reaction of sodium with chlorine exemplifies the marvel of chemistry: a highly reactive and dangerous metal reacts with a toxic gas to form sodium chloride, an essential compound for life:

$$2Na_{(l)} + Cl_{2\,(g)} \rightarrow 2NaCl_{(s)}$$

Alkali metals exhibit dramatic reactions with water, with reactivity increasing down the group. The reaction of potassium with water is particularly striking:

$$2K_{(s)} + 2H_2O_{(l)} \rightarrow 2KOH_{(aq)} + H_{2\,(g)}$$

Due to their heightened reactivity compared to typical metals, alkali metals are sometimes referred to as "supermetals."

An overview of the elements of the alkali metals

Lithium

Lithium is the lightest of all metals and can effortlessly float on water. In its pure form, lithium is highly reactive and naturally occurs only in minerals like **lepidolite** and **petalite**. Numerous lithium-containing minerals are highly soluble in water, leading to the presence of millions of tonnes of dissolved lithium in the world's seawater. Lithium can also be found in various foods, including mushrooms, prawns, nuts, and seeds.



Lithium



Mushrooms



Petalite



lepidolite



nuts



Drinking water



Prawns

Uses

Lithium has numerous practical applications. Glass containing lithium is heat-resistant and used in scientific equipment, such as mirrors in telescopes. The primary use of lithium is in rechargeable batteries; lithium-ion batteries are compact yet powerful, making them ideal for smartphones and tablets. Larger lithium batteries can power electric cars, which are more environmentally friendly than gasoline-powered vehicles. Lithium stearate, a soapy compound, is used to manufacture grease that helps automobile engines operate smoothly. Additionally, lithium forms hard ceramics used to produce durable artificial teeth and is also found in some medications.



Lithium coating on the inside of some syringes delays the clotting of the blood sample.





Lithium-rich grease is used to keep mechanical parts of engines running smoothly, even when hot.







This air scrubber used lithium hydroxide (LiOH) filters to remove excess carbon dioxide (exhaled by humans as part of normal respiration) from the atmosphere inside the Apollo 13 spacecraf

Sodium

Sodium, the 11th element on the periodic table, is a soft, silvery-gray metal with a density of 0.97 g/cm³, lower than that of water, allowing it to float. Despite its softness, which permits it to be easily cut with a butter knife, sodium is highly reactive and will burst into flames upon contact with water, as it readily forms compounds with other elements. Sodium is the most abundant alkali metal and is easily extracted from seawater, making it the most widely produced and used alkali metal in industry.



Sodium

Most people recognize sodium as the element responsible for the "saltiness" in table salt, a valuable trade and commerce commodity for centuries. The most common sodium-containing mineral is halite, or rock salt, which forms when inland salty seas evaporate, leaving the salt behind. Sodium also forms other compounds, such as the soft blue stone sodalite, which can be shaped and polished.

In its pure form, sodium is a soft metal that reacts with oxygen in the air to form sodium oxide, a process that can cause it to burst into flames when it comes into contact with water. Sodium compounds are also used in fireworks, where they produce a yellow-orange color, and were utilized in ancient Egypt to preserve mummies. Another useful sodium compound is sodium bicarbonate, or baking soda, which releases carbon dioxide bubbles to help dough rise. Refined sodium chloride, or common salt, has various practical applications, such as melting ice on slippery, frozen roads and as a seasoning for meals.

Bright yellow lights in fireworks get their colour from burning sodium compounds



Ancient Egyptians believed in life after death and so preserved the bodies of their dead. A dead body was washed and the organs removed, then crystals of sodium compounds were used to dry it out. Finally, the body was wrapped, which completed the process of mummification





Spraying salt keeps roads free from ice and frost



Baking soda

The chemistry of sodium

Be Careful: Sodium Reacts Violently with Water!

Sodium metal is a real firecracker when it comes to water! As the equation shows:

$$2\,Na_{(s)} + 2\,H_2O_{(l)} \rightarrow 2\,NaOH_{(dissolved)} + H_{2\,(g)}$$

- It reacts with a burst of energy, hot enough to ignite the hydrogen gas it produces, causing a potential explosion.

While this reaction is a common classroom demo, it's important to take serious safety precautions. The container needs to be strong enough to hold everything in, and only tiny amounts of sodium should be used to avoid injuries from hot, caustic sodium hydroxide (lye) splashing around.

- Even though pure sodium can be dangerous, sodium as a positively charged ion (Na^+) is a common and important part of many useful compounds.

Here are some examples:

Table salt: This familiar shaker staple is sodium chloride (NaCl).

Drain cleaner: Sodium hydroxide (NaOH), a strong base, is a key ingredient in products like Drano®.

Baking essentials: Baking powder and baking soda are both various forms of sodium bicarbonate ($NaHCO_3$).

Laundry booster: Washing soda, or sodium carbonate (Na_2CO_3), can be added to laundry for extra cleaning power.

Scouring power: Packaged as trisodium phosphate (TSP, Na_3PO_4), this compound is a strong cleaner used in hardware stores.

Sodium also forms various phosphate compounds used in:

Fertilizers: Sodium nitrate ($NaNO_3$) helps plants grow.

Photography: Sodium thiosulfate ($Na_2S_2O_3$) stops the development process in film photography.

Airbags: Sodium azide (NaN_3) helps inflate airbags in cars with a rapid burst of nitrogen gas.

So, while pure sodium is best left to the professionals, sodium compounds play a big role in our everyday lives.

Production of sodium

Industrial production of sodium involves electrolysis, a process that uses electricity to separate elements from a compound. Sodium metal isn't typically the desired end product, but rather a byproduct of this process. Here's a breakdown:

Raw Material: Sodium chloride (NaCl), also known as common table salt, is the primary source of sodium in industrial settings.

Process: The most common method is the electrolysis of molten sodium chloride. This is done in a Downs cell, a specialized container that can withstand high temperatures. The molten salt is mixed with calcium chloride ($CaCl_2$) to lower its melting point, making the process more efficient. Electricity is passed through the molten mixture, causing the sodium (Na) and chlorine (Cl) ions to separate.

Products: The main product of this electrolysis is chlorine gas (Cl_2), which has numerous industrial applications like water purification and bleach production. Sodium metal (Na) forms at the cathode (negative electrode) but due to its reactivity, it often needs further processing or is converted into a more stable compound like sodium hydroxide (NaOH) for industrial use.

Potassium

Potassium has a fascinating history! It was first spotted in the ashes of burnt plants, a substance called potash. Sir Humphry Davy, a curious scientist, explored this potash and discovered the element we now call potassium (named after potash) with the symbol K (from the Latin word for "ash").



Potassium

Unlike some elements, pure potassium isn't found naturally. But it's hiding in minerals like **sylvite** and **aphthitalite**. This hidden gem plays a vital role in our bodies, keeping muscles and nerves functioning properly. Luckily, we can get our daily dose of potassium from delicious sources like bananas, avocados, and sweet potatoes.

Potassium's benefits extend beyond the dinner table. Farmers use potassium-rich fertilizers to boost plant growth, while manufacturers include potassium compounds in soda water for a flavor boost. In hospitals, potassium chloride helps regulate blood pressure, and potassium solutions keep patients hydrated.

This versatile element even finds its way into everyday objects. Liquid soap uses potassium hydroxide for cleaning power, while strengthened glass screens for phones contain potassium nitrate. So next time you bite into a banana or use a smartphone, remember the hidden power of potassium!



Sylvit



This cylinder contains a compound called potassium superoxide

Rebreather



Saline drip



Aphthitalite



Fertilizer



Liquid soap





Gunpowder

This explosive mixture contains powdered potassium nitrate



Soda water

Alkaline Earth Metals



Alkaline Earth Metals

The alkaline earth metals stand in stark contrast to transition and post-transition metals. Unlike most metals in the periodic table, which form insoluble precipitates with sulfide ions (S^{2-}) and result in common sulfide ores in Earth's crust, alkaline earth metals do not form sulfides. Examples of metal sulfides include **galena** (lead sulfide), **cinnabar** (mercury sulfide), **greenockite** (cadmium sulfide), **acanthite** (silver sulfide), **cobaltite** (cobalt arsenic sulfide), **sphalerite** (zinc sulfide), **stibnite** (antimony sulfide), various copper sulfides, orpiment and realgar (both arsenic sulfides), and **pyrite** (iron sulfide). In contrast, alkaline earth metals are frequently found in nature as sulfates (SO_4^{2-}), unlike transition and post-transition metals, which are rarely found in this form. Notable alkaline earth sulfates include minerals such as **gypsum** (calcium sulfate), **epsomite** (magnesium sulfate), and **barite** (barium sulfate). This group consists of reactive metals, historically discovered in compounds within common minerals in Earth's crust. These minerals, previously referred to as "earths," are alkaline, giving the group its name. The purification of all alkaline earth metals occurred in the 19th century.

Properties of elements of Alkaline Earth Metals



Atomic structure

The alkaline earth metals have two electrons in their outer most electron shell. Radium (Ra) is the most radioactive member



Physical properties

All members of this group are soft and shiny when pure. They are solid at room temperature.



Chemical properties

These metals are similar to the alkali metals, but not as reactive. Except for beryllium (Be), all alkaline earth metals react with hot water or steam.



Compounds

These elements form compounds with non-metals by losing their outermost electrons. Several compounds are found in teeth and bones.

The alkaline earth metals are a group of silvery elements that are lighter than most metals. They share some similarities with the alkali metals, but are generally less reactive. Here's a breakdown:

Density: Like the alkali metals, their density increases as you move down the group (Table IX.2).

Strength: They have stronger metallic bonds compared to alkali metals, making them harder and with higher melting points. However, the melting point trend isn't as clear as the density increase.

Reactivity: While less reactive than alkali metals, they're still more reactive than most other metals. For instance, calcium, strontium, and barium react with water (barium most vigorously). Reactivity increases down the group, so magnesium only reacts with hot water, not cold.

Non-metal Reactions: They readily react with many non-metals. For example, calcium burns in chlorine gas to form calcium chloride.

Nitrogen Reaction: Uniquely, they can react with nitrogen gas when heated. Magnesium, for example, forms magnesium nitride.

In short, these shiny elements are a less reactive bunch compared to their alkali metal cousins, but still have their own interesting reactions with water, non-metals, and even nitrogen gas.

Table IX.3 Melting points and densities of the alkaline earth metals

Element	Melting point (C°)	Density (g/cm^{-3})
Mg	649	1.74
Ca	839	1.55
Sr	768	2.63
Ba	727	3.62

Beryllium

A Lightweight Gem with a Dark Side

Beryllium, the fourth lightest element, is a rare visitor in the universe, only forged in giant stellar explosions. This metal, named after the mineral beryl (emeralds are a type of beryl!), has been around for millennia, prized for its beauty but not understood until the late 18th century.



Beryllium

Two common beryllium minerals are **chrysoberyl** and **beryl**. Beryl has different forms, such as **aquamarine** and emerald.

Rare and Precious: Beryllium is scarce on Earth, forming only during supernovas. Despite its beauty in minerals like beryl, it wasn't identified as a separate element until the 1700s.



Chrysoberyl

Danger Lurks Within: While beautiful, beryllium dust is highly toxic when inhaled, causing a serious lung condition. This danger became clear in the mid-20th century when workers making fluorescent lights were exposed. Thankfully, safer alternatives were found.

A Star in Science: Beryllium played a crucial role in unlocking the secrets of the atom. By bombarding beryllium with alpha particles, scientists discovered the neutron, a key building block of the atom.

Strength and Transparency: Beryllium's lightness, high melting point, and resistance to corrosion make it ideal for spacecraft and missile components. It's also transparent to X-rays, making it valuable in X-ray equipment.

A Double-Edged Sword: Beryllium's ability to reflect neutrons makes it a key component in nuclear weapons, intensifying the destructive power.

Beryllium's story is a fascinating mix of beauty, danger, and scientific importance. While its unique properties make it valuable in many applications, its toxicity requires careful handling.

The chemistry of beryllium

The chemistry of beryllium is notably distinct from other Group 2 elements due to its predominance of covalent bonding. The very small beryllium cation has an extremely high charge density, which causes it to polarize approaching anions, resulting in electron density overlaps. Consequently, simple ionic compounds of beryllium are often found as tetrahydrates, such as $BeCl_2 \cdot 4H_2O$, consisting of $[Be(OH_2)_4]^{2+}$ and $2Cl^-$ ions in the crystal lattice. The tetraaquaberyllium ion, $[Be(OH_2)_4]^{2+}$, with four covalently bonded oxygen atoms from water molecules, is also the predominant species in aqueous solution. Beryllium typically exhibits four coordination due to its small ionic size.

Although beryllium is metallic, it possesses a characteristic more typical of nonmetals: the ability to form oxyanion species. Unlike "normal" metal oxides that react with acids to form cations but not with bases to form oxyanions, beryllium oxide is amphoteric. It reacts with hydronium ions to form the tetraaquaberyllium ion, $[Be(OH_2)_4]^{2+}$, and with hydroxide ions to form the tetrahydroxidoberyllate ion, $[Be(OH_2)_4]^{-2}$:

$$BeO_{(s)} + 2H_3O^+{}_{(aq)} + H_2O_{(l)} \rightarrow [Be(OH_2)_4]^{2+}{}_{(aq)}$$

$$BeO_{(s)} + 2OH^-{}_{(aq)} + H_2O_{(l)} \rightarrow [Be(OH_2)_4]^{-2}{}_{(aq)}$$

Beryllium and other metals exhibiting amphoteric behavior (such as aluminum and zinc) are sometimes referred to as "weak" metals because they are located near the metalloid/nonmetal

boundary. In the periodic table, beryllium is positioned next to boron, a metalloid. The apparent gap between beryllium and boron only exists because the transition metal groups are placed lower in the short form of the periodic table.

Magnesium

Magnesium was named after the region of Magnesia in Greece, where it was first discovered. This element is primarily found deep within the Earth's mantle, but it can also be extracted from seawater and various minerals in the Earth's crust, including **serpentine**. Another mineral, **dolomite**, is also a source of pure magnesium.



Magnesium

Magnesium has numerous important applications. Magnesium alloys are prized for their combination of strength and lightness, making them useful in products ranging from car wheels to cameras. For centuries, naturally occurring magnesium minerals have been used in traditional medicines.



Serpentine

One such mineral, serpentine, has a distinctive feather-like appearance. Magnesium has 22 known isotopes, and a laboratory sample of the pure element appears white. Another magnesium-containing mineral, dolomite, is a source of the pure metal.



Dolomite

Magnesium is an essential component of chlorophyll, the molecule that gives plants their green color and enables photosynthesis. The magnesium atom at the center of the chlorophyll molecule helps plants convert sunlight into energy.

Magnesium compounds have diverse applications. Magnesium carbonate, or magnesia, can be used to settle indigestion when it reacts with stomach acid. Heating magnesia produces magnesium oxide, an ingredient in cement. Magnesium compounds are also used in fireworks, where they burn with a bright white flame. Salts of magnesium, known as Epsom salts, are used as muscle relaxants. Finally, magnesium silicate, or talc, is a soft mineral used in body powders.

Plant Powerhouse: In plants, magnesium sits at the heart of chlorophyll, the green pigment that lets them capture sunlight and turn it into food (glucose) and oxygen. A lack of magnesium shows up

quickly as leaves lose their green color. Luckily, a simple magnesium spray or adding some minerals to the soil can fix the problem.

Essential for Humans: We get magnesium from plants and animals that eat them. It's crucial for many bodily functions, including building strong bones, regulating blood sugar, and keeping our nerves, muscles, and heart working properly.

Warning Signs of Deficiency: People with digestive issues, uncontrolled diabetes, or who take certain medications may be at risk for magnesium deficiency. Symptoms include fatigue, mood changes, heart problems, and seizures.

Magnesium on the Move: Research suggests magnesium may help with certain medical conditions, and getting enough is important for overall health. Adults need around 200mg daily, found in foods like bran, chocolate, soybeans, and nuts.

Beyond Biology: Magnesium has a long history of medicinal use. Epsom salts, discovered in the 17th century, were named after a town in England where cattle wouldn't drink the bitter water (magnesium sulfate). These salts and magnesium hydroxide (Milk of Magnesia) became popular laxatives and antacids.

Magnesium for a Greener Future: This versatile element is also lightweight and strong, making it a perfect fit for airplanes and cars. Magnesium alloys with aluminum help reduce vehicle weight, leading to better fuel efficiency and lower pollution. Plus, magnesium is recyclable, making it even more eco-friendly.

Reactions of Magnesium

Magnesium exhibits distinct chemical behavior compared to the other lower group 2 metals. A key difference is that magnesium readily forms compounds containing covalent bonds. This can be attributed to magnesium's relatively high charge density compared to calcium.

For example, magnesium metal can react with organic compounds called halocarbons or alkyl halides, such as bromoethane (C_2H_5Br), in a solvent like ethoxyethane ($(C_2H_5)_2O$), commonly known as ether. In this reaction, the magnesium atom inserts itself between the carbon and halogen atoms, forming covalent bonds with its neighbors:

$$C_2H_5Br\ (ether) + Mg(s) \rightarrow C_2H_5MgBr(ether)$$

The resulting organo-magnesium compounds are referred to as Grignard reagents. These compounds are extensively used as important intermediates in synthetic organic chemistry.

The ability of magnesium to form covalent bonds, in contrast to the more ionic bonding exhibited by the lower group 2 metals, reflects its distinct chemical properties and reactivity. This makes magnesium an important and versatile element in various chemical applications and synthetic processes.

The Industrial Extraction of Magnesium

Seawater is a major industrial source of magnesium, as it is the third most common ion in seawater after sodium and chloride. In fact, 1 cubic kilometer of seawater contains about 1 million tonnes of magnesium ions, and with 108 cubic kilometers of seawater on the planet, there is more than enough magnesium available to meet our needs.

The Dow Chemical Company's extraction process is based on the lower solubility of magnesium hydroxide compared to calcium hydroxide. Finely powdered calcium hydroxide is added to seawater, causing magnesium hydroxide to precipitate:

$$Ca(OH)_2(s) + Mg^{2+}(aq) \rightarrow Ca^{2+}(aq) + Mg(OH)_2(s)$$

The magnesium hydroxide is then filtered off and mixed with hydrochloric acid, resulting in a solution of magnesium chloride:

$$Mg(OH)_2(s) + 2\,HCl(aq) \rightarrow MgCl_2(aq) + 2\,H_2O(l)$$

This solution is evaporated to dryness, and the residue is placed in an electrolytic cell similar to the Downs cell used for sodium production. The magnesium metal collects on the surface of the cathode compartment and is siphoned off, while the chlorine gas produced at the anode is reduced back to hydrogen chloride for reuse.

A major challenge in this process is providing an unreactive atmosphere over the molten magnesium to prevent it from reacting with atmospheric gases. Nitrogen gas is typically used for other reactive metal syntheses, but it reacts with magnesium. Currently, most plants use the expensive greenhouse gas sulfur hexafluoride (SF_6) to blanket the molten magnesium, although a lesser-used alternative is sulfur dioxide.

Uses:

Talcum Powder



Alloy Weel





Magnesium fireworks

Portland cement





This indigestion medicine is a mixture of water and magnesium carbonate

Milk of magnesia

Calcium

Beyond Bones: The Many Lives of Calcium

While we picture calcium as the white stuff in bones and seashells, it's actually a silvery gray metal rarely seen in pure form. This is because calcium loves to react with air and water, quickly forming the familiar white compounds like calcium carbonate (think: white cliffs and eggshells).



Calcium

Calcium: The Body's Builder: This essential element is the building block of our bones (calcium phosphate) and seashells. Our bones aren't static - they're constantly being broken down and rebuilt, with calcium playing a key role. Children, pregnant women, and seniors need more calcium (1000-1500mg daily) to support this process. Dairy products, leafy greens, and beans are all great sources.

The Calcium Connection: Calcium is crucial for other bodily functions too. If our bodies lack calcium, they'll steal it from our bones, potentially leading to osteoporosis later in life. Vitamin D, found in fish and some dairy products, helps our bodies absorb calcium.

From Mortar to Masterpieces: Calcium oxide, also known as lime, has a long history. Since Roman times, lime has been used as a key ingredient in mortar, a building material that hardens by absorbing carbon dioxide from the air (forming calcium carbonate again!). The beautiful honey-colored limestone buildings of Bath, England, are a testament to the enduring use of calcium.

A Gardener's Ally (or Enemy): Lime-rich soil can be tricky for gardeners. It can be dry and lack nutrients. However, lime can also be helpful by raising the pH of acidic soil, allowing plants to better absorb nutrients.

Calcium's Many Uses: Calcium isn't just for bones and buildings! It's used in water treatment, fertilizer, and steel-making. In steel production, calcium acts as a flux, binding with impurities to create a removable slag.



Writing chalk



Marble statue



Plaster cast

Despite its otherworldly appearance, the **vibrant Fly Geyser** in Nevada isn't entirely a natural wonder. While similar colorful formations arise from hot springs rich in calcium, this particular geyser was created by accident in 1964. During a geothermal well drilling project, engineers stumbled upon hot water but capped it to continue searching elsewhere. Over time, the persistent hot water from deep underground found its way to the surface, forming a natural geyser. Over decades, dissolved calcium has steadily deposited around the vent, building a central mound nearly 5 feet tall and 13 feet wide. The hot water continues to erupt, reaching heights of 5 feet and contributing to the vibrant colors thanks to the algae and bacteria thriving in its warm, mineral-rich environment.



Strontium

Strontium's story begins in a Scottish village called Strontian. In 1790, a local doctor stumbled upon a new mineral while examining ores from nearby lead mines. This discovery sparked further investigation, leading chemist Thomas Charles Hope to identify a previously unknown element within the mineral – strontium. Notably, Hope observed that this element turned flames a fiery red.

Another strontium-containing mineral was found in England a decade later, used for decorative garden paths. This discovery yielded strontium sulfate, known as celestite. Finally, in 1808, Sir Humphry Davy successfully isolated pure strontium through electrolysis, a process he had previously used for barium and calcium.

Strontium is a soft, silvery metal with a fiery side. It reacts readily with water and air, and finely powdered forms can even ignite spontaneously. However, a more concerning aspect of strontium is its association with the radioactive isotope, strontium-90.



Strontium

Fallout from above-ground nuclear tests in the mid-20th century significantly contaminated the environment with strontium-90, a potent emitter of radiation with a long half-life of 29 years. Studies revealed a dramatic increase in strontium-90 levels in children's teeth after the peak testing period, ultimately contributing to the signing of the Partial Nuclear Test Ban Treaty to end such practices. The Chernobyl disaster further highlighted the dangers of strontium-90 contamination.

Despite its radioactive counterpart, ordinary strontium is not radioactive. However, its uses remain somewhat limited. It finds application in specialized glass for old-fashioned televisions to prevent radiation emission and in "getter" materials for vacuum tubes. Interestingly, strontium chloride is sometimes used in toothpaste for sensitive teeth, creating a protective barrier on exposed areas.

The human body absorbs strontium similarly to calcium due to their chemical resemblance. This has led to the use of strontium supplements as "bonemakers," with some studies showing promise for promoting bone cell growth.

Strontium's story is a fascinating mix of scientific discovery, environmental concerns, and potential medical applications. While its radioactive shadow looms large, this silvery metal continues to hold potential for specialized uses.

Barium

Barium, named after the Greek word for "heavy," might surprise you. While the pure metal itself isn't particularly hefty, many of its compounds are real weightlifters. Barium sulfate, for instance, is so dense that it helps clean out oil wells! A slurry of this compound is pumped down the wellbore, and the pressure forces rock chips back up to the surface.



Barium

This soft, silvery metal is a real social butterfly – it loves to react with air! So much so, that you won't find it hanging around in nature unattached. However, its compounds are plentiful. The story of barium starts in 17th century Italy, where a curious alchemist stumbled upon some glowing pebbles. These "Bologna stones" were actually a type of barium sulfate, and their ability to capture sunlight and emit a spooky glow in the dark made quite a splash.

Fast forward to the 18th century, and scientists figured out these glowing stones contained a new element – barium. By the 19th century, barium was popping up in all sorts of unexpected places – plant ash, vegetables, even seaweed! Finally, in 1808, Sir Humphry Davy managed to isolate the element itself.



Desert- rose: Petal-like shapes form in the desert when sand mixes with barite or with gypsum.

Today, barium's main source comes from minerals like barite and witherite, mined in places like the UK, USA, and Germany. Barium's eagerness to react with other elements makes it a great "getter" – it can suck up the last traces of air from a vacuum, creating a super-perfect vacuum.

However, a word of caution: some barium compounds are quite poisonous. In fact, one teenager tragically used barium acetate to harm her father. Luckily, there's a much safer use for barium – the barium meal! This medical workhorse uses barium sulfate's X-ray absorbing properties to light up the digestive system in scans. Since it's insoluble, it passes through the body safely, allowing doctors to see potential problems in the stomach and intestines. While endoscopies are becoming more common, barium meals are still a valuable diagnostic tool.

Beyond its medical uses, barium compounds have niche roles in glassmaking and even add a touch of green magic to firework displays. So, the next time you see a dazzling green firework or get an X-ray, remember the fascinating story of barium – from glowing pebbles to medical marvel.

Radium

Radium's story is a cautionary tale of scientific discovery gone wrong. Discovered in 1898 by the Curies, this silvery white metal captivated Marie with its faint glow, a result of its inherent radioactivity. However, radium's power soon morphed into a public health nightmare.



This is the material that radium is made from. It's a sample of black uraninite (uranium oxide)—along with a deposit of yellowish-brown gummite (uranium hydroxide). Sharp-cornered black crystals of uraninite are occasionally found in nature, but it usually occurs in lustrous, black masses (as here), when it is known as pitchblende

Early on, radium was hailed as a miracle cure. Unscrupulous figures peddled dubious radium-laced "tonics" and devices, promising everything from better health to virility. Meanwhile, radium needles were used to treat cancer, a practice that tragically exposed both patients and medical workers to harmful radiation.

The allure of radium's luminescence also had a dark side. Young women, often unaware of the dangers, were employed to paint luminous watch faces with radium-containing paint. This practice had devastating consequences, with many of these "radium girls" developing cancer and tragically succumbing to its effects. Even Marie Curie, a pioneer in radioactivity research, eventually fell victim to radiation exposure.

Radium's legacy reveals a stark lesson. While scientific curiosity can lead to groundbreaking discoveries, the potential risks must be carefully considered and managed. The story of radium serves as a reminder of the importance of safety protocols and responsible handling of hazardous materials.

Transition Metals



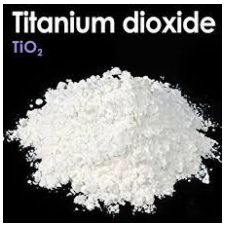
$FeSO_4$

The periodic table has a special category called transition metals. These elements sit between the first two groups (think lithium and sodium) and the last six (like the halogens). What makes them stand out? They have a specific type of electron orbital, the "d orbital," that's only partially filled with electrons.

There are three main groups of transition metals based on which d orbital is partially filled. These groups are further categorized as first-row, second-row, and third-row depending on the specific d orbital involved (3d, 4d, or 5d). You might see them written as Groups 3-12 or "B" group elements.

While the second and third rows have important metals, the first row takes the spotlight for its practical uses. These first-row transition metals are the building blocks of strong structures. Not only are they valuable on their own, but countless alloys containing them are essential for various applications.

Among transition metal compounds, titanium dioxide (TiO_2) is the king of production, with a whopping 2 billion pounds produced annually! Its wide use in paints makes it a champion of the chemical industry.



TiO_2

Titanium tetrachloride ($TiCl_4$) is a strong Lewis acid and forms many adducts with a variety of Lewis bases. It reacts with alcohols to produce alkoxide compounds, which can be considered salts of the acid H_4TiO_4.

Potassium dichromate ($K_2Cr_2O_7$) is a useful oxidizing agent, employed in synthetic reactions and analytical chemistry titrations. It can oxidize Fe^{2+} and Cl^-. The equilibrium between chromate (CrO_4^{2-}) and dichromate ($Cr_2O_7^{2-}$) ions is pH-dependent, resulting in color changes. Chromates and dichromates have applications in pigments, textiles, and leather tanning, but the Cr(VI) oxidation state is carcinogenic.



$K_2Cr_2O_7$ and K_2CrO_4

Potassium permanganate ($KMnO_4$) is another important oxidizing agent. Its deep purple color and the colorless Mn^{2+} reduction product make it useful as a self-indicating titrant.



$KMnO_4$

Various iron compounds like $FeCO_3$, $FeCl_2$, and $FeSO_4$ have industrial uses. $FeSO_4$ is used in inks and dyes. Reactions between Fe^{2+}/Fe^{3+} and ferrocyanide complexes produce distinctive "Turnbull's blue" and "Prussian blue" solids.

Copper sulfate has applications in dyeing, insecticides, and other industrial processes. It can be dehydrated to produce the trihydrate and monohydrate forms.



$FeSO_4$



Calamine

Zinc carbonate (calamine) and zinc oxide are used in skin ointments and creams to treat rashes. Many ternary compounds of nickel and cobalt also exist, exhibiting typical properties of the contained anions.

Titanium

Imagine a metal as strong as steel yet 45% lighter. That's titanium, the ninth most abundant element on Earth, and a gift for engineers and medical professionals alike.



Strength Takes Flight: This wonder metal isn't just strong, it's also a champion of lightness. No surprise then, that airplanes, especially jet engines, rely heavily on titanium. A single Boeing 777 boasts a whopping 59 tons of it!



Corrosion? Not a Chance: Titanium defies the enemy of metals – corrosion. Unlike iron that succumbs to rust, titanium forms a protective oxide film, a microscopic shield that grows stronger over time. This makes it perfect for withstanding the harsh environment of the sea – from propeller shafts on ships to the hulls of submarines.



The Body's Perfect Match: Because titanium is both strong and biocompatible (doesn't harm living tissue), it's a lifesaver in the medical field. Artificial hip joints, bone screws, and skull plates crafted from titanium can last for decades within the body. And here's the secret sauce – titanium seems to bond well with bone, thanks to its oxide film. To ensure this perfect fit, medical-grade titanium gets a special treatment – a high voltage zap that removes any surface layers and promotes a fresh, protective oxide coating.

Beyond the Basics: From lightweight sports equipment like golf clubs and bicycles to self-cleaning window coatings, titanium's applications extend far and wide. Its compounds are equally impressive. Titanium dioxide, for instance, is the brilliant white pigment that keeps paint and paper opaque, and even protects us from harmful UV rays in sunscreen. Another cool fact – titanium and nickel join

forces to create nitinol, a shape-memory alloy that can be bent out of shape but miraculously springs back!


Nitinol

The discovery of this mighty metal goes back to 1791, thanks to a curious vicar-geologist in England. He named his discovery after the Titans of Greek mythology, perhaps a fitting tribute to the strength and potential he saw in this element. Today, titanium continues to live up to its name, a true marvel in the world of materials.

Vanadium

Vanadium, a seemingly ordinary silvery metal, has played an extraordinary role in shaping our modern world. Its impact stretches from the cars we drive to the wars we fight.

Vanadium's true strength lies in its ability to make steel stronger and lighter. This quality didn't go unnoticed by Henry Ford, who, in his quest for an affordable car for the masses, stumbled upon vanadium in the wreckage of a French race car. This discovery revolutionized car manufacturing, leading to the iconic Model T and ultimately putting millions of Americans on the road. However, this convenience came with a cost – the environmental impact of mass car usage.

Vanadium also played a crucial role in World War I. Fighter planes could now carry powerful, lightweight cannons thanks to vanadium steel. This same steel provided better protection for soldiers through helmets and armor.



Today, vanadium remains a vital component in our everyday lives. It strengthens the tools we use, from drill bits to pliers, often leaving its mark with the label "vanadium steel."



The story of vanadium's discovery is quite interesting. Initially found in Mexico in 1801, it was mistaken for chromium. It wasn't until 1831 that a Swedish chemist rediscovered it and named it after the Scandinavian goddess of beauty, Vanadis.

Vanadium even plays a tiny but essential role in our bodies, regulating sodium levels and potentially promoting growth. While we only need trace amounts, it's surprisingly abundant in soil, plants, and even some fungi like toadstools!

Vanadium's story is a reminder that sometimes the most unexpected things can have a profound impact on our world, for better or worse.

Chromium


Chromium

Chromium, a shiny silver metal, lives up to its Greek name for "color." It has a fascinating history, both for its vibrant applications and its potential dangers.

Once a favorite pigment for artists and even school buses because of its brilliant yellow color (chrome yellow), chromium was later replaced by safer alternatives when scientists discovered its toxic nature. This discovery highlights the delicate balance between progress and safety.

Chromium's story starts in 1797 with French chemist Nicolas Vauquelin, who was intrigued by a bright red mineral. He isolated a new element from it, one that produced a range of colors in solution – hence the name "chromium." Interestingly, Vauquelin also found chromium to be the secret ingredient behind the emerald's green hue!

Today, South Africa, Zimbabwe, and Finland are the main sources of chromium, the 21st most abundant element on Earth. While chromium is vital for human health in tiny amounts, some chromium compounds can be harmful. In the 1800s, Scottish workers handling chromium developed painful ulcers, a condition named "chrome ulcers." This risk extends to people in chrome-plating, dyeing, and tanning industries.


Ruby: This red colour is due to the presence of tiny amounts of chromium oxide in the crystal.

On the positive side, chromium is a key component in stainless steel. When alloyed with iron and nickel, chromium creates a strong and corrosion-resistant material. Chrome plating, a trend for car bumpers in the mid-20th century, also utilizes chromium's ability to create a shiny, protective surface.

Chromium's story reminds us that even the most colorful elements can have a dark side. We must be mindful of its potential dangers while appreciating its contributions to our world.

Manganese

A Long History with Humanity:

Our connection with manganese stretches back at least 17,000 years. Our artistic ancestors used black manganese oxide pigments to create their captivating cave paintings. Even the Romans used

manganese minerals in glassmaking, highlighting its versatility. The element itself was isolated in 1774 by Swedish scientist Johan Gottlieb Gahn.



Cave paintings

The Strength Within:

Despite its brittleness in pure form, manganese becomes incredibly strong when alloyed with other metals. In 1883, a 24-year-old Briton named Robert Hadfield patented this revolutionary alloy, Hadfield steel. This discovery is why we see manganese in prison bars, railway tracks, safes, and even helmets – its strength is unmatched.



Railway tracks

Essential But Tricky:

Manganese is vital for all living beings, but only in trace amounts for humans. It plays a role in enzyme function and glucose metabolism. We can get our daily dose from various sources like tea, nuts, cereals, and vegetables. However, excessive exposure can be harmful. Manganese dust or fumes can lead to respiratory problems and even neurological disorders in miners.

Mining and Maritime Marvels:

South Africa, Russia, Ukraine, and Australia are the main sources of manganese ore, but the most abundant deposits lie on the ocean floor. Here, trillions of tons of manganese nodules are scattered across vast areas. This abundance fueled a bizarre episode in 1974. Entrepreneur Howard Hughes, in a CIA-orchestrated cover story, started a fake “manganese fever” by collecting these nodules. The real mission? To recover a sunken Russian submarine and its valuable code books, a mission that ultimately failed.

Beyond the Basics:

Manganese's applications extend far beyond strengthening steel. It's a key component in dry cell batteries and helps remove impurities from glass. In the past, manganese dioxide was even used to create the dark pigments in prehistoric cave paintings.



Dry cell batteries

Manganese's story reminds us that seemingly ordinary elements can have extraordinary tales to tell. From the artistry of our ancestors to the high-stakes world of espionage, manganese continues to leave its mark on our world.

Iron

Iron is more than just a common metal – it's a force that has shaped our planet and our history. Here's why iron deserves all the superlatives:



Iron

Earth's Core and Our Shield: It's the most abundant element on Earth, forming most of our planet's molten core. This molten iron churns and creates Earth's magnetic field, which protects us from harmful radiation from space.

A Star-Forged Marvel: Iron is the heaviest element naturally produced by stars. This mighty metal is literally forged in the fires of the cosmos!

From Tools to Warships: The Hittites first smelted iron around 1500 BC, ushering in the Iron Age. This revolutionized tool-making and construction, propelling civilization forward. However, iron's strength also fueled warfare, from swords to cannons, as Pliny the Roman philosopher wisely observed.



Nuts and bolts

Strength in Structure: Pure iron is strong but brittle. The secret to its legendary strength lies in its crystal structure. By working iron at high temperatures, we refine the grain size, creating a more uniform and stronger metal.

Nature's Built-in GPS: Earth's magnetic field, guided by iron's flow in the core, acts as a natural navigation tool. From compasses to migrating birds, many rely on this invisible force.

Iron's Everyday Uses:

While most iron is locked away in Earth's core, we mine and process it for various purposes:

Essential for Life: Our bodies use iron to make hemoglobin, which carries oxygen-rich blood throughout our system. Spinach and meat are good dietary sources of iron.

From Rust to Resilience: Pure iron rusts easily. To combat this, we add small amounts of carbon and other elements like nickel and titanium, creating steel. Steel's strength and versatility make it a cornerstone of our infrastructure, from buildings to tractors. Adding chromium to steel creates the even more resistant stainless steel.

Iron's story is a testament to its remarkable properties. It's a crucial element for our planet, our bodies, and the tools and structures that define our world.

Cobalt

Cobalt's story is one of mistaken identity and unexpected benefits. Medieval miners, thinking they had found precious metals, were instead fooled by cobalt ores. The nasty fumes released during their attempts to purify these "treasures" made them sick, leading them to call the culprit "kobold" – the German word for a mischievous goblin.



Cobalt

Despite this initial frustration, cobalt itself is a valuable metal. It's hard and shiny, and when added to alloys like steel, it creates incredibly strong materials. These alloys are used in the high-pressure blades of jet engines and even in artificial joints like hips and knees, offering exceptional strength where it's needed most.

One of cobalt's unique properties is its ability to form permanent magnets. Large magnets used in industry are often made from a tough alloy of cobalt, nickel, and aluminum called alnico. There's even a radioactive form of cobalt, cobalt-60, used to safely sterilize food through a process called irradiation.



Artificial joints

And beyond its industrial applications, cobalt offers a beautiful blue hue. Cobalt blue paints and dyes, created by combining aluminum with cobalt oxide, have been used for centuries to add a vibrant touch to art and everyday objects.

So, while cobalt may have caused some trouble for early miners, it has become a vital element in our modern world, contributing to advancements in medicine, engineering, and even the visual arts.

Nickel

Much of Earth's nickel might have come crashing down from space! Giant meteorites, like one believed to be as big as Mount Everest, may have pelted our planet billions of years ago. It's no surprise then that Canada's Sudbury basin, where a massive meteorite is thought to have struck, holds a whopping 30% of the world's nickel reserves. While the meteor might be a major source, nickel also bubbles up naturally from Earth's core. Today, mining for this valuable element extends beyond Canada to Russia, South Africa, Australia, and Cuba.

Nickel's history is filled with interesting twists. Early civilizations unknowingly mixed it with iron for tools and weapons. Its name, "kupfernickel," comes from German miners who mistook it for copper

(another reddish mineral) and considered it worthless – literally "devil's copper" or "St. Nicholas's copper"! They could only use it to make green glass.

In 1751, a Swedish scientist finally unlocked nickel's true identity. He was studying a different mineral when he isolated this unknown metal, also present in kupfernickel. Despite his discovery, recognition of nickel as a distinct element took a few years.



kupfernickel

Pure nickel is a gleaming silver metal that resists rust and corrosion. This makes it a perfect partner for steel. Over half of all nickel goes into creating stainless steel, the versatile material used in everything from cars and airplanes to our kitchenware. Nickel's heat resistance also makes it valuable in gas turbines and rocket engines.

Beyond stainless steel, special nickel alloys like Inco 276 can withstand harsh environments. This particular alloy tackles the challenge of hydrogen sulfide gas, making it useful for deep drilling projects.



This silver-coated fork is made of an alloy of nickel, copper, and zinc

Nickel plays a vital role for some living things, and humans need just a tiny amount daily. A cup of tea actually provides more than enough, with tea leaves boasting a small amount of nickel.

However, nickel exposure can be risky. Nickel dust and gas can be harmful, primarily impacting miners and industrial workers. For some people with sensitive skin, nickel can cause irritation, especially from jewelry or watches. The good news is that nickel's durability makes it a champion of recycling, allowing products to be reused many times over.



The Algerian five dinars coin is made of an alloy of copper and nickel

These nickel-plated guitar strings help create a clear tone.



Copper

Copper is an incredibly useful metal, used for thousands of years. Evidence suggests its use began around 10,000 years ago. It's strong, beautiful, and lasts a long time. Archaeologists even found working copper pipes in an Egyptian pyramid that were thousands of years old!



Unmixed native copper in its oxidized state. The corroded parts have a green hue. Copper is one of the most-used metal elements we have—with applications in plumbing, electrical wiring, coinage and many branches of engineering

Copper was especially important during the Bronze Age, when it was mixed with tin to create a strong metal for tools and weapons. Later, in Roman times, copper was everywhere – in coins, razors, instruments, and more. This created a big demand for copper and trade around the Mediterranean.

Copper's name comes from the island of Cyprus, a major source of the metal in ancient times. It's a good conductor of electricity, second only to silver. This makes copper wiring essential in our modern world, just like it was in the past. Copper was also once used in coins, though it was the least valuable of the precious metals.

Today, most copper goes into electrical equipment, buildings, and plumbing. It's also an important part of many alloys, like brass. Copper weathers well and forms a green patina that protects it. This is why you see copper roofs and statues, like the Statue of Liberty. Copper was even used to protect ships from clinging organisms, making them faster and longer-lasting.



Statue of Liberty

Incredibly, copper is also essential for living things! It helps our bodies function in many ways. We only need a tiny amount each day, but it's important to get it from our food.

Zinc

Zinc is a tiny but vital ingredient for us, animals, and plants. It's found in over 200 enzymes that help us grow, digest food, fight off germs, and even have babies. Men with low zinc levels may have lower sperm counts.


Zinc

We get zinc from foods like meat, cheese, oysters, and even maple syrup. Not enough zinc can cause problems like stunted growth, as discovered by a scientist named Ananda Prasad. He studied this in Egypt, where zinc is scarce in the soil. People there often grew poorly. Prasad found that adding zinc to their diets fixed the problem.

Low zinc in soil is a big issue for crops, especially grains like rice and wheat. This is a problem in places like Africa and India. Adding zinc to the soil helps farmers grow more food and gives people more zinc in their diet.

We've known about zinc for a long time. There's evidence of zinc being used in ancient ointments for wounds. A scientist named Andreas Marggraf officially identified zinc in the 1700s, although people had been making zinc for centuries before that.

Zinc is also used in medicines for skin problems like eczema and sunburn. It's even an ingredient in diaper rash cream!

Over 11 million tons of zinc are produced every year, mostly used to protect steel from rust and make alloys. But zinc isn't just useful, it's also beautiful! The zinc roofs in Paris create a unique silvery sheen that artists love.

EXERCISES

Exercise1:

a) Explain the general properties of alkali metals, such as reactivity, melting and boiling points, and electronic configuration.

b) Describe two important uses of alkali metals.

Exercise 2:

a) Explain the general properties of alkaline earth metals, such as reactivity, melting and boiling points, and electronic configuration.

b) Describe two important uses of alkaline earth metals.

Exercise 3:

1.Compare and contrast the physical and chemical properties of alkali metals and alkaline earth metals.

2. Explain why alkali metals are more reactive than alkaline earth metals.

3. Discuss the characteristic properties of transition metals, highlighting their differences from alkali and alkaline earth metals.

Exercise 4:

1. Write balanced chemical equations for the reactions of sodium and magnesium with water.

2. Explain the formation of ionic compounds by alkali and alkaline earth metals.

3. Describe the concept of variable oxidation states in transition metals and give examples.

Exercise 5:

1. Discuss the common uses of sodium and potassium compounds in everyday life.

2. Explain the role of magnesium and calcium in human health.

3. Describe the importance of transition metals in catalysis and industry.

Exercise 6:

a) Explain the general properties of transition metals, such as variable oxidation states, high melting and boiling points, and catalytic activity.

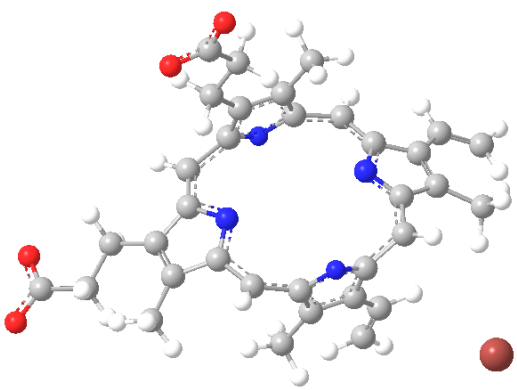
b) Describe two important uses of transition metals.

CHAPTER X

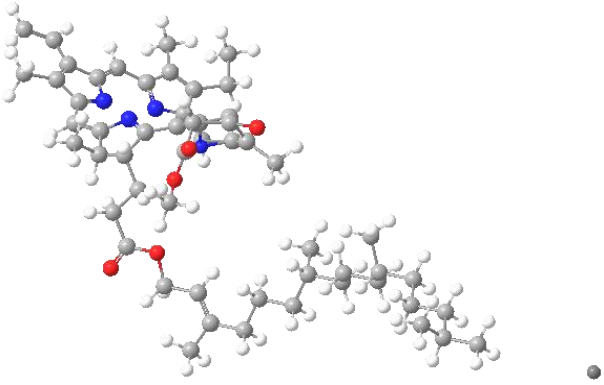
coordination compounds

An Introduction to coordination compounds

Coordination compounds, also known as metal complexes, are a class of chemical compounds that students are introduced to early in their chemistry coursework. These compounds consist of a central atom or ion, usually a metal, surrounded by several ions or molecules. The complex generally maintains its identity even in solution, although it may undergo partial dissociation. The complex can be a cation, an anion, or be non-ionic, depending on the sum of the charges of the central atom and the surrounding ions and molecules.



Hemoglobin



Chlorophyll

Coordination compounds play a crucial role in both chemical industry and life itself. The importance of metal complexes becomes evident when one considers that chlorophyll, essential for photosynthesis in plants, is a magnesium complex, and hemoglobin, which transports oxygen to animal cells, is an iron complex.

The nature and properties of metal complexes have been the subject of extensive research for many years, captivating some of the world's leading chemists. **Alfred Werner** was awarded an early Nobel Prize in 1913 for developing the fundamental concepts of coordination chemistry. In 1983, Henry Taube of Stanford University received the Nobel Prize in Chemistry for his pioneering work on the mechanisms of inorganic oxidation-reduction reactions.

Coordination compounds are extensively utilized in qualitative analysis for separating and positively identifying certain metal ions. For example, the addition of chloride ion to a solution containing silver ion results in the formation of a white precipitate of silver chloride, which then dissolves in an excess of aqueous ammonia. If an excess of nitric acid is subsequently added to this clear solution, the white precipitate forms again. This behavior is due to equilibria:

$$Ag^+ + Cl^- \leftrightarrow AgCl\downarrow \qquad (1)$$

$$AgCl + 2NH_3 \leftrightarrow [Ag(NH_3)_2]^+ + Cl^- \quad (2)$$

The white precipitate of AgCl forms, as described in reaction (1), because silver chloride is not soluble in water. However, the precipitate can dissolve in an excess of ammonia (NH_3) due to the formation of the stable complex ion $[Ag(NH_3)_2]^+$, as shown in reaction (2). When excess nitric acid (HNO_3) is added to the clear solution, equilibrium (2) shifts to the left, causing the white precipitate of AgCl to reappear. This is due to the lowering of the concentration of ammonia, as it reacts with the H+ ions from the nitric acid to form ammonium ($NH_4{}^+$) ions.

The formation of metal complexes is often accompanied by significant changes in color. One example is the use of aqueous solutions of cobalt (II) chloride ($CoCl_2$) as invisible ink. This ink appears essentially colorless, but when the paper on which it was applied is heated, the ink becomes a visible blue color. This blue color gradually fades as the paper absorbs moisture from the atmosphere. The phenomenon responsible for the appearance and disappearance of the color is represented by the equilibrium (3).

$$\underbrace{[Co(H_2O)_6]Cl_2}_{Pink} \leftrightarrow \underbrace{[CoCl_2(H_2O)_2]}_{Blue} + 4H_2O \quad (3)$$

The pink octahedral complex is almost colorless when in a dilute solution, making any writing done with it practically invisible. However, when heat is applied, the water is driven off, and a blue tetrahedral complex $CoCl_2(H_2O)_2$ is formed. This blue complex has a sufficiently intense color that the writing can easily be seen. Over time, as the paper absorbs moisture from the atmosphere, the original pink complex is regenerated, and the writing becomes invisible again.

These examples illustrate that coordination compounds are widely encountered and common. Until the early 20th century, the nature of these materials was not well understood, and they were referred to as "complex compounds." This term is still used, but it no longer carries the same connotation of complexity.

As a result of extensive research on such systems, our knowledge has increased significantly, and these compounds are no longer considered complicated. In fact, understanding the properties of complexes is necessary to obtain a comprehensive understanding of the chemistry of metals.

In a complex, the ligands are directly attached to the central metal atom or ion, forming the primary coordination sphere. The number of ligands is called ***the coordination number*** *of the central metal.*

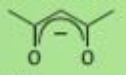
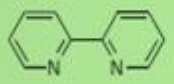
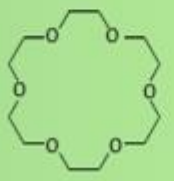
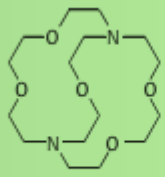
*Complexes can also form **outer-sphere associations**, where the ligands are not directly bound to the metal, but are instead electrostatically associated or weakly interacting.*

Many different molecules and ions can act as ligands, and a wide variety of metal ions can form complexes. Understanding the nature of these complexes, both inner-sphere and outer-sphere, is crucial for comprehending the chemistry of metals.

Ligands

Table X.1 lists the names and formulas of several common simple ligands, while Table X.2 provides the common prefixes used for ligands. Some ligands possess only a single donor pair of electrons, resulting in only one point of attachment to the metal; these are classified as monodentate ligands (from the Latin 'one-toothed'). Ligands with multiple points of attachment are classified as polydentate. Specifically, ligands with two points of attachment are called bidentate, those with three points are tridentate, and so forth.

Table X.2 Common simple ligands

Name	Formula	Abbreviation	Donor atoms	Number of donors
Acetylacetonato		$acac^-$	O	2
Ammine	NH_3		N	1
Aqua	H_2O		O	1
2,2-Bipyridine		bpy	N	2
Bromido	Br^-		Br	1
Carbanato	CO_3^{2-}		O	1 or 2
Carbonyl	CO		C	1
Chlorido	Cl^-		Cl	1
1,4,7,10,13,16-Hexaoxa-cyclooctadecane		18-crown-6	O	6
4,7,13,16,21-Pentaoxa-1, 10-diaza-bicyclo [8.8.5]tricosane		2.2.1 crypt	N, O	2N, 5O
Cyanido	CN^-		C	1

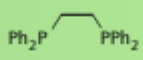
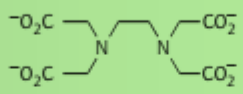
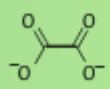
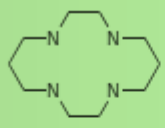
Diethylenetriamine	$NH(CH_2CH_2NH_2)_2$	dien	N	3
Bis(diphenylphosphino)ethane		dppe	P	2
Bis(diphenylphosphino)methane		dppm	P	2
Cyclopentadienyl	$C_5H_5^-$	Cp^-	C	5
Ethylenediamine (1,2-diaminoethane)	$NH_2CH_2CH_2NH_2$	en	N	2
Ethylenediaminetetraacetato		$edta^{4-}$	N, O	2N, 4O
Fluorido	F^-		F	1
Glycinato	$NH_2CH_2CO_2^-$	gly	N, O	1N, 1O
Hydrido	H^-		H	1
Hydroxido	OH^-		O	1
Iodido	I^-		I	1
Nitrato	NO_3^-		O	1 or 2
Nitrito—κO	NO_2^-		O	1
Nitrito—κN	NO_2^-		N	1
Oxido	O^{2-}		O	1
Oxalato		ox	O	2
Pyridine		py	N	1
Sulfido	S^{2-}		S	1
Tetraazacyclotetradecane		cyclam	N	4
Thiocyanato—κN	NCS^-		N	1
Thiocyanato—κS	SCN^-		S	1
Thiolato	RS^-		S	1
Triaminotriethylamine	$N(CH_2CH_2NH_2)_3$	tren	N	4
Tricyclohexylphosphine	$P(C_6H_{11})_3$	PCy_3	P	1
Trimethylphosphine	$P(CH_3)_3$	PMe_3	P	1
Triphenylphosphine	$P(C_6H_5)_3$	PPh_3	P	1

Table X.3 Common prefixes used for ligands

Prefix	Meaning	Prefix	Meaning
mono-	1	hepta-	7
di-, bis-	2	octa-	8
tri-,tris-	3	nona-	9
tetra-, tetrakis-	4	deca-	10
penta-	5	undeca-	11
hexa-	6	dodeca-	12

Naming Coordination Compounds

Traditionally, coordination compounds were named after their discoverers or their color. However, with the vast number of these compounds, a more systematic approach was needed. This section outlines the modern naming rules for coordination compounds.

Here's a breakdown of the key points:

1. **Cation First, Anion Second:** Just like any ionic compound, the name starts with the cation (positive ion) followed by the anion (negative ion). Both can be complex ions.
2. **Ligands by Alphabet:** Within a complex ion, list the ligands alphabetically. Prefixes indicating the number of ligands (di, tri, etc.) don't affect the order. For example, "trichloro" comes after "chloro" even though it means "three chlorides."
    - Anions as ligands end in "-o" (e.g., chloro for Cl^-, cyano for CN^-).
    - Neutral ligands use their normal names (e.g., ethylenediamine) with some exceptions like aqua (H_2O) and ammine (NH_3). See a reference table for common ligand names.
    - Cations as ligands end in "-ium" (e.g., hydrazinium for $NH_2NH_3^+$).
3. **Number Prefixes:** Indicate the number of each ligand type with prefixes like di- (two), tri- (three), etc., for simple ligands (Cl^-, Br^-, etc.). For ligands with built-in prefixes (e.g., ethylenediamine), use bis- (two), tris- (three), etc.
4. **Metal and Oxidation State:** After listing the ligands, name the metal followed by its oxidation state in Roman numerals (e.g., Co(III)).
5. **Metal Anions End in "-ate":** If the complex ion is an anion (negative), the metal name ends in "-ate" (e.g., cobalt(III) sulfate).

These are the core rules for naming most coordination compounds. The passage provides additional details and examples for further clarification.

Additional Considerations for Complex Ligands:

Ligand Bonding Modes: Some ligands can attach to metals in multiple ways, through different atoms. To avoid confusion, the bonding mode is indicated by a letter after the ligand name. For example, thiocyanate (SCN^-) can bind through nitrogen or sulfur. These are distinguished as "thiocyanato-N-" and "thiocyanato-S-" in the name. Sometimes, "(N-thiocyanato)" is used for clarity.

Bridging Ligands: Certain ligands can connect two metal ions simultaneously. These "bridging ligands" are indicated by "m-" before the ligand name. For instance, $[(NH_3)_3Pt(SCN)Pt(NH_3)_3]Cl_3$ is named as "hexammine-m-thiocyanatodiplatinum(II) chloride".

An Overview of Bonding Theories of Transition Metal Compounds

Chemists have struggled for a long time to explain how transition metals bond with other atoms. These bonds create colorful compounds, interesting shapes, and magnetic properties.

There have been a few different ideas about how this bonding works.

- **Lewis acid-base theory:** This theory treats the metal ion like an electron acceptor and the surrounding atoms (ligands) like electron donors. It can predict the structure of some compounds, but it doesn't explain color or magnetism.
- **Valence bond theory:** This theory suggests metals bond similarly to other elements by sharing electrons. It explains some shapes, but not color or unpaired electrons.
- **Crystal field theory:** This theory assumes the bonding is purely electrostatic. It's been very successful at explaining the properties of these compounds and will be a major focus in our study. However, we know there's also some covalent character to the bonding.
- **Ligand field theory:** This is an improved version of crystal field theory that considers some covalent character in the bonding.
- **Molecular orbital theory:** This is the most complex theory and considers the electrons to be completely shared between the metal and ligands. It's not necessary for understanding most transition metal compounds.

The text suggests crystal field theory is a good starting point for understanding bonding in transition metals, with ligand field theory providing a more nuanced view.

Magnetic susceptibility

Before beginning the discussion of bonding in complexes, their magnetic properties will be considered because the magnetic character of a complex tells us about how the electrons are distributed in the partially filled d orbitals. The essential measurement to determine the magnetism of a complex involves determining the attraction of the sample to a magnetic field.

The magnetic moment is related to the molar magnetic susceptibility by the equation:

$$\mu = \frac{3k}{N_0}\chi_M T$$

where k is Boltzmann's constant, N_0 is Avogadro's number, and T is the absolute temperature.

For a single unpaired electron, the magnetic moment due to its spin is $\mu_s = 1.73$ Bohr magneton (BM). The orbital motion may also contribute to the magnetic moment, and for a single electron the total magnetic moment is represented in terms of both the spin and orbital contributions by the equation

$$\mu_{s+l} = \sqrt{4s(s+1) + l(l+1)}$$

where s is the spin of one electron and l is the angular momentum quantum number for the electron. For several unpaired electrons having parallel spins:

$$\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$$

For many complexes of first row metal ions, the contribution is so small that it is ignored and the spin only magnetic moment is used. However, the sum of the spins, S, is related to the number of unpaired electrons, n, by $S = n/2$. Thus, the spin only magnetic moment can be written as:

$$\mu_s = \sqrt{n(n+2)}$$

Valence-Bond Theory

In a previous chapter, we discussed valence-bond theory (VBT) and orbital hybridization in the context of main group elements. This theory can also explain some bonding aspects in transition metal complexes. According to VBT, the interaction between a metal ion and its ligands is considered a Lewis acid-base interaction, where the ligand's electron pairs occupy the metal ion's empty higher orbitals. For instance, in the tetrahedral tetrachloridonickelate (II) ion, $[NiCl_4]^{2-}$, the free nickel (II) ion has an electron configuration of [Ar]3d^8 with two unpaired electrons. The 4s and 4p orbitals of nickel hybridize to form four sp^3 hybrid orbitals, each occupied by an electron pair from a chloride ion (the Lewis bases).

This explanation accounts for the two unpaired electrons in the complex ion and the expected tetrahedral shape for sp^3 hybridization. However, constructing the VBT orbital diagram requires prior determination of the crystal structure and magnetic measurements to ascertain the shape and number of unpaired electrons. Ideally, a theory should be predictive, but VBT is not. For example, VBT cannot

predict or explain why the hexaaquairon (II) ion, $[Fe(OH_2)_6]^{2+}$, has four unpaired electrons while the hexacyanidoferrate (II) ion, $[Fe(CN)_6]^{4-}$, has none.

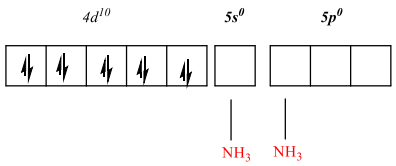
VBT also has conceptual flaws. It doesn't explain why electron pairs occupy higher orbitals when there are vacancies in the 3d orbitals. For some Period 4 transition metal complexes, ligand electron pairs are assigned to 4d, 4s, and 4p orbitals, despite available space in the 3d orbitals.

Table X.3 Important Hybrid Orbital Types in Complexes

Atomic Orbitals	Hybrid Type	Number of Orbitals	Orientation
s, p_x	sp	*2*	*Linear*
s, p_x, p_y	sp^2	*3*	*Trigonal planar*
s, p_x, p_y, p_Z	sp^3	*4*	*Tetrahedral*
d_{z^2}, s, p_x, p_y	dsp^2	*4*	*Square planar*
$d_{z^2}, s, p_x, p_y, p_Z$	dsp^3	*5*	*Trigonal bipyramid*
$d_{x^2-y^2}, d_{z^2}, s, p_x, p_y, p_Z$	d^2sp^3	*6*	*Octahedral*
$s, p_x, p_y, p_Z, d_{x^2-y^2}, d_{z^2}$	sp^3d^2	*6*	*Octahedral*

WORKED EXAMPLES

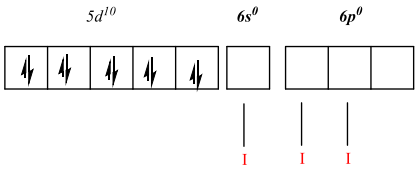
❖ $[Ag(NH_3)_2]^{1+}$

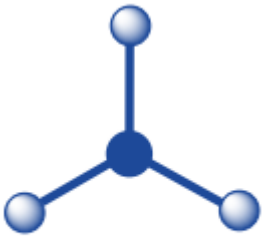
1. **Oxidation State:** $x + (2 * 0) = 1 \Longrightarrow x = 1$
2. $_{47}Ag[_{36}Kr]\ 5s^1 4d^{10}$
3. $_{47}Ag^+[_{36}Kr]\ 5s^0 4d^{10}$
4. 

5. **hybridization:** sp (linear)
6. **Magnetic properties:** Diamagnetic
7. **Magnetic moment:**

$\mu_s = \sqrt{0(0+2)} = 0\ MB$



1. $[HgI_3]^{1-}$ **(The f orbital is not considered)**
2. **Oxidation State:** $x + (-1 * 3) = -1 \Longrightarrow x = +2$
3. $^{\square}_{80}Hg[^{\square}_{54}Xe]\ 6s^2 4f^{14} 5d^{10}$
4. $^{\square}_{80}Hg^{2+}[^{\square}_{54}Xe]\ 6s^0 4f^{14} 5d^{10}$
5. 

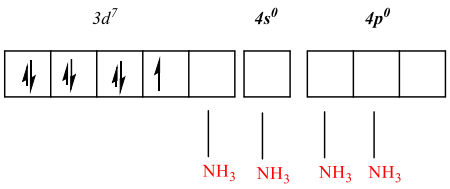


three-coordination
trigonal planar

6. **hybridization:** sp^2 (Trigonal planar)
7. **Magnetic properties:** Diamagnetic
8. **Magnetic moment:**

$\mu_s = \sqrt{0(0+2)} = 0\ MB$

❖ $[Co(NH_3)_4]^{2+}$ **(Strong field ligand)**

1. **Oxidation State:** $x + (4 * 0) = 2 \Longrightarrow x = 2$
2. $^{\square}_{27}Co[^{\square}_{18}Ar]\ 4s^2 4d^7$
3. $^{\square}_{27}Co[^{\square}_{18}Ar]\ 4s^0 4d^7$
4. 



square planar

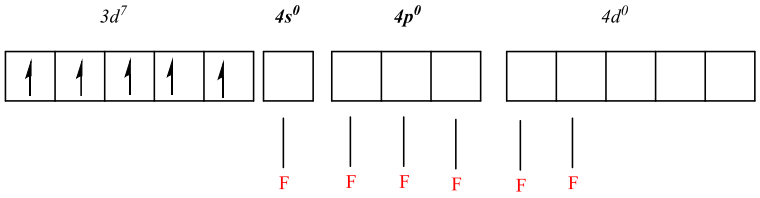
5. **hybridization:** dsp^2 (Square planar)
6. **Magnetic properties:** Paramagnetic
7. **Magnetic moment:**

$\mu_s = \sqrt{1(1+2)} = 1.73\ MB$

❖ $[FeF_6]^{3-}$

1. **Oxidation State:** $x + (-1 * 6) = -3 \Longrightarrow x = 3$
2. $^{\square}_{26}Fe[^{\square}_{18}Ar]\ 4s^2 4d^6$
3. $^{\square}_{26}Fe^{3+}[^{\square}_{18}Ar]\ 4s^0 4d^5$

4.



5. **hybridization:** sp^3d^2 (Octahedral)
6. **Magnetic properties:** Paramagnetic
7. **Magnetic moment:**

$\mu_s = \sqrt{5(5+2)} = 5.91\ MB$



❖ ***TO NOTE:***

1. If a ligand contains an N atom or CO (carbonyl), it is a strong field ligand.

2. If there are two ligands, one being a strong field ligand and the other a weak field ligand, we consider the combination as having strong field ligands.

3.

Table X.4 Commonly known ligands are classified as strong or weak field ligands.

Strong Field Ligands :	**Weak Field Ligands :**
Cyanide (CN^-)	Iodide (I^-)
Carbonyl (CO)	Bromide (Br^-)
Phosphines (PR_3)	Chloride (Cl^-)
Nitro (NO_2^-)	Fluoride (F^-)
Ethylenediamine (en)	Hydroxide (OH^-)
Ammonia (NH_3)	Water (H_2O)

Crystal Field Theory

Crystal field theory assumes that the transition metal ion is in a free, gaseous state, and that the ligands behave as point charges with no interactions between the metal d-orbitals and the ligand orbitals. The theory also relies on the probability model of the d-orbitals, which shows that there are two d-orbitals ($d_{x^2-y^2}$ and d_{z^2}) oriented along the Cartesian axes, and three d-orbitals ($d_{xy}, d_{xz}, and\ d_{yz}$) oriented between the Cartesian axes.

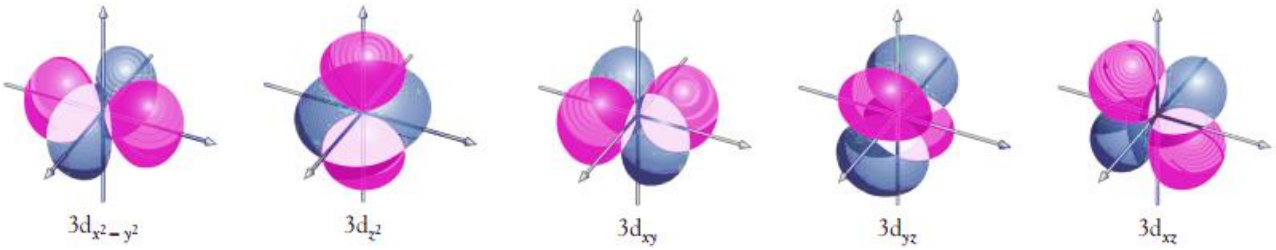


Figure X.3 Representations of the shapes of the 3d orbitals

The process of complex formation can be described in three steps:

1. When the ligand electrons initially approach the metal ion, they form a spherical shell around it. This causes repulsion between the ligand electrons and the metal ion electrons, resulting in an increase in the energy of the metal ion's d-orbitals.
2. The ligand electrons then rearrange to be distributed in pairs along the actual bonding directions (such as octahedral or tetrahedral). This means the mean energy of the metal d-orbitals stays the same, but the orbitals oriented along the bonding directions increase in energy, while those between the bonding directions decrease in energy. This loss of d-orbital degeneracy is the focus of the crystal field theory discussion.
3. Up to this point, complex formation would not be favored, because there has been a net increase in energy as a result of the ligand electron–metal electron repulsion (step 1). Furthermore, the decrease in the number of free species means that complex formation will generally result in a decrease in entropy. However, there will be an attraction between the ligand electrons and the positively charged metal ion that will result in a net decrease in energy. It is this third step that provides the driving force for complex formation.

These three hypothetical steps are summarized in Figure X.2.

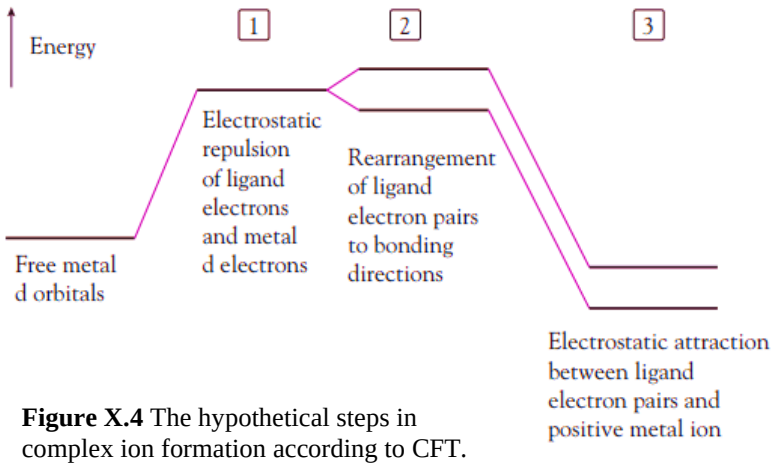


Figure X.4 The hypothetical steps in complex ion formation according to CFT.

Octahedral Complexes

While the final step provides the energy needed for the complex to form, it's actually the second step that matters most for explaining color and magnetism in these compounds.

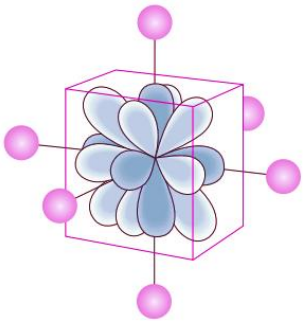


Figure X.5 The orientation of six ligands with respect to the metal d orbitals.

The second step is where the d orbitals lose their degeneracy (become unequal in energy). This is especially important for octahedral complexes, where the ligands are positioned along the x, y, and z axes. (Figure X.3)

As a result of the negative charges of the ligands along the Cartesian axes, the energies of the d-orbitals aligned along these axes ($d_{x^2-y^2}$ and d_{z^2}) are higher than the energies of the d-orbitals oriented between the axes ($d_{xy}, d_{xz}, and\ d_{yz}$). This splitting of the d-orbitals into two sets is represented in Figure 19.18. The energy difference between the two sets of d-orbitals in an octahedral field is given the symbol Δ_{oct}.

The sum of the orbital energies equals the degenerate energy (sometimes called the baricenter). Therefore, the energy of the two higher-energy orbitals ($d_{x^2-y^2}$ and d_{z^2})is $3/5\Delta_{oct}$, and the energy of the three lower-energy orbitals ($d_{xy}, d_{xz}, and\ d_{yz}$) is $2/5\Delta_{oct}$ below the mean.

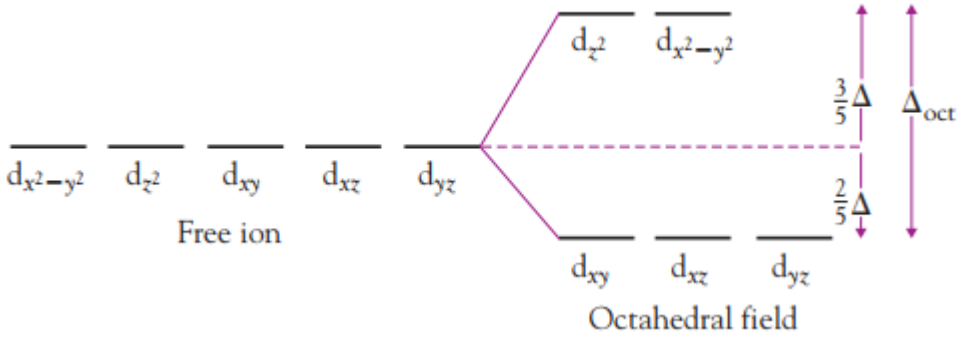


Figure X.6 The splitting of the d-orbital energies that occurs when the metal ion is surrounded by an octahedral array of ligands

When we look at the energy diagrams for different d-electron configurations, we see that for d^1, d^2, and d^3 configurations, the electrons will all fit into the lower-energy set of orbitals. This net energy decrease is known as the crystal field stabilization energy (CFSE). The CFSE for the d^3 configuration is $3(2/5\Delta_{oct})$ or $-1.2\Delta_{oct}$.

For the d^4 configuration, there are two possibilities: the fourth d-electron can either pair up with an electron in the lower-energy level, or it can occupy the upper-energy level, depending on which

situation is more energetically favorable. If the octahedral crystal field splitting, Δ_{oct}, is smaller than the pairing energy, then the fourth electron will occupy the higher orbital. If the pairing energy is less than the crystal field splitting, then it is energetically preferred for the fourth electron to occupy the lower orbital. The two situations are shown in Figure X.5. The result having the greater number of unpaired electrons is called the **high-spin** (or **weak field**) situation, and that having the lesser number of unpaired electrons is called the **low-spin** (or **strong field**) situation.

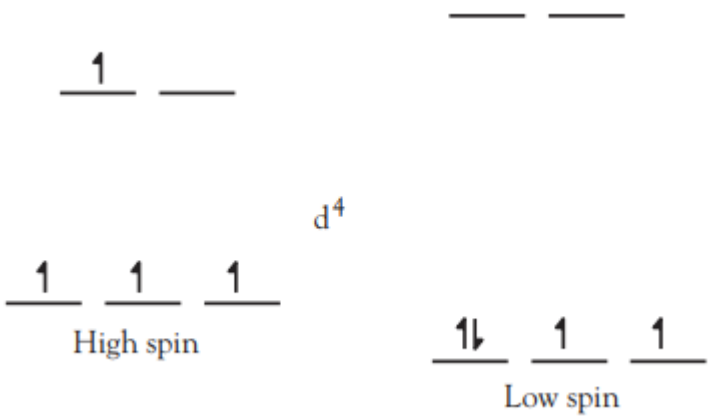


Figure X.7 The two possible spin situations for the d4 configuration.

Tetrahedral Complexes

The next most common arrangement of ligands is tetrahedral, with four ligands around the metal ion (like a pyramid). Here, the $d_{xy}, d_{xz}, and\ d_{yz}$ orbitals point more towards the ligands than the $d_{x^2-y^2}$ and d_{z^2} orbitals. Because of this, the $d_{x^2-y^2}$ and d_{z^2} orbitals have lower energy, flipping the energy order compared to octahedral complexes (imagine the energy level diagram upside down).

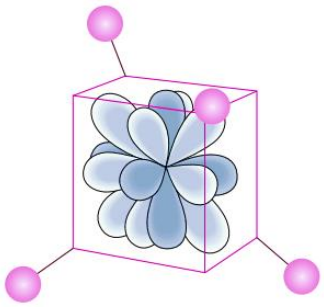


Figure X.8 The orientation of four ligands with respect to the metal d orbitals.

(Figure X.7)

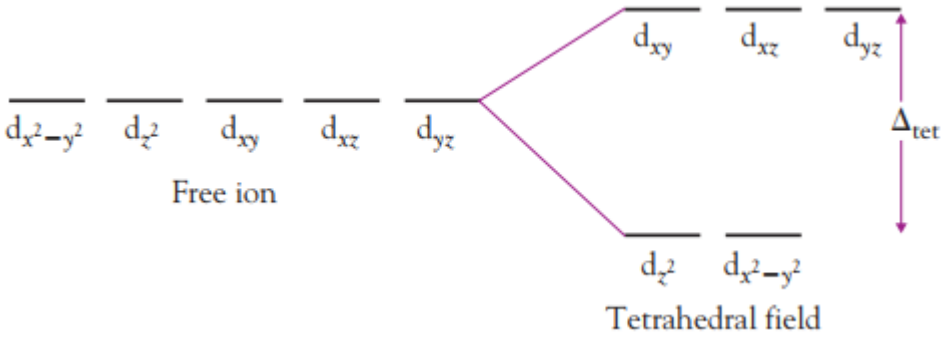


Figure X.9 The splitting of the d-orbital energies that occurs when the metal ion is surrounded by a tetrahedral array of ligands.

Since there are only four ligands and they're not perfectly aligned, the energy difference between the orbitals is much smaller in tetrahedral complexes compared to octahedral ones (about four-ninths the difference). This smaller splitting means ***most tetrahedral complexes have all their electrons unpaired (high spin).***

Tetrahedral geometry is common for compounds with four halide ions (like chlorine) around the metal, such as the tetrachloridocobaltate (II) ion ($[CoCl_4]^{2-}$), and for compounds with four oxygen atoms, like the molybdate ion ($[MoO_4]^{2-}$).

Colors of Transition Metal Complexes

Visible Light and Color Perception:

Transition metal complexes exhibit a vast range of colors due to their ability to absorb specific wavelengths of visible light. Visible light is a portion of the electromagnetic spectrum that our eyes can detect and perceive as different colors. White light is a combination of all visible wavelengths. When a complex absorbs certain wavelengths, the remaining colors are transmitted and combine to create the perceived color.

Example: Hexaaquatitanium(III) Ion ($[Ti(OH_2)_6]^{3+}$)

This complex appears purple because it absorbs light in the green region of the spectrum. The remaining blue and red light pass through and combine to create the perceived purple color.

Electron Energy Levels and Crystal Field Theory:

Light absorption is linked to the energy levels of the metal's d-orbitals. Crystal field theory explains how the arrangement of ligands in a complex (octahedral in this case, with six water molecules) influences these energy levels. The interaction between the metal's d-electrons and the ligands' electrons causes the d-orbitals to split into higher and lower energy levels.

Electron Transitions and Light Absorption:

When light strikes the complex with sufficient energy, it can excite an electron from a lower energy d-orbital to a higher energy d-orbital. This process is called an electronic transition.

The energy of the absorbed light matches the specific energy difference between the initial and final d-orbital levels of the electron.

After the electron is excited, it eventually drops back down to its original lower energy level. This transition releases the absorbed energy, but typically not as light (photons) but rather as heat (vibrations within the molecule).

Broadening of Absorption Bands:

The absorption bands observed in the visible spectrum are often broad due to vibrations within the molecule. These vibrations can slightly alter the energy levels of the d-orbitals, leading to a range of possible energy differences for the electron transition. This range of energies broadens the observed absorption band, making the color appear less sharp.

Lowering the temperature of the complex reduces these vibrations, leading to sharper absorption bands in the spectrum.

Crystal Field Splitting Strength and Color:

The strength of the crystal field splitting, which is the energy difference between the higher and lower energy d-orbitals, also affects the color of the complex.

Weaker crystal field splitting (caused by weaker field ligands like chloride ions) results in smaller energy differences between the d-orbitals. To be excited, the electron requires light with lower energy (longer wavelength) which corresponds to the red end of the visible spectrum. This is why the hexachloridotitanate(III) ion ($[TiCl_6]^{3-}$) appears orange, as it absorbs blue and green light (higher energy) and transmits the remaining red and orange light.

Units of Energy Difference:

Chemists often use wave numbers (cm^{-1}) instead of kilojoules per mole ($kJ\ mol^{-1}$) to express the energy difference between d-orbital levels. The passage provides an example where 230 $kJ\ mol^{-1}$ is equivalent to 19,200 cm^{-1}. Wave numbers are simply the reciprocal of the wavelength expressed in centimeters.

EXERCISES

Exercise 1:

1.1 Write the IUPAC names for the following coordination compounds:

$[Co(NH_3)_6]Cl_3$

$K_3[Fe(CN)_6]$

$[Pt(NH_3)_2Cl_2]$

1.2 Draw the geometrical isomers of

$[Co(NH_3)_4Cl_2]^+$.

1.3 Determine the oxidation state of the central metal ion in the following complexes:

$[Cr(H_2O)_6]Cl_3$

$K_4[Fe(CN)_6]$

Exercise 2:

Provide the systematic names for the following coordination compounds:

$[Co(NH_3)_6]Cl_3$

$[Cr(H_2O)_4Cl_2]Cl$

$[Pt(en)_2Cl_2]Cl$

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