DIRECTORATE OF DISTANCE & CONTINUING EDUCATIONS

MANONMANIAM SUNDARANAR UNIVERSITY

TIRUNELVELI – 627012

OPEN AND DISTANCE LEARING(ODL) PROGRAMMES

(FOR THOSE WHO JOINED THE PROGRMMES FROM THE ACADEMIC YEAR 2023 – 2024)

B.Sc. CHEMISTRY
COURSE MATERIALS
CORE – V – GENERAL CHEMISTRY - III

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UNIT I

Gaseous state

Kinetic molecular model of a gas: postulates and derivation from the kinetic gas equation; The Maxwell –Boltzmann distribution of speed of molecules average, root mean square and most probable velocity and average kinetic energy, law of equipartition of energy, degrees of freedom and molecular basis of heat capacities. Collision frequency; collision diameter; mean free path and viscosity of gases.

Real gases: Deviations from ideal gas behaviour, (Andrew's and Amagat's plots); compressibility factor, Z, and its variation with pressure for different gases. equations of states for real gases-van der Waal's equation; Virial equation; Boyle temperature; Numerical problems based on equations of states

for real gases, isotherms of real gases – critical phenomena – isotherms of CO_2 - continuity of state–Van der waal's equation and the critical state; law of corresponding states-liquefaction of gases; numerical problems involving the core concepts.

Unit-II

Liquid and Solid State

Properties of Liquids- Surface tension, viscosity and their applications. Crystalline and amorphous – differences - geometry, isotropy and anisotropy, melting point; isomorphism, polymorphism. Crystals–size and shape; laws of crystallography; symmetry elements– plane, centre and axis; Miller indices, unit cells and space lattices; classification of crystal systems; Bravais lattices; X – ray diffraction – Bragg's equation Packing in atomic solids – simple cubic, body centered cubic, face centered and hexagonal close packing; Co-ordination number in typical structures - NaCl, CsCl, ZnS, TiO_2; comparison of structure and properties of diamond and graphite; numerical problems involving core concepts Defects in solids - stoichiometric and nonstoichiometric defects. Liquid crystals – classification and applications.

UNIT-III

Nuclear Chemistry

Natural radioactivity - α, β and y rays; half-life period; Fajan–Soddy group displacement law; Geiger–Nattal rule; isotopes, isobars, isotones, mirror nuclei, iso diaphers; nuclear isomerism; radioactive decay series; magic numbers; units – Curie, Rutherford, Roentgen; nuclear stability - neutronproton ratio; binding energy; packing fraction; mass defect. Simple calculations involving mass defect and B.E., decay constant and $t_{1/2}$ and radioactive series.

Isotopes – uses – tracers – determination of age of rocks by radiocarbon dating. (Problems to be worked out) Nuclear energy; nuclear fission and fusion – major nuclear reactors in India; radiation hazards, disposal of radioactive waste and safety measures.

UNIT-IV

Halogen derivatives

Aliphatic halogen derivatives Nomenclature and classes of alkyl halides – isomerism, physical properties, Chemical reactions. Nucleophilic substitution reactions – SN1, SN2 and SNi mechanisms with stereochemical aspects and effect of solvent.

Di, Tri & Tetra Halogen derivatives: Nomenclature, classification, preparation, properties and applications.

Aromatic halogen compounds Nomenclature, preparation, properties and uses Mechanism of nucleophilic aromatic substitution – benzyne intermediate.

Aryl alkyl halides Nomenclature, benzyl chloride – preparation – preparation properties and uses Alcohols: Nomenclature, classification, preparation, properties, use; conversions – ascent and descent of series; test for hydroxyl groups. Oxidation of diols by periodic acid and lead tetraacetate

UNIT-V

Phenols

Nomenclature; classification, Preparation from diazonium salts, cumene, Dow’s process, Reaching process; properties – acidic character and effect of substitution on acidity. Reactions – Fries, Claisen rearrangement, Electrophilic substitution reactions, Reimer - Teimen, Kolbe, Schmidt, Gatermann

synthesis, Libermann, nitro reaction, phthalein reaction.

Resorcinol, quinol, picric acid – preparation, properties and uses.

Aromatic alcohols Nomenclature, benzyl alcohol – methods of preparation – hydrolysis, reduction of benzaldehyde, Cannizzaro reaction, Grignard synthesis, physical properties, reactions – reaction with sodium, phosphorus pentachloride, thionyl chloride, acetic anhydride, hydrogen iodide, oxidation – substitution on the benzene nucleus, uses.

Thiols: Nomenclature, structure, preparation, and properties

Recommended Text

B.R. Puri, L.R. Sharma, M.S. Pathania; Principles of Physical Chemistry, 46th edition, Vishal Publishing, 2020.

B.R. Puri, L.R. Sharma and K.C. Kalia, Principles of Inorganic Chemistry, Milestone Publishers and Distributors, New Delhi, thirtieth edition, 2009.

P.L. Soni and Mohan Katyal, Textbook of Inorganic Chemistry, Sultan Chand & amp; Sons, twentieth edition, 2006.

M. K. Jain, S. C. Sharma, Modern Organic Chemistry, Vishal Publishing, fourth reprint, 2003.

S.M. Mukherji, and S.P. Singh, Reaction Mechanism in Organic Chemistry, Macmillan India Ltd., third edition, 1994.

Reference Books

T. W. Graham Solomons, Organic Chemistry, John Wiley & Sons, fifth edition, 1992.

A. Carey Francis, Organic Chemistry, Tata McGraw-Hill Education Pvt., Ltd.,New Delhi, seventh edition, 2009.

I. L. Finar, Organic Chemistry, Wesley Longman Ltd, England, sixth edition, 1996.

P. L. Soni, and H. M.Chawla - Text Book of Organic Chemistry, New Delhi, Sultan Chand & Sons, twenty ninth edition, 2007.

J.D. Lee, Concise Inorganic Chemistry, Blackwell Science, fifth edition, 2005.

MOOC components

https://nptel.ac.in/courses/104104101 Solid state chemistry

https://nptel.ac.in/courses/103106071 Nuclear industries and safety

https://nptel.ac.in/courses/104106119s Introduction to organic chemistry

UNIT-1

GASEOUS STATE

Kinetic Molecular Model of Gas:

Postulates And Derivation for Kinetic Gas Equation

The kinetic molecular model of a gas a theoretical framework that describes the behaviour of gas as based on the motion of their particles.it is fundamental concept in physics and chemistry that explains the properties and behaviour of gases.

The kinetic molecular model provided a simple and effective way to understand gas behaviour, making it a fundamental tool in physics, chemistry, engineering. It has numerous applications is fields like: chemical, engineering, aerospace, materials science, biology.

Kinetic Molecular Model of Gas:

1. The kinetic molecular theory of gases provides a reasonable explanation of the behaviour of gases. the macroscopic properties from the action of the individual molecules comprising the gas.
2. Gases are made up of small atoms or molecules that are in constant, random motion.
3. The distance of separation among these atoms or molecules. In other words, a gas is mostly empty space.
4. All of the atoms and molecules behave independently. No attractive or repulsive forces exist between atoms or molecules in a gas.
5. Atoms and molecules collide with each other and with the walls of the container without losing energy. The energy is transferred from one atom or molecule to another.
6. The average kinetic energy of the atoms or molecules increases or decreases in proportion to the absolute temperature.

Derivation of Gas Law from Kinetic Gas Equation:

Boyle’s Law: Relationship of Pressure and Volume;

The Irish scientist, Robert boyle, found that the volume of a gas varies inversely with the pressure exerted by the gas if the number of moles and temperature of gas are held constant. this relationship is known as boyle’s law.

Mathematically, the product of pressure (p) and volume(v) is a constant:

$$PV=K1$$

Boyle’s law is often used to calculate the volume resulting from a pressure change or vice versa. We consider.

$$PV_i=K_i$$

the final condition, because pv, initial or final, is constant and is equal to Ki,

$$P_iV_i=PfVf$$

Charles’s Law: Relationship of Temperature and Volume

Jacques Charles, a French scientist, studied the relationship between gas volume and temperature. This relationship, charles’s law, states that the volume of a gas varies directly with the absolute temperature (k) if the pressure and number of moles of gas are constant.

Mathematically, the ratio of volume (v) and temperature (T) is a constant: $V/T=K2$

In a way analogous to boyle’s law, we may establish a set of initial conditions, $Vi/Ti=K2$

and final conditions

$$Vf/TF=K2$$

Because K2 is a constant, we may equate them resulting in $Vi/Ti=VF/TF$

Consider a gas occupying a volume of 10.0L at 273 K. the ratio V/T is a constant, doubling the temperature, to 546K, increases the volume to 20.0L as shown here.

$$10.0L/273K=V1/546K$$

Tripling the temperature, to 819K, increases the volume by a factor of 3: $10.0L/273K=VF/819K$

$$V1=30.0L$$

Combined Gas Law:

Boyle’s law describes the inverse proportional relationship between volume and pressure; charles’s law shows the direct proportional relationship between volume and temperature. Often, a sample of gas (a fixed number of moles of gas). Undergoes change involving volume, pressure, and temperature simultaneously. It would be useful to have none equation that describes such processes. The combined gas law is such an equation. It is derived from boyle’s law and charles’s law and takes the form:

$$PiVi/Ti=PfVf/Tf$$

Avogadro’s Law: Relationship of Number of Moles and Volume;

The relationship between the volume and number of moles of a gas at constant temperatures and pressures is known as Avogadro’s law. It states that equal volumes of any ideal gas contain the same number of moles if measured under the same condition of temperature and pressure.

Mathematically, the ratio of volume (V) to number of moles (n) is a constant: $v/n=k3$ consider 1 mol of gas occupying a volume of 10.0L; using logic similar to the application of boyle’s and charles’s laws, 2 mol of the gas would occupy 20.0L ,3 mol would occupy 30.0L, and so forth. As we have done with the previous laws, we can formulate a useful expression relating initial and final conditions.

$$Vi/ni=Vf/nf$$

$$(3.0\ \text{atm})\ (Vx)=\ (10.0\text{L})\ (1.00\ \text{atm})\ Vx=3.3\text{L}$$

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Maxwell-Boltzmann Distribution of Speed

The Maxwell - Boltzmann law states that:

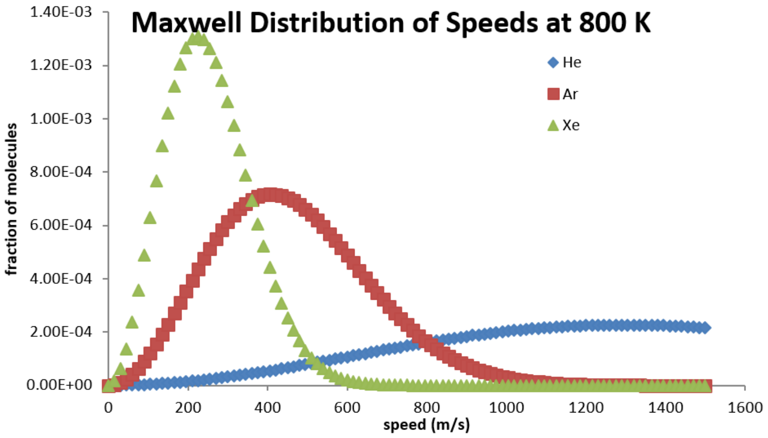
“The distribution of speeds among molecules in a gas is proportional to the square root of the temperature, and is given by the equation

$$f(c) = 4\pi c^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{\frac{-mc^2}{2k_B T}}$$

Where:

- f(v) is the probability density function
- m is the mass of a molecule
- k is the Boltzmann constant
- T is the temperature in Kelvin
- Vis the speed of the molecule

This law describes the statistical distributions of molecular speeds in a gas, and is a fundamental concept in kinetic theory and statistical mechanics.”



Maxwell Distribution of speeds at 800 K for different gasses of differing molecular masses

Velocity Distribution in One Direction*:*

The energy of a molecule of mass *m* moving with velocity v_X is $mv^2{}_X/2$, and so the Boltzmann distribution indicates the probability density $f(v_X)$ that a molecule has velocity v_X is given by

$$F(v_X) = \text{const } e^{-mv2}{}_X/2kT$$

The value of the integration constant can be determined by integrating from ∞ to -∞:

$$\int_{-\infty}^{\infty} f(v_x)dv_x = 1 = const \int_{-\infty}^{\infty} e^{-\frac{mv2_x}{2kT}}\, d\,v\,x$$

So that the **Maxwell-Boltzmann distribution** of molecular velocities is given by

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-mv^2}{2k_B T}\right)$$

The most probable velocity in the x direction is zero because of the form. This can be integrating the velocity in the x direction times its probability over all values of v_X

$$\frac{df(v)}{dv} = 0$$

TYPES OF AVERAGE SPEEDS:

Since there is a distribution of molecular speeds, there are different measures of the average speed. We will discuss the most probable speed $\boldsymbol{v_{mp}}$, the mean speed $\langle \boldsymbol{v} \rangle$, and the root- mean-square speed $\langle \boldsymbol{v^2}^{\mathbf{1/2}} \rangle$.

The most probable speed v_{mp} is the speed at the maximum of F(v). Setting dF/dv equal to zero, we find

$$v_{mp} = \left(\frac{2kT}{m}\right)^{1/2} = \left(\frac{2RT}{M}\right)^{1/2}$$

The **mean speed** $\langle \boldsymbol{v} \rangle$ is calculated as the average of v using the probability distribution F(v):

$$\langle v \rangle = \int_0^\infty vF(v)dv$$

Substituting *equation and performing* the *integration*

$$\langle v \rangle = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty exp-(mv^2/\mathrm{kT})v^3\mathrm{dv}$$

$$\langle v \rangle = (8kT/\pi m)^{1/2} = (8RT/\pi M)^{1/2}$$

The last speed we consider is the **root-mean-square speed,** which is defined as the square root

$\langle v^2 \rangle$:

$$\langle {v^2}^{1/2} \rangle = \left[\int_0^\infty v^2F(v)dv\right]^{1/2}$$

$$\langle {v^2}^{1/2} \rangle = \left(\frac{3kT}{m}\right)^{1/2} = \left(\frac{3kT}{M}\right)^{1/2}$$

From these three calculations, we can see that at any temperature,

$$\langle v^{2^{1/2}} \rangle > \langle v \rangle > v_{mp}$$

Law of equipartition of Energy

According of the law of equipartition of energy, “the total energy of a molecule is equally divided among the different degrees of freedom”.

Each degree of freedom contributes 1/2KT Per molecule or 1/2RT per mole.

The total energy of a molecule is the sum of its translation or (kinetic energy), rotational and vibrational energies.

Translational Energy of Kinetic Energy (K.E.):

It is due to the motion of a molecule in straight line. A molecule moving in space requires x, y, z coordinates to, specify it’s position.

Therefore, the number of degrees of freedom is three. Each degree of freedom contributes energy equal to 1/2RT.

Therefore, Total KE=3×1/2RT=3/2RT per mole.

Rotational energy(R.E.):

This is due to the rotatory motion of a molecule. A diatomic molecule has 2 rotational degrees of freedom.

Therefore, Total R.E = 2×1/2RT=RT Per mole

For polyatomic molecules, there are 3 rotational degrees of freedom.

Therefore, Total R.E=3×1/2RT=3/2RT per mole

Vibrational Energy (V.E.)

It is due to the vibratory motion of a molecule. This is partly kinetic and partly potential.

A diatomic molecule has 2 vibrational degrees of freedom. Therefore, Total V.E=2×1/2RT

=RT Per mole.

According to law of equipartition of energy, the total energy of polyatomic molecule is as follow.

For a non-linear poly atomic molecule, $E=[3+3+(3N-6)\times2]\times1/2RT$ For a linear poly atomic molecule, $E=[3+2+(3N-5)\times2]\times1/2RT$

Degrees of Freedom:

The Degrees of freedom of a molecule is defined as the number of coordinates to describe its position in space. There are three types of degrees freedom.

1. Translational degrees of freedom
2. Rotational degrees of freedom.
3. Vibration degrees of freedom.

Translational Degrees of Freedom:

Translational degree of freedom is the ability of a particle or molecule to move freely in space along the X, Y, and Z axes of a Cartesian coordinate system.

Rotational Degrees of Freedom:

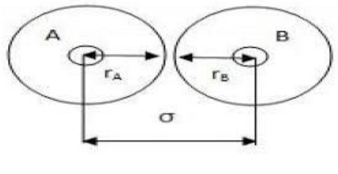
The degree of freedom that a molecule has when it absorbs kinetic energy for rotational motion.

Vibrational Degrees of Freedom:

The degree of freedom that a molecule has when it absorbs kinetic energy for vibrational motion.

Collision diameter:

When two molecules approach one another due to attractive forces. There is a distance of closest approach beyond which the molecules cannot set closet. The repulsive forces become most predominant than the attractive forces, At and beyond this distance. This, it obvious that there is never a physical contact between the molecules. Nevertheless, a collision is said to occur under this situation and the distance between the centers of the molecules when they are closest is called collision diameter. It is denoted by ’σ’. It is not the actual diameter of the molecules. However, the actual diameter of the molecules has no significance in the collision of the molecules and it is the collision diameter which is considered in all calculations. Collision diameter is inversely proportional to the molecular mass of the molecule. This is because the molecules with higher molecular mass have a greater radius.



Collision Number (Z)

The number of molecules with which a single molecule will collide per unit time per unit volume of the gas is called collision number. It is given that,

$Z= \sqrt{2}\pi\ \sigma\ 2\ c\ \rho$

Where,

Z= collision number

σ= diameter of molecule

c = Average velocity

ρ = Number of molecules per unit volume of gas

Collision Frequency

It is the number of molecules collision occurring per unit time per unit volume of the gas. Total number of molecules colliding per unit time per unit volume is obtained by multiplying collision number by number density ρ. Thus, total number of colliding molecules = $\sqrt{2}\pi\ \sigma\ 2\ c\ \rho\ 2$ Since each collision involve two molecules of the same type. Therefore, number of collisions i.e collision frequency is given by one half of the total number of colliding molecules. So $Z11 =1/2$.

$\sqrt{2}\pi\ \sigma\ 2\ c\ \rho\ 2$

Or, $Z11 = 1/\sqrt{2}.\ \pi\ \sigma\ 2\ c\ \rho\ 2$

Collision frequency of different types of molecules– $Z12$

$Z12 = 1/\sqrt{2}.\pi\ \sigma\ 2\ c\ \rho 1\ \rho 2$

Mean Free Path

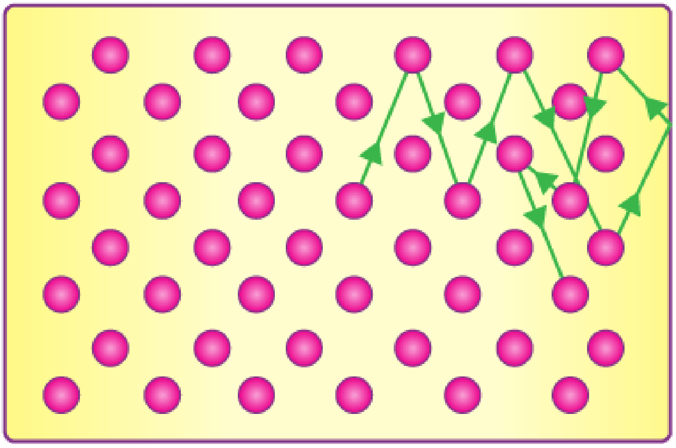
A gas molecule's mean free path λ is its average path length between collisions.

Mathematically the mean free path can be represented as follows:

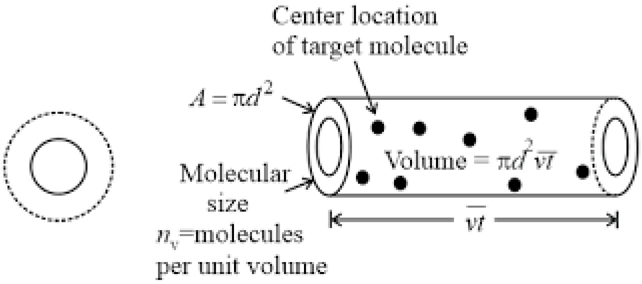
$$\lambda=12\pi d2NV$$

Let's look at the motion of a gas molecule inside an ideal gas; a typical molecule inside an ideal gas will abruptly change its direction and speed as it collides elastically with other molecules of the same gas. Though between the collisions, the molecule will move in a straight line at some constant speed, this is applicable for all the molecules in the gas.

It is difficult to measure or describe this random motion of gas molecules thus, we attempt to measure its mean free path λ.



As its name says, λ is the average distance travelled by any molecule between collisions, we expect λ to vary inversely with N/V, which is the number of molecules per unit volume or the density of molecules because if there are more molecules, more are the chances of them colliding with each other hence reducing the mean free path, and also λ would be inversely proportional to the diameter d of the molecules, because if the molecules were point masses, then they would never collide with each other, thus larger the molecule smaller the mean free path. It should be proportional to π times the diameter square and not the diameter itself because we consider the circular cross-section and not the diameter itself.



Derivation of Mean Free Path

We will derive the equation using the following assumptions, let's assume that the molecule is spherical, and the collision occurs when one molecule hits the other. Only the molecule we are going to study will be in motion, and the rest molecules will be stationary.

Let's consider our single-molecule to have a diameter of d and all the other molecules to be points this does not change our criteria for collision. As our single-molecule moves through the gas, it sweeps out a short cylinder of cross-section area $\pi\ d^2$ between successive collisions. For a small-time t, it will move a distance of vt where v is the velocity of the molecule, now if we sweep this cylinder, we will get a volume of $\pi\ d^2$*vt, so the number of point molecules inside this volume will give us the number of collisions the molecule might have.

Since N/V is the number of molecules per unit volume, the number of molecules in the cylinder will be N/V multiplied by the volume of the cylinder, i.e. πd^2vt, and the mean free path can be derived as follows,

$$\text{Mean free path estimate} = \frac{\overset{\text{Distance traveled}}{\bar{v}t}}{\underbrace{\pi d^2 \bar{v}t}_{\text{Volume of interaction}}\ \underset{\text{Number of molecules per unit volume}}{n_V}} = \overset{\text{Mean distance per collision}}{\frac{1}{\pi d^2 n_V}}$$

We have approximated the equation because we have assumed that all the particles are stationary with respect to the particle we are studying. In fact, all the molecules are moving relative to each other, we have cancelled two velocities in the above equation, but actually, the v in the numerator is the average velocity and v In the denominator is relative velocity hence they both differ from each other with a factor √ 2. Therefore, the final equation would be,

λ=12πd2NV

The mean free path at sea level is 0.1 micrometres.

Viscosity of Gas

The viscosity of gases refers to the resistance of a gas to flow and is primarily caused by the transfer of momentum between gas molecules. Unlike liquids, where intermolecular forces dominate, the viscosity of gases depends on the molecular collisions and the kinetic theory of gases.

Real Gas

A real gas refers to a gas whose behavior deviates from the assumptions of the ideal gas law due to intermolecular interactions and finite molecular volumes. Unlike ideal gases, real gases exhibit deviations, particularly at high pressures and low temperatures.

Deviations from Ideal Gas Behavior

The ideal gas law:

$$PV=nRTPV=nRT$$

assumes:

1) Gas molecules have no volume (point particles).

2) No intermolecular forces exist between molecules.

3) All collisions are perfectly elastic.

For real gases:

1) Molecules have finite volumes.

2) Intermolecular forces (attractive and repulsive) are significant.

These deviations are especially noticeable:

1) At high pressures: Molecules are compressed, so their finite volume cannot be ignored.

2) At low temperatures: Intermolecular attractions reduce the pressure exerted by the gas.

The Van der Waals equation is an equation relating the relationship between the pressure, volume, temperature, and number of real gases. For a real gas containing ‘n’ moles, the equation is written as;

$$(P+an2/V2)(V-nb)=nRT$$

Where P, V, T, and n are the pressure, volume, temperature and moles of the gas, respectively, and ‘a’ and ‘b’ constants specific to each gas.

The equation can further be written as:

Cube power of volume:

$$V3-(b+RTP)\ V2+aPV-abP=0$$

Reduced equation (Law of corresponding states) in terms of critical constants:

$$\left(\pi+\frac{3}{\varphi^2}\right)(3\varphi-1)=8\tau:\ where\ \pi=\frac{P}{Pc},\varphi=\frac{V}{Vc}\ and\ \tau=\frac{T}{Tc}$$

Volume Correction in Van der Waals Equation

As the particles have a definite volume, the volume available for their movement is not the entire container volume but less.

Volume in the ideal gas is hence an overestimation and has to be reduced for real gases.

The volume of the real gas V_R = Volume of the container/ideal gas (V_I) – Correction factor(b)

$$V_R = V_I - b.$$

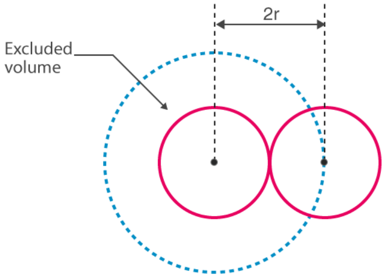
If the particles are independent, then,

Total volume of the particle = number of particle x volume of one particle

$=(n4/3\pi r^3)$

But the particles are not independent, and they do interact.

Van der Waals considered two hard-sphere particles can come as close as to touch each other, and they will not allow any other particle to enter into that volume, as shown in the diagram.



The two-sphere model has a total radius of ‘2r’ (r is the radius of the sphere particle) and volume of

$4/3\pi 2r^3 = 8\times 4/3\pi r^3 = 8\times$ (volume of a single particle)

Then, each of the two particles has a sphere of influence of 4 times the volume of the particle. Volume correction for each particle is not the volume of the particle but four times of it

$=b=4\times4/3\pi r^3$

Volume correction for ‘n’ particles

$=nb=4n\times4/3\pi r^3$

Volume (V) of the real gas = Vi – nb

Pressure Correction in Van der Waals Equation

Gaseous particles do interact. For inside particles, the interactions cancel each other. But, the particles on the surface and near the walls of the container do not have particles above the surface and on the walls. So, there will be net interactions or pulling of the bulk molecules towards the bulk that is away from the walls and surface. The molecules experiencing a net interaction away from the walls will hit the walls with less force and pressure. Hence, in real gases, the particles exhibit lower pressure than shown by ideal gases.

The reduction in pressure α square of the particle density in bulk α $(\text{particle density/volume})^2$

$\alpha n^2/V^2=an^2/V^2$

where, a is the proportionality constant.

Pressure of the real gas,

$Pi=Pr+an^2/V^2$

Substituting the pressure and volume correction in the ideal gas equation, we get the Van der Waals equation for real gases as:

$(Pr+an^2/V^2)(Vi-nb)=nRT$

or in general,

$(P+an^2/V^2)(V-nb)=nRT$

Here, ‘a’ and ‘b’ are Van der Waals constants and contain positive values. The constants are characteristic of the individual gas. When gas is ideal, or it behaves ideally, then both the constants will be zero. Generally, a constant helps in the correction of the intermolecular forces, while the b constant helps in making adjustments for the volume occupied by the gas particles.

Ideal Gas Equation and Van der Waals Equation

Ideal gas equation is given as $PV = nRT$

Van der Waals equation is

$(P+an^2/V^2)(V-nb)=nRT$

At constant temperature, a decrease in pressure increases the volume (V). Hence at low pressures, the volume will be larger. So, the correction factor in pressure (an^2/V^2)

becomes very small and negligible.

Again, the volume of the gas will be larger compared to the volume of the molecules (n, b). Hence, the volume correction also will be small and negligible.

As the correction factor becomes negligible, the pressure and volume of the real gases will be equal to that of ideal gases. Interestingly, all real gases behave like ideal gases at low pressures and high temperatures.

Boyle’s Temperature

Boyle's Temperature (TB) is the temperature at which a real gas behaves most closely to an ideal gas over a range of pressures. At this temperature, the gas obeys Boyle's law (PV=constant) more precisely than at other temperatures because the effects of intermolecular attractions and repulsions balance each other.

$TB=a/bR$

Where,

a and b: Van der Waals constants.

R: Universal gas constant.

Compressibility Factor:

- The compressibility factor ($Z=PV/nRT$) at TB is approximately 1 for a range of pressures.
- Real gas behavior improves at TB

Second Virial Coefficient:

The second virial coefficient B(T) becomes zero at TB

$B(T)=b-a/RT$

Here, a and b are the Van der Waals constants:

a: Corrects for intermolecular attractions.

b: Corrects for the finite volume of gas molecules.

Isotherms of Real gases

Isotherms are P-V curves that represent the relationship between the concentration of a solid and fluid at a constant temperature. When pressure is increased at a constant temperature, the volume decreases, and vice versa.

At high temperatures and low pressures, real gases behave like ideal gases and follow the ideal gas equation $PV = RT$. However, at temperatures below 215 K, real gases begin to deviate from ideal behavior. For example, if a container of gas at 185 K is decreased in volume, the gas will eventually condense. As the gas condenses, the pressure remains constant, but once the gas has completely condensed, the pressure increases rapidly because the liquid is incompressible. The isotherm will then appear almost vertical.

Critical phenomena

Critical phenomena can refer to a variety of phenomena, including phase transitions, gravitational collapse, and atmospheric precipitation:

Phase transitions

Critical phenomena can occur near second-order phase transitions and are characterized by thermodynamic singularities and long-range spatial correlations. They can include scaling relations, power-law divergences, universality, fractal behavior, and ergodicity breaking. For example, in chemistry, critical phenomena can include the liquefaction of a gas, which occurs when the temperature is reached above which no second phase appears, regardless of pressure.

Gravitational collapse

Critical phenomena can also refer to phenomena that occur during gravitational collapse, such as universality, power-law scaling of black hole mass, and scale echoing. These phenomena can be described by a critical surface that separates basins of attraction, and a spacetime that is self-similar. They can be observed in systems such as axisymmetric gravitational waves in a vacuum, and the grazing collision of two black holes.

Atmospheric precipitation

Critical phenomena can also refer to phenomena that occur in atmospheric precipitation, such as extreme precipitation in the tropics, and episodic deluges in simulated hothouse climates.

Isotherms of (CO_2):

Isotherms of carbon dioxide (CO_2) are graphs that show how the pressure of CO_2 gas varies with its volume at different temperatures. Here are some things to know about CO_2 isotherms:

At high temperatures: The isotherm of a real gas looks similar to that of an ideal gas.

As temperature decreases: The curve's shape changes and deviates from ideal behavior.

Liquefaction temperature: At the liquefaction temperature, or critical temperature of CO_2, the gas will completely liquefy.

Continuity of state: At the critical temperature, the substance remains in one phase, which is called continuity of state between the liquid and gaseous states.

Here are some observations about CO_2 isotherms:

Gaseous state: At temperature T1, CO_2 will exist as a gas between points a and b.

Liquefaction: At point b, the plot becomes linear, indicating the start of CO_2 liquefaction.

Complete liquefaction: At point c, CO_2 will be completely liquefied.

Vander waal's equation

It's a thermodynamic equation that describes the behavior of real gases.

It's an improvement over the ideal gas law, which assumes no interactions between molecules.

The equation takes into account;

Attractive forces between molecules (a/v^2)

Repulsive forces between molecules(b)

The equation is:

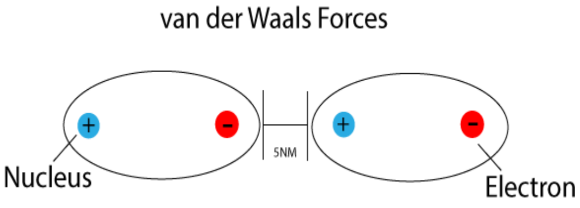
$$(P+a/V^2)(V-b)=RT$$

Where,

P = pressure V = volume

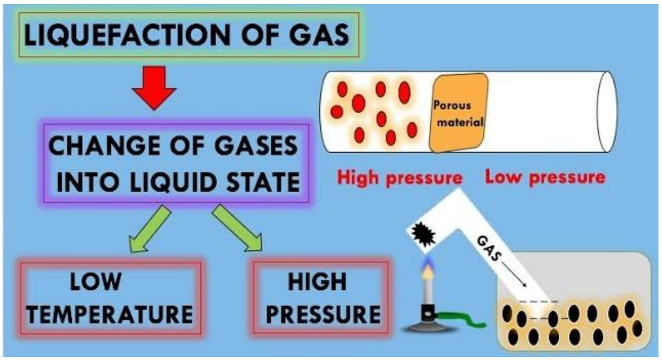
A = attraction parameter b = repulsion parameter R = gas constant

T = temperature



Liquefaction of Gases

Gases are difficult to transport. Due to their physical properties, it is almost impossible to transfer them from one place to another. For the same purpose, the gas is transformed into a liquid. Study of liquefaction of gases tells us about changes in the properties and structure of a gas. It also gives valuable information about the structure of matter in general.



Liquefaction

Liquefaction is the transformation of a gaseous substance into its liquid state. This change is the outcome of change in physical conditions like temperature, pressure, and volume. Thomas Andrew was the first person to study the change of state from gases to liquids in Carbon Dioxide. It was later discovered that most real gases behave like Carbon Dioxide (CO_2) and change from gases to liquids if optimum physical changes in temperature and pressure are achieved.

In his experiment on CO_2, Andrews came to a conclusion that at high temperatures, despite high pressure, the gases cannot be liquefied. Also, with the increase in temperature, the gases show significant deviation from the ideal behavior. In the case of carbon dioxide, at 30.98° C, the gas started changing into a liquid.

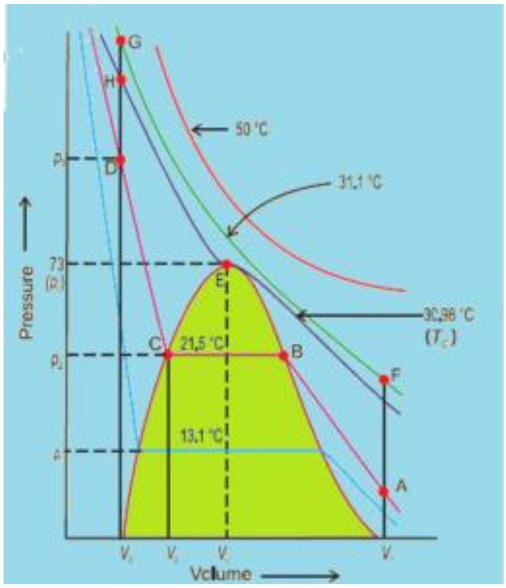
Critical Temperature, Volume, and Pressure

Andrews in his experiment observed that above a specific temperature, the gas sample couldn't be liquefied, howsoever high the pressure becomes. The critical temperature is the temperature at which a gas changes into liquid. With the increase in temperature, the pressure required to liquefy a gas also increases. This temperature was the highest temperature at which a gas appears in the form of a liquid. It is the critical temperature or T_C.

Critical constants play an essential role in the change of states of matter. Critical constants are critical pressure, temperature, and volume. The volume of one mole of a gas volume liquefied at critical temperature is known as the critical volume (V_c) while the pressure required to liquefy the gas at critical temperature is called as the Critical pressure (p_c).

Isotherm of Carbon Dioxide

The graph between the Pressure and Volume at a given constant temperature is the isotherm. On studying the isotherm of Carbon dioxide, we get to know the different intervals of temperatures at which a gas can show signs of liquefaction:



On studying the isotherm above we get to know the physical change of state temperature wise. Volume and pressure play a vital role in the change of state. In the above isotherm, we study the liquefaction of Carbon dioxide. We see that the gaseous state of carbon dioxide changes to liquid at 30.98° C. The curve changes at a lower temperature, while at the higher temperature it does not show any change. At 30.98°C, the gas shows considerable deviation from the ideal gas behavior.

Equilibrium state

The curve at increased pressure signifies compressibility of liquid CO_2 while the steep line pertains to the isotherm of the liquid, slightest of compression results in a sharp rise in the pressure, thus indicating the amount of compressibility of CO_2. On attaining 21.5° Carbon dioxide behaves like a gas until point B.

The point B shows signs of liquid CO_2. The gas now exists in the dual form i.e both liquid and gas. At this stage compressing further does not affect the pressure on the gas, rather it results in condensation**.** At point C, all the CO_2 gas has condensed and further compression results in the rise in pressure.

From the above isotherm it is clear that at point A, CO_2 exists in the gaseous state while at point D it exists in a liquid state. At point D the compression of the liquid CO_2 is almost impossible. At point C an equilibrium state between the two states of matter is seen.

Further find that the behavior of all the gases is similar to CO_2 and this is because of the constant temperature or isothermal compression. This similar behavior shown by gases, in compression, at constant temperature is known as isothermal compression.

Gases to liquids

- The critical temperature of the gas is the highest temperature at which the first occurrence of liquefaction of gas is seen. The critical temperature signifies the force of attraction between the molecules. The higher the critical temperature, higher is the intermolecular force of attraction and easier is the liquefaction of the gas.
- Gases require cooling and compression both for liquefaction.

Now what gases need cooling and compression both for liquefaction? The gases which display a positive deviation from compressibility factor (Z) are permanent gases and they need both cooling and compression for the change in state.

The compressibility factor is the ratio of the original volume of a gas to the molar volume, now if the value of Z is in positive or greater than 0 then it shall need both cooling and compression for the change of state.

Effect of Compression and Cooling

Compression is the process of increasing pressure on the molecules of the gas. It brings the molecules close to each other. As soon as the molecules come in the vicinity of each other the reduced temperature slows the random movement of the molecules. This dual action of compression and cooling instigates intermolecular interactions. With the start of this intermolecular interaction, the molecules gradually and closely move toward each other leading to a change in the state.

Solved Example

Q: The Critical temperature of N_2 is 126 K and He is 5.3 K. Which of the gases will liquify first?

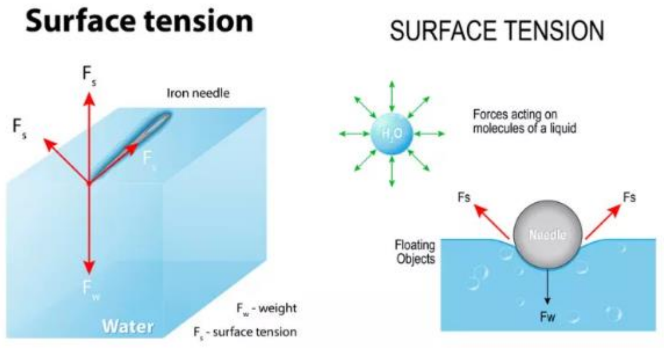
Ans. N_2 (nitrogen) liquifies easily. Intermolecular forces are high for gases which have a high critical temperature, making the change of state fast.

UNIT-2

LIQID AND SOLID STATE

Surface Tension

Surface tension is the tension of the surface film of a liquid caused by the attraction of the particles in the surface layer by the bulk of the liquid, which tends to minimise surface area.



Liquid and Solid State

Properties of Liquids

- Liquids do not fill up the space provided to them but occupy their own volume.
- In liquids, the molecules are close to each other. They are held together by a strong intermolecular force of attraction. Hence liquid molecules cannot be separated from their close neighbours. However, the cluster can move.
- Liquids are virtually incompressible. Their compressibility coefficient 'ß' is very small about 10-15 per atmosphere.
- Liquids diffuse very slowly since the available space for movement is much smaller.
- Liquids with similar internal pressure mix with each other easily in all proportions.
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- Liquids with similar internal pressure mix with each other easily in all proportions.

Applications of surface tension:

- Surface tension plays a crucial role in various chemical phenomena. Here are some applications in chemistry:
- Emulsification: Surface tension helps to stabilize emulsions, where immiscible liquids (like oil and water) are mixed together. This is important in processes like making mayonnaise or pharmaceutical formulations.
- Bubble Formation and Stability: Surface tension influences the formation and stability of bubbles in solutions, which is essential in processes like fermentation in beverages or carbonation in soft drinks.
- Capillary Action: Surface tension allows liquids to move against gravity in narrow tubes, a process known as capillary action.

- Emulsification: Surface tension helps to stabilize emulsions, where immiscible liquids (like oil and water) are mixed together. This is important in processes like making mayonnaise or pharmaceutical formulations.
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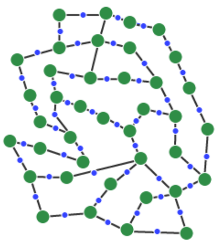
- Capillary Action: Surface tension allows liquids to move against gravity in narrow tubes, a process known as capillary action. This is significant in areas such as chromatography, where it helps to separate components of a mixture.
- Wetting and Spreading: Surface tension affects how liquids spread on solid surfaces. This is important in applications like coatings, adhesives, and inkjet printing.
- Biological Processes: Surface tension plays a role in biological systems, such as the movement of fluids in plants and the functioning of alveoli (tiny air tubes) in the lungs.
- Nanotechnology: Surface tension can be manipulated to control the assembly of nanoparticles, which is important in the fabrication of nanomaterials and devices.

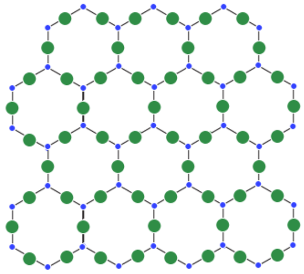
CRYSTALLINE AND AMORPHOUS:

In crystalline solids the particles are arranged in a 3-dimensional order. The particles have equal intermolecular forces. They have sharp melting point and are anisotropic. They are called true solids. Example: Benzoic acid, Diamond.

Amorphous solids: Amorphous means shapeless. This word is derived from Greek. It has an irregular arrangement of solid particles. The intermolecular forces are not equal. Also, the distance between particles varies. They have an undefined geometric shape. They are also called supercooled liquids. They are isotropic. Example: Naphthalene, glass



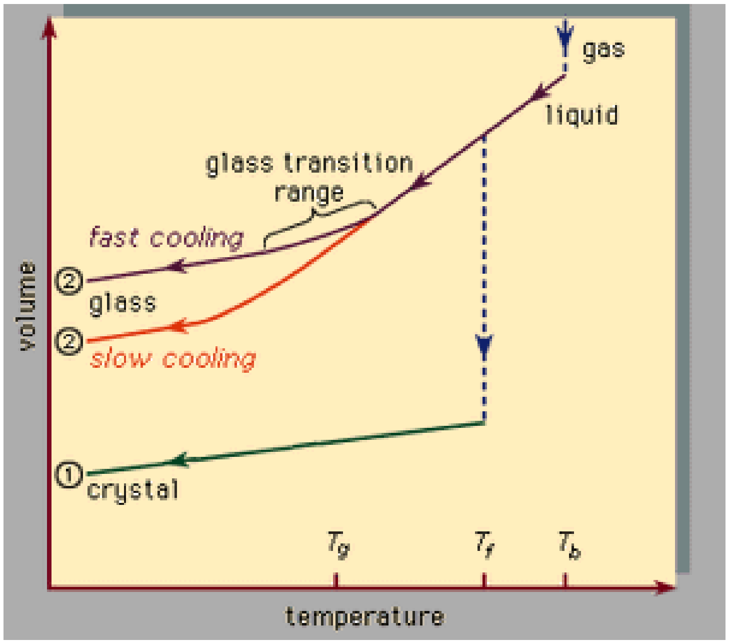
Amorphous Solids



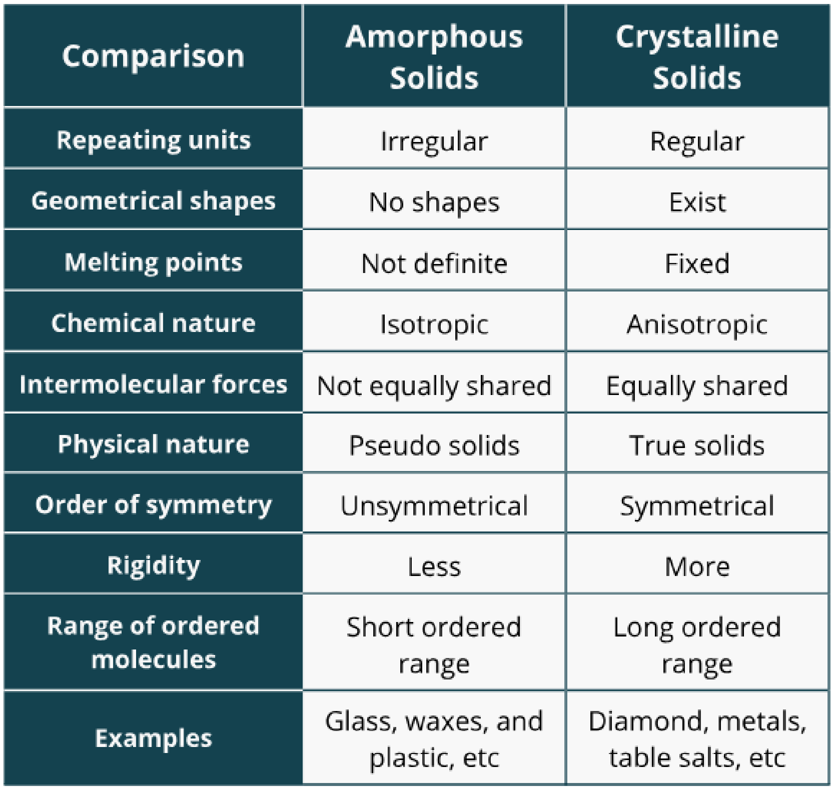
Crystalline Solids

Atomic positions in a crystal exhibit a property called long-range order or translational periodicity; positions repeat in space in a regular array . In an amorphous solid, translational periodicity is absent. There is no long-range order. The atoms are not randomly distributed in space, however, as they are in the gas. In the glass example illustrated in the figure, each atom has three nearest-neighbour atoms at the same distance (called the chemical bond length) from it, just as in the corresponding crystal. All solids, both crystalline and amorphous, exhibit short-range (atomic-scale) order. (Thus, the term amorphous, literally "without form or structure," is actually a misnomer in the context of the standard expression amorphous solid.) The well-defined short-range order is a consequence of the chemical bonding between atoms, which is responsible for holding the solid together. In addition to the terms amorphous solid and glass, other terms in use include non-crystalline solid and vitreous solid. Amorphous solid and non-crystalline solid are more general terms, while glass and vitreous solid have historically been reserved for an amorphous solid prepared by rapid cooling (quenching).

The below figure, which should be read from right to left, indicates the two types of scenarios that can occur when cooling causes a given number of atoms to condense from the gas phase into the liquid phase and then into the solid phase. Temperature is plotted horizontally, while the volume occupied by the material is plotted vertically. The temperature T_b is the boiling point, T_f is the freezing (or melting) point, and T_g is the glass transition temperature. In scenario 1 the liquid freezes at T_f into a crystalline solid, with an abrupt discontinuity in volume. When cooling occurs slowly, this is usually what happens. At sufficiently high cooling rates, however, most materials display a different behaviour and follow route 2 to the solid state. T_f is bypassed, and the liquid state persists until the lower temperature T_g is reached and the second solidification scenario is realized. In a narrow temperature range near T_g, the glass transition occurs: the liquid freezes into an amorphous solid with no abrupt discontinuity in volume.



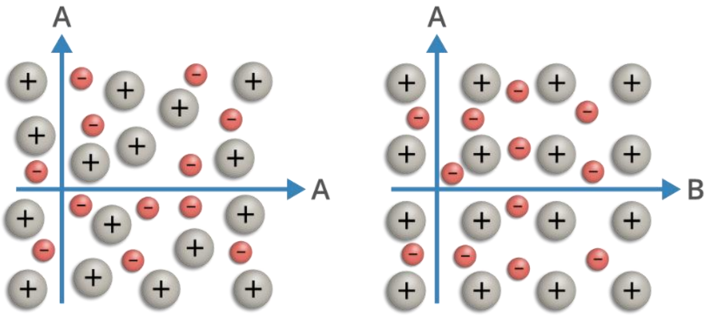
The glass transition temperature T_g is not as sharply defined as T_f; T_g shifts downward slightly when the cooling rate is reduced. The reason for this phenomenon is the steep temperature dependence of the molecular response time, which is crudely indicated by the order-of-magnitude values shown along the top scale of the figure.



Comparison	Amorphous Solids	Crystalline Solids
Repeating units	Irregular	Regular
Geometrical shapes	No shapes	Exist
Melting points	Not definite	Fixed
Chemical nature	Isotropic	Anisotropic
Intermolecular forces	Not equally shared	Equally shared
Physical nature	Pseudo solids	True solids
Order of symmetry	Unsymmetrical	Symmetrical
Rigidity	Less	More
Range of ordered molecules	Short ordered range	Long ordered range
Examples	Glass, waxes, and plastic, etc	Diamond, metals, table salts, etc

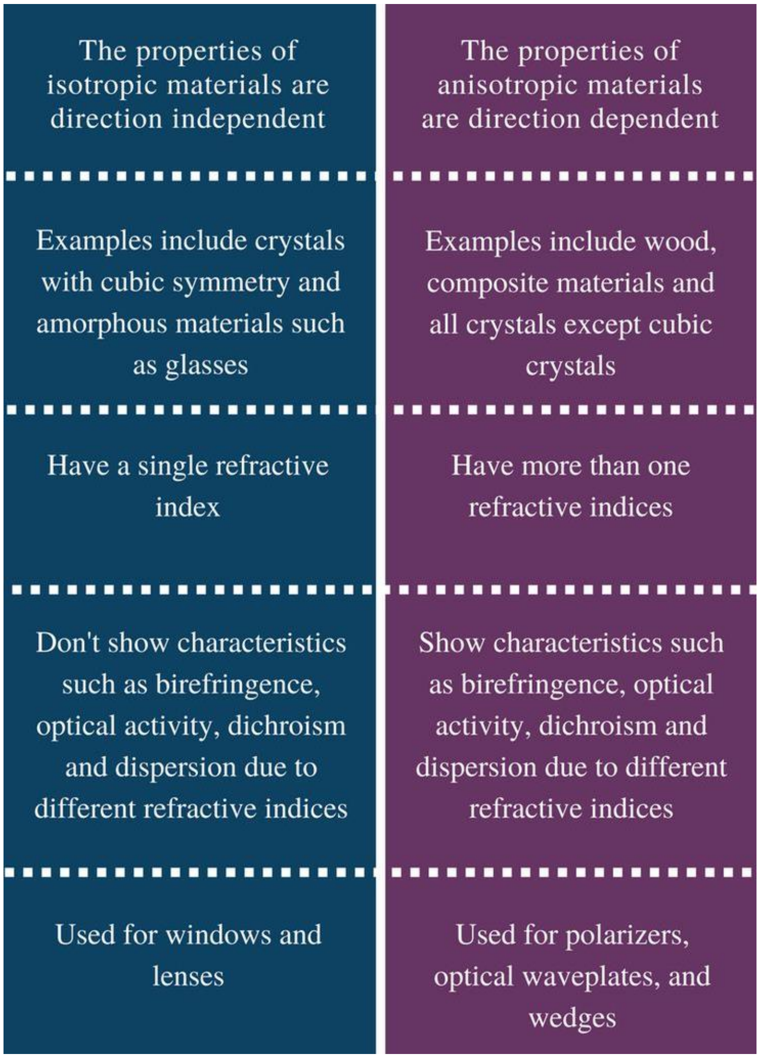
Isotropy and Anisotropy

Isotropy is the property of being uniform in all directions, while anisotropy is the property of being dependent on direction.



Isotropy in amorphous solids

Anisotropy in crystalline solids



The properties of isotropic materials are direction independent	The properties of anisotropic materials are direction dependent
Examples include crystals with cubic symmetry and amorphous materials such as glasses	Examples include wood, composite materials and all crystals except cubic crystals
Have a single refractive index	Have more than one refractive indices
Don't show characteristics such as birefringence, optical activity, dichroism and dispersion due to different refractive indices	Show characteristics such as birefringence, optical activity, dichroism and dispersion due to different refractive indices
Used for windows and lenses	Used for polarizers, optical waveplates, and wedges

Melting point

Melting point, temperature at which the solid and liquid forms of a pure substance can exist in equilibrium. As heat is applied to a solid, its temperature will increase until the melting point is reached. More heat then will convert the solid into a liquid with no temperature change. When all the solid has melted, additional heat will raise the temperature of the liquid. The melting temperature of crystalline solids is a characteristic figure and is used to identify pure compounds and elements. Most mixtures and amorphous solids melt over a range of temperatures.

The melting temperature of a solid is generally considered to be the same as the freezing point of the corresponding liquid; because a liquid may freeze in different crystal systems and because impurities lower the freezing point, however, the actual freezing point may not be the same as the melting point. Thus, for characterizing a substance, the melting point is preferred.

Isomorphism and Polymorphism

In nature, elements and compounds can exist in different combinations, having different structures or morphologies. The structure of a compound determines most of the physical properties and sometimes chemical properties of that compound. The term “morphism” refers to the morphology. It is the external appearance. Therefore, isomorphism and polymorphism are two terms used to describe the morphology of chemical substances. The existence of a substance in more than one crystalline form is known as polymorphism. If this substance is a single element, then it is called allotropy rather than polymorphism. If two or more different substances show the same morphology, then it is called isomorphism. The main difference between isomorphism and polymorphism is that isomorphism describes the presence of the same morphology in different substances whereas polymorphism describes the presence of different morphologies of the same substance.

What is Isomorphism?

Isomorphism is the similarity in the crystal structure of different compounds. These compounds are called isomorphous substances. In the simplest definition, isomorphous substances are nearly same in their shape.

Isomorphous substances are comprised of the same atomic ratio. Therefore, the empirical formulas of these isomorphous substances are the same. However, since these substances are composed of combinations of different atoms, the chemical and physical properties of isomorphous substances are different from each other. Such properties include mass, density, chemical reactivity, etc.

Examples of Isomorphism

Some of the examples for substances that show isomorphism are shown below.

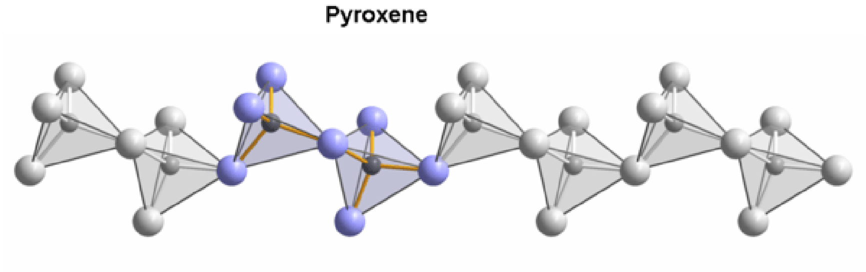
- **$CaCO_3$ and $NaNO_3$**

Both these substances exist in trigonal shape. The atomic ratio of these isomorphous substances is the same (1: 1: 3).

But the physical and chemical properties are different. For example, the molar mass of CaCO3 is 100 g/mol whereas the molar mass of NaNO3 is about 85 g/mol.

- **Na_3PO_4 and N_3AsO_4**

Both substances are tetrahedral in shape. The atomic ratio of both structures is 3: 1: 4. But the physical and chemical properties are different.



Different isomorphous compounds are crystallized together to form Pyroxene

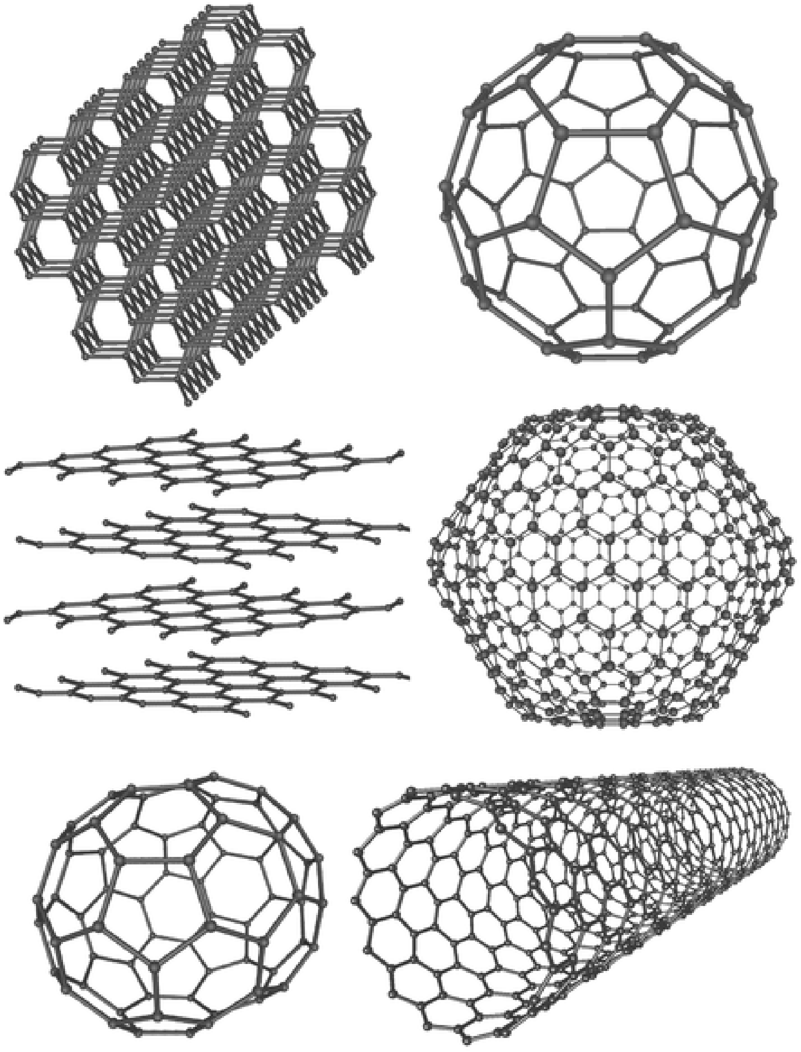
Isomorphism can be often found in minerals. Since the crystal structures are similar to each other, these isomorphous substances can sometimes be crystallized together. Most minerals are composed of this type of structure which has several different compounds mixed together, forming the equal crystal structure. Some of the examples include Feldspar, Garnet, and pyroxene.

What is Polymorphism?

Polymorphism is the presence of different crystalline forms of the same compound. In other words, if a particular compound can be found in different shapes, this phenomenon is called polymorphism. The compound showing polymorphism is called a polymorphic substance.

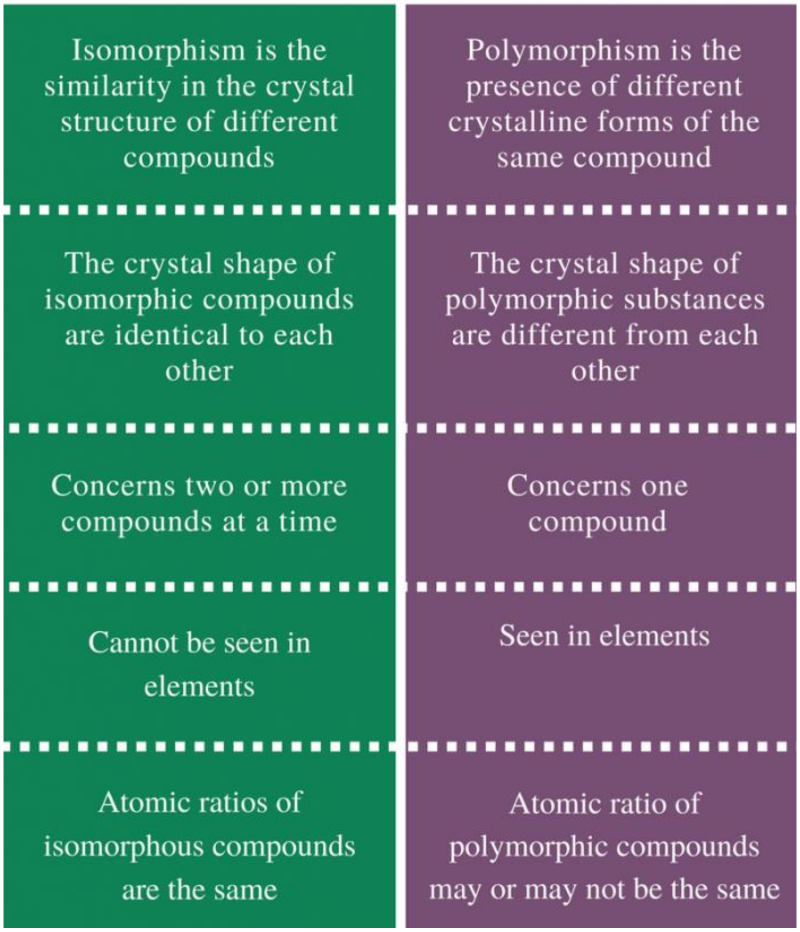
Polymorphic substances show similarities as well as differences. Most of the times, chemical properties of these polymorphic form of a particular substance is the same, but physical properties can be different. However, the chemical formulas of polymorphic forms are the same since it is the same compound. For example, the $CaCO_3$ compound may exist either in orthorhombic form or in hexagonal form.

When an element show polymorphism, it is called allotropy. When an element is found in different forms of arrangements, those compounds are called allotropes. For example, carbon can be found as either diamond or graphite. They have different chemical and physical properties but are composed only of carbon atoms.



Allotropes of carbon

The above image shows the polymorphism of carbon elements. These different forms or compounds are called allotropes.



Isomorphism is the similarity in the crystal structure of different compounds	Polymorphism is the presence of different crystalline forms of the same compound
The crystal shape of isomorphic compounds are identical to each other	The crystal shape of polymorphic substances are different from each other
Concerns two or more compounds at a time	Concerns one compound
Cannot be seen in elements	Seen in elements
Atomic ratios of isomorphous compounds are the same	Atomic ratio of polymorphic compounds may or may not be the same

Crystals

Crystals are fascinating structures that exhibit a highly ordered arrangement of atoms, ions, or molecules. This internal organization is what gives crystals their distinct shapes and unique physical properties. To understand crystals better, we can explore their size, shape, and the fundamental laws that govern their formation and characteristics.

Crystal Size

The size of a crystal can varies greatly, from tiny microscopic structures to massive specimens visible to the naked eye. The size largely depends on the conditions under which the crystal grows. For instance, when a substance cools slowly from its molten state, the atoms or ions have more time to arrange themselves into a well-organized lattice. This slower process often results in larger, well-defined crystals. Conversely, rapid cooling leads to the formation of smaller crystals, as there is insufficient time for the orderly arrangement of particles.

Impurities present in the environment can also play a significant role in determining crystal size. Pure materials tend to form larger and more regular crystals because there are fewer disruptions in the lattice structure. In contrast, the presence of impurities can inhibit crystal growth, resulting in smaller and sometimes irregularly shaped crystals.

The availability of space is another crucial factor. In environments where growth is unrestricted, such as in large cavities, crystals can expand freely and achieve impressive sizes. However, in confined spaces, their growth is limited, producing smaller structures.

Crystal Shape

Crystals are renowned for their geometric shapes, which reflect the underlying atomic arrangement within. This external appearance, known as the crystal habit, can vary widely even for crystals of the same material, depending on growth conditions. For example, quartz can form long, slender prismatic crystals under certain conditions, or short, stubby shapes under others.

The shape of a crystal is not random but is dictated by its internal symmetry. The atoms or ions within the crystal lattice are arranged in a repeating pattern that determines its external geometry. These shapes are often classified into one of seven crystal systems: cubic, tetragonal, hexagonal, orthorhombic, monoclinic, triclinic, and trigonal. Each system has its distinct characteristics based on the angles between the faces and the relative lengths of the crystal axes.

Laws of Crystallography

The study of crystals is guided by several fundamental laws that describe their behavior and structure. These laws provide a framework for understanding how crystals form and why they exhibit specific properties.

Steno’s Law (Law of Constancy of Interfacial Angles): One of the earliest observations in crystallography, Steno’s law states that the angles between corresponding faces of crystals of the same substance are always constant. This constancy arises because the internal arrangement of atoms remains consistent regardless of the external size or conditions of formation. For example, all quartz crystals, regardless of their size, will have the same interfacial angles between equivalent faces.

Haüy’s Law (Law of Rational Indices): This law explains the relationship between the faces of a crystal and its internal lattice. According to Haüy, the intercepts of crystal faces on the crystallographic axes are simple whole-number ratios. These ratios are used to define the orientation of the crystal faces and are represented by Miller indices, a shorthand notation in crystallography.

Symmetry in Crystals: Symmetry is a defining characteristic of crystals. They possess various symmetry elements, including planes of symmetry, axes of symmetry, and centers of symmetry. A plane of symmetry divides the crystal into two identical halves, while an axis of symmetry allows the crystal to rotate around it and repeat its shape. A center of symmetry exists when every point on the surface of the crystal has an equivalent point on the opposite side.

Bravais’ Law: Bravais’ law categorizes the 14 distinct types of crystal lattices, known as Bravais lattices, based on their symmetry and unit cell dimensions. These lattices form the fundamental building blocks of crystals and determine their overall structure.

Applications of Crystallography

Crystals play a vital role in various scientific and industrial applications. The precise study of their structure through techniques like X-ray diffraction has allowed scientists to understand the properties of materials ranging from metals and semiconductors to biological molecules like DNA. Crystals are also essential in the development of technologies such as lasers, optical fibers, and electronic components.

In addition, the understanding of crystal growth and structure has applications in geology, where it helps in identifying minerals, and in pharmaceuticals, where the crystalline form of a drug can influence its solubility and bioavailability.

Symmetry Elements in Crystals

Symmetry is a fundamental characteristic of crystals, reflecting the repetitive and orderly arrangement of atoms, ions, or molecules within the crystal lattice. Symmetry elements are specific features within a crystal that describe how its structure can be manipulated through reflection, rotation, or inversion while remaining unchanged. These elements form the basis for classifying crystals into different symmetry groups and systems.

1. Plane of Symmetry (Mirror Plane)

A plane of symmetry, also known as a mirror plane, divides a crystal into two halves such that one half is the mirror image of the other.

Crystals may have one or more mirror planes.

The presence of a mirror plane signifies that the atomic arrangement on one side of the plane is identical to the arrangement on the opposite side.

Example: A cube has multiple planes of symmetry, each passing through its center.

2. Axis of Symmetry (Rotation Axis)

An axis of symmetry is an imaginary line about which a crystal can be rotated by a specific angle, and after the rotation, it appears indistinguishable from its original orientation.

Types of Rotation Axes:

Twofold axis (2-fold): Rotation by 180^0 produces an identical appearance.

Threefold axis (3-fold): Rotation by 120^0 restores symmetry.

Fourfold axis (4-fold): Rotation by 90^0 produces the same appearance.

Sixfold axis (6-fold): Rotation by 600 restores symmetry.

Example: In a hexagonal crystal, a sixfold rotation axis is present along the vertical direction.

3. Centre of Symmetry (Inversion Center)

A center of symmetry, or inversion center, is a point within the crystal such that any line drawn from it to the surface of the crystal will intersect an equivalent point on the opposite side at an equal distance.

If a crystal possesses a center of symmetry, it remains unchanged upon inversion through this central point.

Example: A sphere or cube inherently possesses a center of symmetry.

4. Roto inversion Axis

A rotoinversion axis combines rotation and inversion. A crystal is rotated by a specific angle about an axis, and then every point is inverted through the centre of the crystal.

Example: Certain trigonal and hexagonal crystals exhibit rotoinversion symmetry.

5. Symmetry Operations and Combinations

In many crystals, symmetry elements occur in combination, leading to complex patterns and classifications. Symmetry operations involve performing actions such as reflection, rotation, or inversion using these elements, leaving the crystal unchanged.

Point Groups: Crystals are classified into 32-point groups based on the combination of their symmetry elements.

Space Groups: These extend point group classification by incorporating translational symmetry, resulting in 230 unique space groups**.**

Applications of Symmetry Elements

1. Classification of Crystals: Symmetry elements are used to categorize crystals into one of the seven crystal systems: cubic, tetragonal, hexagonal, trigonal, orthorhombic, monoclinic, and triclinic.

2. Material Properties: Symmetry governs various physical properties of crystals, such as optical behavior, piezoelectricity, and thermal conductivity.

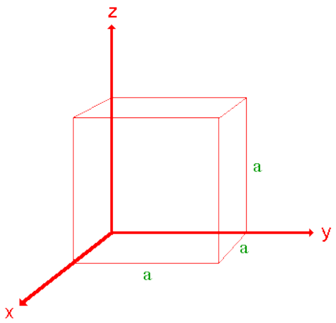
3. Crystallography Techniques: Symmetry elements are crucial in interpreting X-ray diffraction patterns and understanding the arrangement of atoms within a crystal lattice.

4. Molecular Structures: Symmetry is not limited to crystals; it is also vital in analysing molecular structures, particularly in spectroscopy and chemical bonding studies.

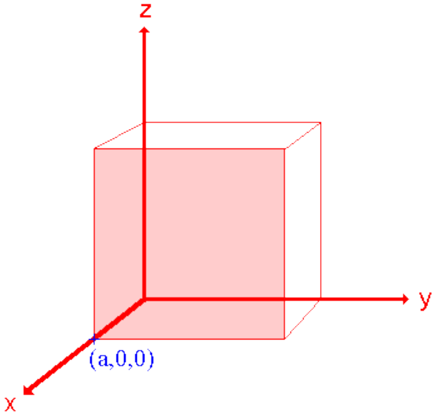
Miller indices (hkl)

The orientation of a surface or a crystal plane may be defined by considering how the plane (or indeed any parallel plane) intersects the main crystallographic axes of the solid. The application of a set of rules leads to the assignment of the Miller Indices (hkl), which are a set of numbers which quantify the intercepts and thus may be used to uniquely identify the plane or surface.

The following treatment of the procedure used to assign the Miller Indices is a simplified one (it may be best if you simply regard it as a "recipe") and only a cubic crystal system (one having a cubic unit cell with dimensions a x a x a) will be considered.



The procedure is most easily illustrated using an example so we will first consider the following surface/plane



Step 1: Identify the intercepts on the x-, y- and z- axes.

In this case the intercept on the x-axis is at x = a (at the point (a,0,0)), but the surface is parallel to the y- and z-axes - strictly therefore there is no intercept on these two axes but we shall consider the intercept to be at infinity (∞) for the special case where the plane is parallel to an axis. The intercepts on the x-, y- and z-axes are thus

Intercepts: a, ∞, ∞

Step 2: Specify the intercepts in fractional co-ordinates

Co-ordinates are converted to fractional co-ordinates by dividing by the respective cell-dimension - for example, a point (x,y,z) in a unit cell of dimensions a x b x c has fractional co-ordinates of (x/a, y/b, z/c). In the case of a cubic unit cell each co-ordinate will simply be divided by the cubic cell constant, a. This gives

Fractional Intercepts: a/a, ∞/a, ∞/a i.e. 1, ∞, ∞

Step 3: Take the reciprocals of the fractional intercepts

This final manipulation generates the Miller Indices which (by convention) should then be specified without being separated by any commas or other symbols. The Miller Indices are also enclosed within standard brackets (….) when one is specifying a unique surface such as that being considered here.

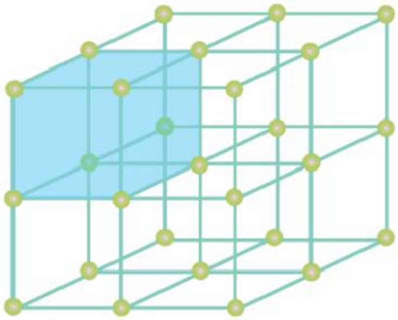
The reciprocals of 1 and ∞ are 1 and 0 respectively, thus yielding

Miller Indices: (100)

So, the surface/plane illustrated is the (100) plane of the cubic crystal.

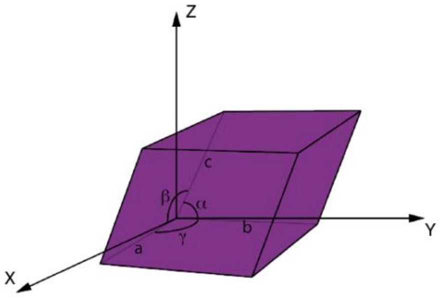
What is Crystal Lattice?

The crystal lattice is the *symmetrical three-dimensional structural arrangements of atoms, ions or molecules (constituent particle) inside a crystalline solid as points.* It can be defined as the geometrical arrangement of the atoms, ions or molecules of the crystalline solid as points in space.



Unit Cell

Unit Cell is the smallest part (portion) of a crystal lattice. It is the simplest repeating unit in a crystal structure. The entire lattice is generated by the repetition of the unit cell in different directions.



There are six parameters of a unit cell. These are the 3 edges which are a, b, c and the angles between the edges which are α, β, γ. The edges of a unit cell may be or may not be perpendicular to each other.

Bravais Lattices

Bravais Lattice refers to the *14 different 3-dimensional configurations into which atoms can be arranged in crystals.* The smallest group of symmetrically aligned atoms which can be repeated in an array to make up the entire crystal is called a unit cell.

There are several ways to describe a lattice. The most fundamental description is known as the Bravais

lattice. In words, a Bravais lattice is an array of discrete points with an arrangement and orientation that look exactly the same from any of the discrete points, that is the lattice points are indistinguishable from one another. Thus, a Bravais lattice can refer to one of the 14 different types of unit cells that a crystal structure can be made up of. These lattices are named after the French physicist Auguste Bravais.

Types of Bravais Lattices

Out of 14 types of Bravais lattices some 7 types of Bravais lattices in three-dimensional space are listed in this subsection. Note that the letters a, b, and c have been used to denote the dimensions of the unit cells whereas the letters **α**, ***β***, and **γ** denote the corresponding angles in the unit cells.

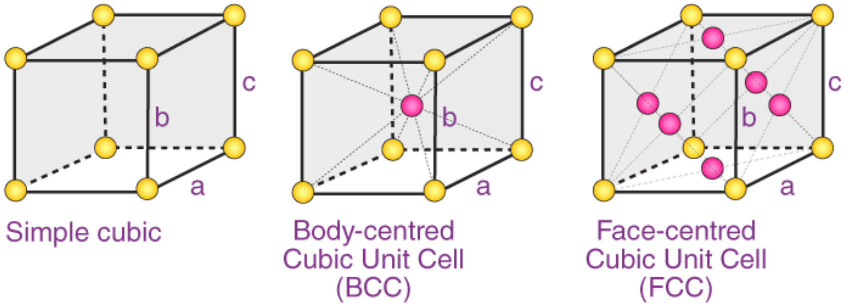
1. Cubic Systems

In Bravais lattices with cubic systems, the following relationships can be observed.

a = b = c

α = *β* = γ = 90º

The 3 possible types of cubic cells have been illustrated below.



<u>Examples:</u> Polonium has a simple cubic structure, iron has a body-centered cubic structure, and copper has a face-centered cubic structure.

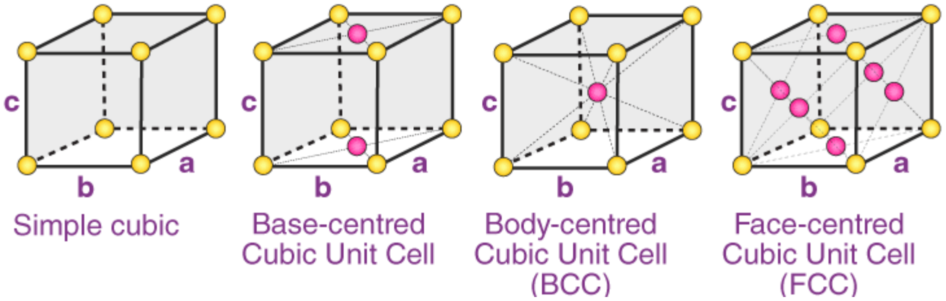
2. Orthorhombic Systems

The Bravais lattices with orthorhombic systems obey the following equations:

$a \neq b \neq c$

$\boldsymbol{\alpha = \beta = \gamma = 90^o}$

The four types of orthorhombic systems (***simple, base centered, face-centered, and body-centered orthorhombic cells***) are illustrated below.



Examples of Orthorhombic Systems:

Rhombic Sulphur has a simple orthorhombic structure

Magnesium sulfate heptahydrate ($MgSO_4.7H_2O$) is made up of a base centred orthorhombic structure.

Potassium Nitrate has a structure which is body-centered orthorhombic.

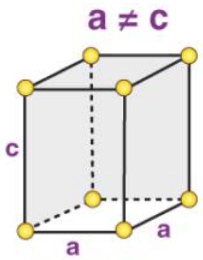
An example of a substance with a face-centered orthorhombic structure is barium sulfate.

3. Tetragonal Systems

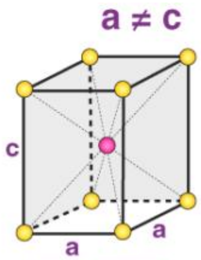
In tetragonal Bravais lattices, the following relations are observed:

$a = b \neq c$ $\boldsymbol{\alpha = \beta = \gamma = 90^o}$

The two types of tetragonal systems are ***simple tetragonal cells and body-centered tetragonal cells***, as illustrated below.



Simple cubic



Body-centred
Cubic Unit Cell

Examples of tetragonal Bravais lattices are – stannic oxide (simple tetragonal) and titanium dioxide (body-centered tetragonal)

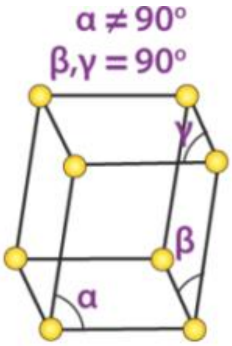
4. Monoclinic Systems

Bravais lattices having monoclinic systems obey the following relations:

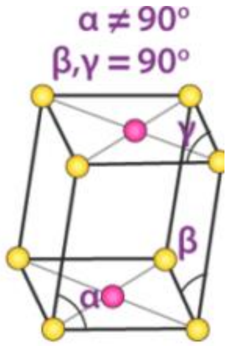
$a \neq b \neq c$

$\beta = \gamma = 90^o$ and $\alpha \neq 90^o$

The two possible types of monoclinic systems are ***primitive and base centered monoclinic cells***, as illustrated below.



Simple



Centered

Cubic cells are – Monoclinic sulphur (simple monoclinic) and sodium sulfate decahydrate (base centered monoclinic)

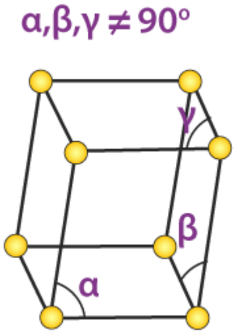
5. Triclinic System

There exists only one type of triclinic Bravais lattice, which is a ***primitive cell***. It obeys the following relationship.

$a \neq b \neq c$

$\alpha \neq \beta \neq \gamma \neq 90^o$

An illustration of a simple triclinic cell is given below.



Such unit cells are found in the structure of potassium dichromate (Chemical formula $K_2Cr_2O_7$).

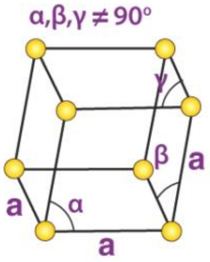
6. Rhombohedral System

Only the primitive unit cell for a rhombohedral system exists. Its cell relation is given by:

a = b = c

α = β = γ ≠ 90º

An illustration of the primitive rhombohedral cell is provided below.



Calcite and sodium nitrate are made up of simple rhombohedral unit cells.

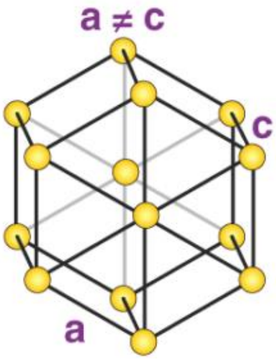
7. Hexagonal System

The only type of hexagonal Bravais lattice is the *simple hexagonal cell*. It has the following relations between cell sides and angles.

a = b ≠ c

α = **β** = 90º and **γ** = 120º

An illustration of a simple hexagonal cell is provided below.



Zinc oxide and beryllium oxide is made up of simple hexagonal unit cells. Thus, it can be noted that all 14 possible Bravais lattices differ in their cell length and angle relationships.

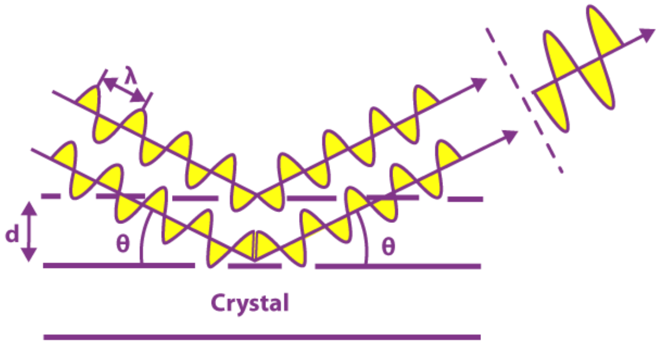
X-Ray Diffraction

X-ray diffraction, phenomenon in which the atoms of a crystal, by virtue of their uniform spacing, cause an interference pattern of the waves present in an incident beam of X-rays. The atomic planes of the crystal act on the X-rays in exactly the same manner as does a uniformly ruled diffraction grating on a beam of light. A beam of X-rays contacts a crystal with an angle of incidence θ. It is reflected off the atoms of the crystal with the same angle θ. The X-rays reflect off atomic planes in the crystal that are a distance *d* apart. The X-rays reflecting off two different planes must interfere constructively to form an interference pattern; otherwise, the X-rays would interfere destructively and form no pattern. To interfere constructively, the difference in path length between the beams reflecting off two atomic planes must be a whole number (*n*) of wavelengths (λ), or *n*λ. This leads to the Bragg law $n\lambda = 2d \sin\theta$. By observing the interference pattern, the internal structure of the crystal can be deduced.

What is Bragg's Law?

Bragg's law is a special case of Laue diffraction, which determines the angles of coherent and incoherent scattering from a crystal lattice. When X-rays are incident on a particular atom, they make an electronic cloud move like an electromagnetic wave. The movement of these charges radiates waves again with similar frequency, slightly blurred due to different effects, and this phenomenon is known as Rayleigh scattering. Basically, this law explains the relationship between an x-ray light shooting and its reflection from a crystal surface.

Bragg's Equation



According to Bragg Equation:

nλ = 2d sinΘ

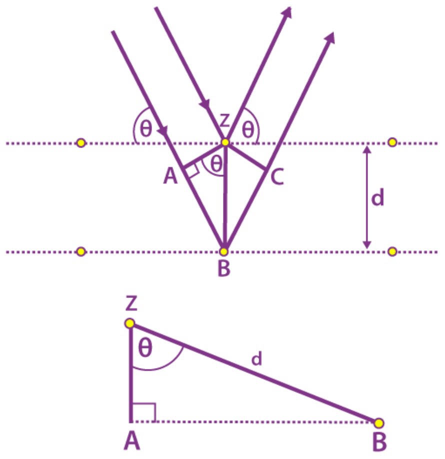
Therefore, according to the equation of Bragg’s Law:

The equation explains why the faces of crystals reflect X-ray beams at particular angles of incidence (Θ, λ).

The variable d indicates the distance between the atomic layers, and the variable The variable d indicates the distance between the atomic layers, and the variable λ specifies the wavelength of the incident X-ray beam and n as an integer. This observation illustrates the X-ray wave interface, called X-ray diffraction (XRD) and proof of the atomic structure of crystals. Bragg was also awarded the Nobel Prize in Physics for identifying crystal structures starting with NaCl, ZnS, and diamond. In addition, to understand the structure of every state of matter by any beam, e.g., ions, protons, electrons, neutrons, with a wavelength similar to the length between the molecular structures, diffraction was developed.

Derivation of Bragg’s Law

Consider the following figure of beams in which the phases of the beams coincide when the incident angle is equal to the reflecting angle. The incident beams are parallel to each other until they reach point z. When they are at point z, they strike the surface and travel upwards. At point B, the second beam scatters. AB + BC is the distance travelled by the second beam. The extra distance is known as the integral multiple of the wavelength.



$n\lambda = AB + BC$

We also know that $AB = BC$

$n\lambda = 2AB$ (equation 1)

d is the hypotenuse of the right triangle Abz. Ab is the opposite of the angle θ.

$AB = d \sin\theta$ (equation 2)

Substituting equation 2 in equation 1

$n\lambda = 2d \sin\theta$

Applications of Bragg's Law

There are numerous applications of Bragg's law in the field of science. Some common applications are given in the points below.

In the case of XRF (X-ray fluorescence spectroscopy) or WDS (Wavelength Dispersive Spectrometry), crystals of known d-spacings are used for analysing crystals in the spectrometer.

In XRD (X-ray diffraction) the inter-planar spacing or d-spacing of a crystal is used for characterization and identification purposes.

Solved Examples

Example 1:

The wavelength of the X-rays is 0.071 nm which is diffracted by a plane of salt with 0.28 nm as the lattice constant. Determine the glancing angle for the second-order diffraction. Assume the value of the salt plane to be 110, and the given salt is rock salt.

Solution:

Given:

Wavelength of the X-rays = 0.071 nm, Lattice constant = 0.28 nm

Plane = 110, Order of diffraction = 2

Glancing angle =?

Using Bragg's law: $2d \sin \Theta = n\lambda$

Rock salt has FCC, therefore, $d=a/\sqrt{}h^2+k^2+l^2$

Substituting the values, $d=0.28\times10^{-9}/\sqrt{}1^2+1^2+0^2=0.28\times10^{-9}/\sqrt{}2$ x m

Substituting in the Bragg's equation,

$\Theta = 21°$

Example 2:

The wavelengths of first-order X-rays are 2.20 Å at 27°8'. Find the distance between the adjacent Miller planes.

Solution:

Using Bragg's law,

$2d \sin \Theta = n\lambda$

Where, $n = 1$, $\lambda = 2.20$ Å, $\Theta = 27°8'$

Substituting the values, we get

$d = 2.20$ Å

What is Packing in Solids?

Packing in solids defines crystalline solid structures. When comes to the crystal structure, the centres of ions, molecules, and atoms are located on the lattice points. The lattice points are decided by how the constituent atoms, ions or molecules are arranged or packed in a solid. Atoms are presumed to be spherical to describe the structures and bonding of metallic crystals.

Principle of Packing in Solids

- ✓ Particle whether ions, atoms, or molecules in a crystal, is filled with lattice points in a crystal lattice.
- ✓ The constituent particles try their best to be packed together very closely, to attain the maximum closed-packed structure.
- ✓ The packing is such that the which is empty between the constituent atoms, molecules or ions is minimum.
- ✓ Because of this arrangement, the maximum possible crystal density is attained
- ✓ Close packing relates to crystal stability.

What are Voids in Crystal Structure?

In the case of a crystal lattice formed by a simple cubic unit cell the occupied space by constituent particles is to the extent of 52.4% and 47.6% space is unoccupied empty space is called void. In body centered cubic structure, the space occupied is about 68% and the void is about 32%. While in the case of face centered cubic structure the occupied space is to the extent of 74% and the void is reduced to 26%. Closest packing deals with the most efficient arrangement of spheres occupying most of the available space and reducing the empty space to a minimum in the crystal lattice.

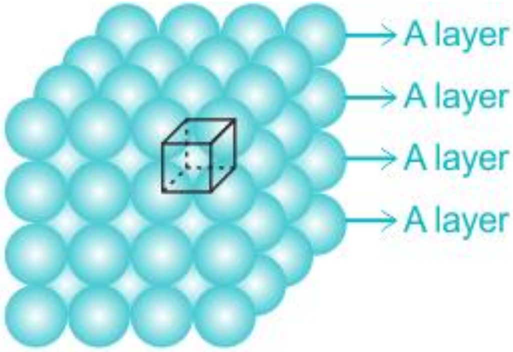
Stages of Packing

The arrangement may be made in three systematic stages. The first stage consists of a linear arrangement of the constituent particles in a row. This constitutes a one-dimensional arrangement of particles. Repeating linear one-dimensional arrangements one after another, a planar two-dimensional structure is obtained. Finally, in the third stage, the planar arrangement of the particles is extended to a three-dimensional arrangement by placing conveniently the planar layers one over another.

Stage I: Linear packing in one direction

The constituent particles of the crystalline solids are represented by spheres of equal size. The linear arrangement of spheres in one dimension can be made in a unique way by arranging the spheres in one row touching one another. Each sphere in a row has two neighbouring spheres on either side to make the contact.

The spheres at the two ends are exceptions. The coordination number of the particles in one dimension is two, as each particle is in contact with two neighbouring particles in one dimension. The linear arrangement in one dimension may be in any one direction i.e. about x, y, z or any other direction is as follows

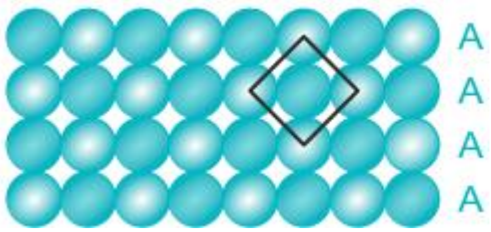


Stage lI: Planar packing arrangement of spheres

Ona linear crystal structure may be employed to generate two-dimensional planar crystal structure by placing one dimensional linear structure one over the other to form multiple rows. This stacking of rows can be done in two different ways.

AAAA Type Arrangement

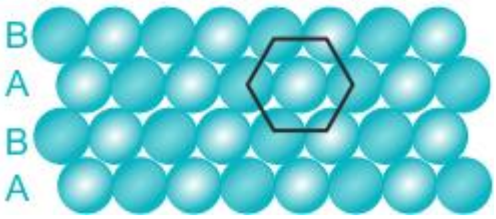
Different one-dimensional identical rows of spheres are placed one over the other in such a way that each sphere in a row is placed over another sphere of another row and so on. So finally, all spheres of different rows align vertically as well as horizontally as shown in the figure. In this structure arrangement, all crests of the spheres are aligned and all the depressions formed by the arrangement are also aligned. The locations of spheres in each row are identical in all rows in a planar structure. Hence, if the first row is called A type then all other rows are also called A type and the planar two dimensional arrangement is called AAAA type as shown in the figure.



The planar structure is said to be square close packing. It is evident from the figure that the coordination number of the sphere is 4. If the centres of 4 neighbouring spheres surrounded by any central sphere are joined then a square is formed. Hence packing is called square close packing.

ABAB type arrangement

A firm and closest type of arrangement may be made by arranging successive rows by placing crests of the spheres of one row into depression or troughs formed between adjacent spheres of the next row and the arrangement is continued. In this arrangement, the unoccupied area is reduced considerably and the arrangement becomes closest and firm. The arrangement of spheres in neighbouring rows does not match with each other. The crests of the sphere in one row are in contact with the troughs or depressions between spheres of another row and so on. If the first row is of A type then the second row is of B type and the third row will again be of A type and the fourth row will again be of B type and so on. Hence, this planar form of arrangement is called ABAB type of arrangement. Each sphere is in contact with 6 spheres. Therefore, in two-dimensional arrangements, the coordination number is 6. The arrangement is as shown below



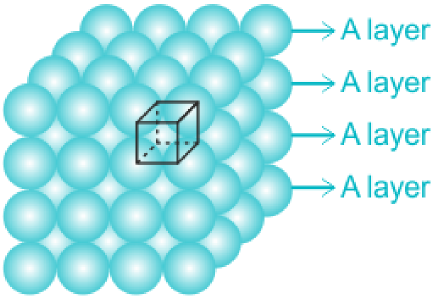
On careful observation, we can see that the holes are present between the two adjacent rows. In square close packing, the size of the holes is comparable with the size o the spheres and the shape of the square and each sphere is surrounded by four square-shaped holes. In hexagonal close packing, the size of the hole becomes very small as compared to size of the spheres and its shape becomes triangular. The numbers of triangular holes are doubled. The apices of the triangular holes are alternately pointing upward and downward. Each sphere is surrounded by six triangular holes.

Stage Ill: Three-dimensional packing

Two dimensional AAAA type of square close-packed crystal structures or ABAB type of hexagonal close-packed crystal structures can be used separately to build three-dimensional crystal structures.

AAAA type: Simple cubic structure

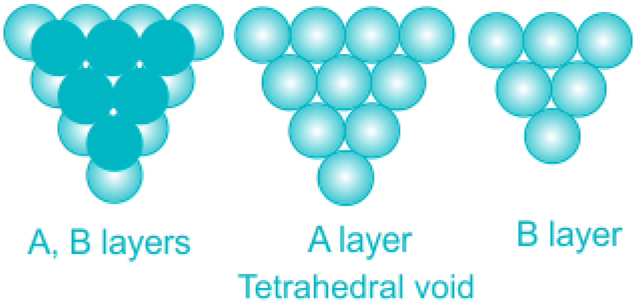
AAAA type of two-dimensional crystal layers is placed one over the other such that all the spheres of the successive layers are exactly above the spheres of the lower layers. All spheres of different layers of the crystal structures are perfectly aligned horizontally and also, vertically so that any unit cell of the crystal has a simple cubic structure as shown in the figure.



It is evident from the figure that each sphere is surrounded by six spheres, 4 in the layer of the sphere and one in the layer above and one below the layer. Hence coordination number of the sphere participating in this formation of a simple cubic structure is six. There is more empty space in the simple cubic structure.

ABAB type: Hexagonal close packed structure

The empty space present in the simple cubic crystal structure can be reduced and packing is made most efficient by staking ABAB types of two-dimensional crystal layers. Consider two ABAB type planar two-dimensional crystal structures as shown in the figure. In both, structures the central spheres are surrounded by six spheres in each layer. Now consider that the spheres of the second layer are packed into depressions between the spheres of the first layer. This makes the packing of two layers efficient and it also reduces the empty space between the adjacent layers and spheres that are closest packed. The first layer, though it is of ABAB type, is now conveniently called A type. The second ABAB layer spheres are fitted in the depressions of the A type layer and conveniently called the B type layer and the arrangement of two layers is called AB type and is shown in the figure.



If AB type arrangement of two layers is viewed from the top it may appear as shown in the figure.

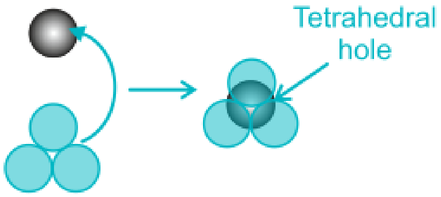
Thus we can conclude that,

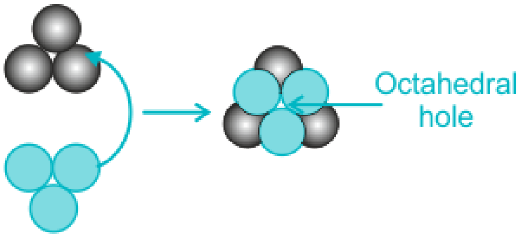
✓ Only half the number of triangular open spaces of lower layer A are completely covered by spheres of upper layer B. This constitutes a tetrahedral hole in the lower layer A formed by four spheres, three in the lower layer A and one sphere in the upper layer B.

✓ Simultaneously new tetrahedral holes (voids) are also created by three neighbouring spheres of the top layer and one sphere of the lower layer.

✓ The remaining half of the triangular open spaces of the lower layer are partially covered by the three neighbouring spheres of the upper layer and a new type of open space is formed by a total of six spheres. This open space is called an octahedral void.

The formation of tetrahedral and octahedral voids is shown in the figure.

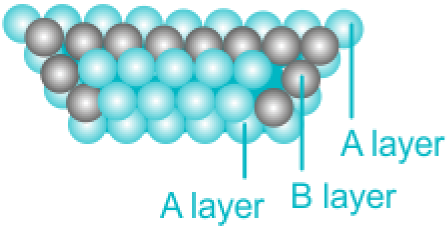


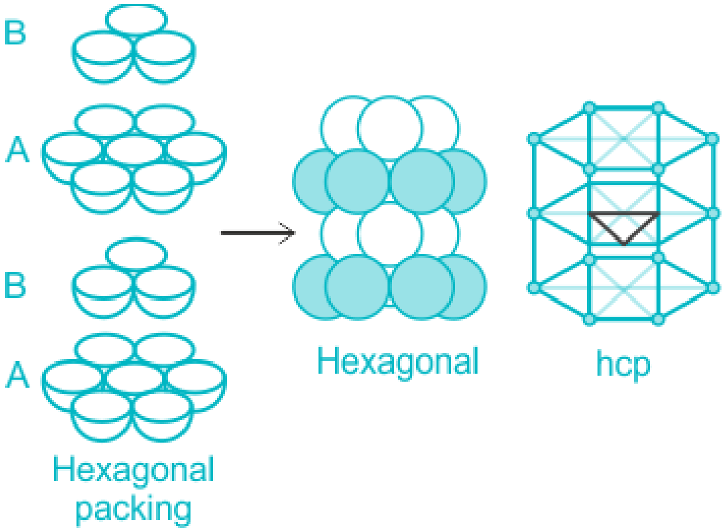


In short, there are two types of depressions formed at the end of fixing B layer over A layer, the octahedral voids and tetrahedral voids. Hence, the third layer can be fitted into the second layer in two ways.

1. Placing the spheres of the third layer into the tetrahedral voids

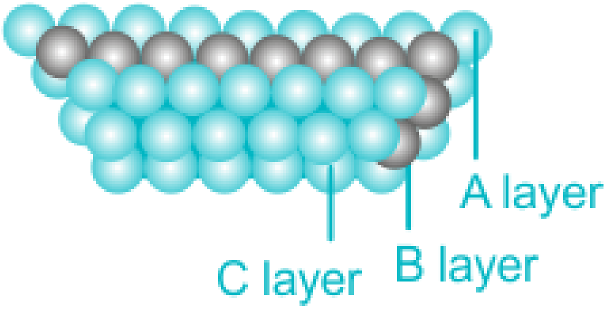
The tetrahedral voids of the second layer are covered by the spheres of the third layer, then it is evident that all spheres of the third layer are exactly over the spheres of the first layer and the fourth layer has to be fitted like the second layer i.e. the overall arrangement becomes ABAB type. The generated crystal structure is called hexagonal close packed (hcp) structure. The three-laver crystal structure of the ABAB type and the exploded view is shown in the figure below.





2. Placing the spheres of the third layer into octahedral voids

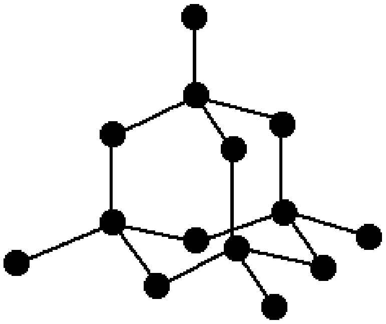
The third layer may be placed over the second layer such that all the spheres of the third layer fit in octahedral voids. This arrangement of the third layer is different from than arrangements of layers A and layer B. The different arrangement is called C type and the structure is called ABC type If the stacking of layers is continued then it is found that every fourth layer is aligned with the first layer spheres. Hence the complete arrangement is called ABCABC type. This is shown in the figure below. The ABC type arrangement is called a cubic close packed (ccp) structure. This structure is the same as face-centered cubic structure The exploded view of ABCABC type of arrangement is shown below.



In the hcp and ccp structures, each sphere has 6 neighbouring spheres in its own layer, 3 spheres in the layer above and 3 spheres in the layer below it. Thus, a single sphere is surrounded by twelve spheres. Therefore, the coordination number of spheres in ABAB type or ABCABC type is the same. The packing cannot be made more efficient as it is not possible to increase the coordination number beyond 12.

Diamond

Carbon has an electronic arrangement of 2,4. In diamond, each carbon shares electrons with four other carbon atoms - forming four single bonds.



In the diagram some carbon atoms only seem to be forming two bonds (or even one bond), but that's not really the case. We are only showing a small bit of the whole structure. This is a giant covalent structure - it continues on and on in three dimensions. It is not a molecule, because the number of atoms joined up in a real diamond is completely variable - depending on the size of the crystal.

Physical Properties of Diamond

✓ has a very high melting point (almost 4000°C). Very strong carbon-carbon covalent bonds have to be broken throughout the structure before melting occurs.

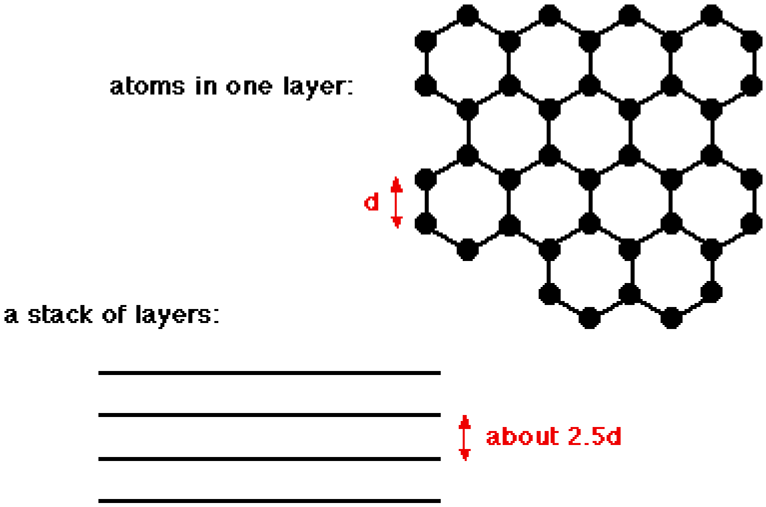
✓ It is very hard. This is again due to the need to break very strong covalent bonds operating in 3-dimensions.

✓ It doesn't conduct electricity. All the electrons are held tightly between the atoms, and aren't free to move.

- ✓ It insoluble in water and organic solvents. There are no possible attractions which could occur between solvent molecules and carbon atoms which could outweigh the attractions between the covalently bound carbon atoms.

Graphite

Graphite has a layer structure which is quite difficult to draw convincingly in three dimensions. The diagram below shows the arrangement of the atoms in each layer, and the way the layers are spaced.



Notice that you cannot really draw the side view of the layers to the same scale as the atoms in the layer without one or other part of the diagram being either very spread out or very squashed. In that case, it is important to give some idea of the distances involved. The distance between the layers is about 2.5 times the distance between the atoms within each layer. The layers, of course, extend over huge numbers of atoms - not just the few shown above. You might argue that carbon has to form 4 bonds because of its 4 unpaired electrons, whereas in this diagram it only seems to be forming 3 bonds to the neighbouring carbons. This diagram is something of a simplification, and shows the arrangement of atoms rather than the bonding.

The Bonding in Graphite

Each carbon atom uses three of its electrons to form simple bonds to its three close neighbors. That leaves a fourth electron in the bonding level. These "spare" electrons in each carbon atom become delocalized over the whole of the sheet of atoms in one layer. They are no longer associated directly with any particular atom or pair of atoms, but are free to wander throughout the whole sheet. The important thing is that the delocalized electrons are free to move anywhere within the sheet - each electron is no longer fixed to a particular carbon atom. There is, however, no direct contact between the delocalized electrons in one sheet and those in the neighboring sheets. The atoms within a sheet are held together by strong covalent bonds - stronger, in fact, than in diamond because of the additional bonding caused by the delocalized electrons. So what holds the sheets together? In graphite you have the ultimate example of van der Waals dispersion forces. As the delocalized electrons move around in the sheet, very large temporary dipoles can be set up which will induce opposite dipoles in the sheets above and below - and so on throughout the whole graphite crystal. Graphite has a high melting point, similar to that of diamond. In order to melt graphite, it isn't enough to loosen one sheet from another. You have to break the covalent bonding throughout the whole structure. It has a soft, slippery feel, and is used in pencils and as a dry lubricant for things like locks. You can think of graphite rather like a pack of cards - each card is strong, but the cards will slide over each other, or even fall off the pack altogether. When you use a pencil, sheets are rubbed off and stick to the paper. Graphite has a lower density than diamond. This is because of the relatively large amount of space that is "wasted" between the sheets. Graphite is insoluble in water and organic solvents - for the same reason that diamond is insoluble. Attractions between solvent molecules and carbon atoms will never be strong enough to overcome the strong covalent bonds in graphite. conducts electricity. The delocalized electrons are free to move throughout the sheets. If a piece of graphite is connected into a circuit, electrons can fall off one end of the sheet and be replaced with new ones at the other end.

Imperfection in solids

There is no such thing as a perfect crystal. Crystalline imperfections (or defects) are always present. In addition, impurity atoms are always present. Any irregularity in the pattern of crystal arrangement in a solid lattice is called imperfection in solids. The occurrence of defects takes place when crystallization (the process of formation of crystals) occurs at a very fast or at an intermediate rate. This is because particles don’t get enough time to arrange themselves in a regular pattern. It is useful to classify crystal lattice defects by their dimension. The 0-

dimensional defects affect isolated sites in the crystal structure, and are hence called point defects. An example is a solute or impurity atom, which alters the crystal pattern at a single point. The 1-dimensional defects are called dislocations. They are lines along which the crystal pattern is broken. The 2-dimensional defects are surfaces, such as the external surface and the grain boundaries along which distinct crystallites are joined together. The 3-dimensional defects change the crystal pattern over a finite volume. They include precipitates, which are small volumes of different crystal structure, and also include large voids or inclusions of second phase particles.

POINT DEFECTS

A point defect disturbs the crystal pattern at an isolated site. It is useful to distinguish intrinsic defects, which can appear in a pure material, from extrinsic defects, which are caused by solute or impurity atoms. Intrinsic defects There are 4 types of point defects:

1. Stoichiometric defect

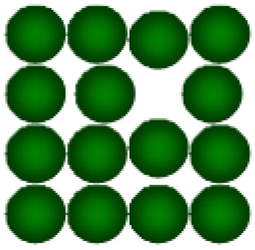
2. Frenkel defect

3. Schottky defect

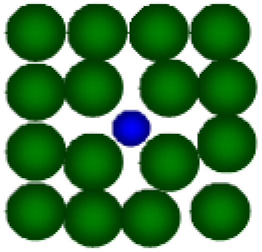
4. Non-Stoichiometric defect

1. Stoichiometric Defect:

In this kind of point defect, the ratio of positive and negative ions (Stoichiometric) and electrical neutrality of a solid is not disturbed. Sometimes it is also known as intrinsic or thermodynamic defects. Fundamentally, they are of two types: • Vacancy defect: When an atom is not present at their lattice sites, then that lattice site is vacant and it creates a vacancy defect. Due to this, the density of a substance decreases. • Interstitial defect: It is a defect in which an atom or molecule occupies the intermolecular spaces in crystals. In this defect, the density of the substance increases. A non-ionic compound mainly shows vacancy and interstitial defects. An ionic compound shows the same in Frenkel and Schottky defect.



Vacancy



Interstitial impurity

2. Frenkel Defect:

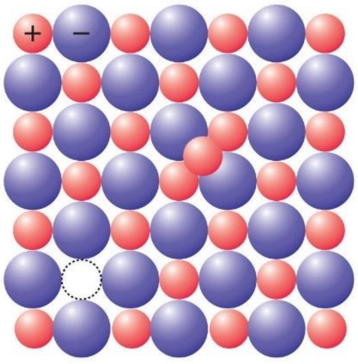
In ionic solids generally, the smaller ion (cation) moves out of its place and occupies an intermolecular space. In this case, a vacancy defect is created on its original position and the interstitial defect is experienced at its new position.

- It is also known as dislocation defect.

- The density of a substance remains unchanged.

- It happens when there is a huge difference in the size of anions and cations.

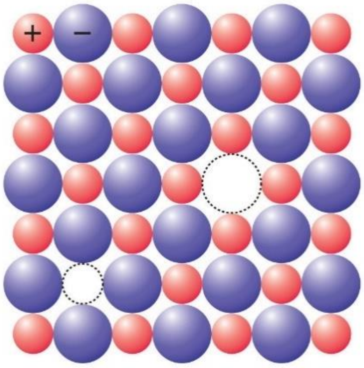
- Example: ZnS and AgCl.



(b) Frenkel defect

3. Schottky Defect

- This kind of vacancy defects is found in Ionic Solids. But in ionic compounds, we need to balance the electrical neutrality of the compound so an equal number of anions and cations will be missing from the compound. • It reduces the density of the substance. • In this, the size of cations and anions are of almost the same. • Examples: NaCl, CsCl



(a) Schottky defect

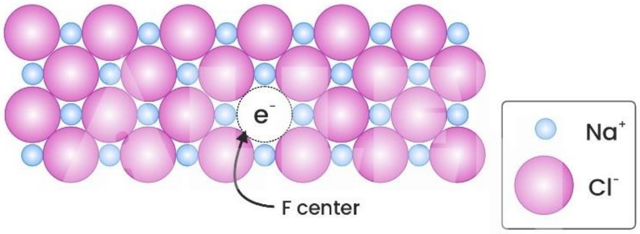
Non-Stoichiometric Defects

The defects discussed so far do not disturb the stoichiometry of the crystalline substance. However, a large number of non-stoichiometric inorganic solids are known which contain the constituent elements in non-stoichiometric ratio due to defects in their crystal structures. These defects are of two types:

(a) Metal Excess Defect and

(b) Metal Deficiency Defect.

(i) Metal Excess Defect Metal excess defect due to anionic vacancies: In this case, negative ions may be missing from their lattice sites leaving holes in which the electrons remain entrapped to maintain the electrical neutrality. This type of defect is observed in those crystals which are likely to form Schottky Defects. For example, Alkali metal halides like NaCl and KCl show this type of defect. When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl– ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form Na+ ions. The released electrons diffuse into the crystal and occupy anionic sites. As a result, the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called F centres (from the German word Farbenzenter for colour centre). They impart yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals. Similarly, excess of lithium makes LiCl crystals pink and excess of potassium makes KCl crystals violet.



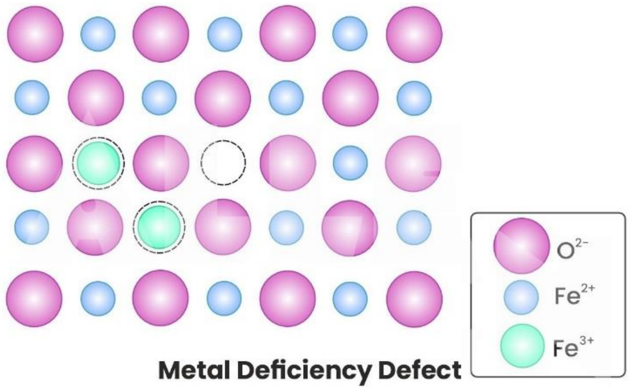
Metal Excess Defect

Metal excess defect due to the presence of extra cations at interstitial sites: In this case, there are extra positive ions occupying interstitial sites and the electrons in another interstitial sites to maintain electrical neutrality. The defect may be visualised as the loss of non-metal atoms which leave their electrons behind. The excess metal ions occupy interstitial positions. The common example is Zinc Oxide. Zinc oxide is white in colour at room temperature. On heating it loses oxygen and turns yellow.

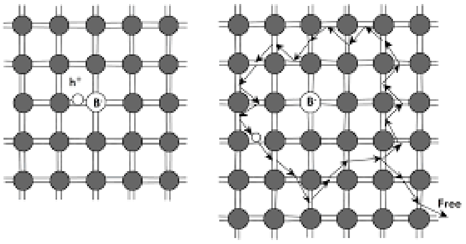
ZnO —-> Zn2+ + ½ O2 +2e–

Now there is excess of zinc in the crystal and its formula becomes Zn1+xO. The excess Zn2+ ions move to interstitial sites and the electrons to neighbouring interstitial sites.

b) Metal Deficiency Defects These contain a smaller number of positive ions than negative ions. These arise due to two ways: (i) Cation Vacancies: In some cases, the positive ions may be missing from their lattice sites. The extra negative charge may be balanced by some nearby metal ion acquiring two positive charges instead of one. This type of defect is possible in metals which show variable oxidation states. The common examples of compounds having this defect are ferrous oxide, ferrous sulphide, nickel oxide etc. (ii) Extra anions occupying interstitial sites: In the case, the extra anions may be occupying interstitial positions. The extra negative charge is balanced by the extra charges on the adjacent metal ions. Such type of defect is not common because the negative ions usually very large and they cannot easily fit into the interstitial sites.



Extrinsic defects The extrinsic point defects are foreign atoms, which are called solutes if they are intentionally added to the material and are called impurities if they are not. The foreign atom may occupy a lattice sites, in which case it is called a substitutional solute (or impurity) or it may fill an interstitial site, in which case it is called an interstitial solute. Since the interstitial sites are relatively small, the type of the solute is largely determined by its size. Small atoms, such as hydrogen, carbon and nitrogen are often found in interstitial sites. Larger atoms are usually substitutional. Extrinsic point defects affect almost all engineering properties, but they are particularly important in semiconducting crystals, where extrinsic defects are used to control electrical properties, and in structural metals and alloys, where extrinsic defects are added to increase mechanical strength. Effects of Substitutional defects in solids: • If the foreign atom is smaller in size as compared to the original atom of the solid, the neighbouring atoms will remain in tensile stress. • If the foreign atom is larger in size as compared to the original atom of the solid, the neighbouring atoms will remain in compressive stress. • So, presence of foreign atom may distort the original lattice structure. • Presence of substantial number of foreign atoms can change the mechanical and thermal properties of the solid. However, this is sometime beneficial, and thus substitutional defects can be applied in a controlled way to enhance various properties of the solid.



UNIT-3

NUCLEAR CHEMISTRY

Radioactivity

Nucleons two subatomic particles that reside in the nucleus known as protons and neutrons Isotopes Differ in number of neutrons only. They are distinguished by their mass numbers. 233 92U Is Uranium with an atomic mass of 233 and atomic number of 92. The number of neutrons is found by subtraction of the two numbers nuclide applies to a nucleus with a specified number of protons and neutrons. Nuclei that are radioactive are radionuclides and the atoms containing these nuclei are radioisotopes.

Nuclear equations

Some atoms are unstable. Emission of particles or electromagnetic radiation is one way to gain stability.

Alpha radiation

Uranium 238 undergoes alpha decay in attempt to be stable

$$^{238}_{92}U \rightarrow {}^{234}_{90}Th + {}^{4}_{2}He$$

daughter nuclide: the nuclide formed from the decay

Parent nuclide: the original nuclide undergoing decay

Beta radiation

Consists of a stream of beta particles which are high speed electrons. Represented by the symbol $^{0}_{-1}e$

Iodine-131 is an example of a radioactive isotope that undergoes Beta emission. (an antineutrino also emitted)

$$^{131}_{53}I \rightarrow {}^{131}_{54}Xe + {}^{0}_{-1}e$$

Notice the atomic number increases. Beta emission results in the conversion of a neutron ($^{1}_{0}n$) to a proton ($^{1}_{1}p$)

$$^{1}_{0}n \rightarrow {}^{1}_{1}p + {}^{0}_{-1}e$$

(the electron comes from the neutron being converted NOT from the electron cloud)

Gamma radiation

High energy photons (electromagnetic radiation of a short wavelength) Gamma radiation does not change the mass or atomic number and is represented as $^{0}_{0}$ It almost always accompanies other radioactive emission because it represents the energy lost when the remaining nucleons reorganize into more stable arrangements. Generally, you do not show gamma rays when writing nuclear equations.

Positron emission

A positron is a particle that has the same mass as an electron but opposite charge. The positron is represented as $^{0}_{1}e$. Carbon-11 is an example of a particle that undergoes positron emission.

$$^{11}_{6}C \rightarrow {}^{11}_{5}B + {}^{0}_{1}e$$

Notice the atomic number goes down. Positron emission is the effect of converting a proton to a neutron

$$^{1}_{1}p \rightarrow {}^{1}_{0}n + {}^{0}_{1}e$$

Electron capture

Capture by the nucleus on an inner shell electron of the electron cloud. Rubidium-81 does this

$$^{81}_{37}Rb + {}^{0}_{-1}e \text{ (orbital electron) } \rightarrow {}^{81}_{36}Kr$$

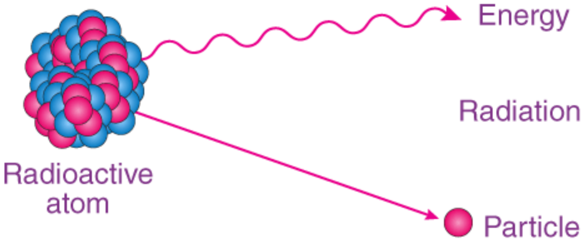
Electron capture has the effect of positron emission, converting a proton to a neutron

$$^{1}_{1}p \rightarrow {}^{1}_{0}n + {}^{0}_{1}e$$

Half-life period

Half-Life or previously known as Half-Life Period is one of the common terminologies used in Physics to describe the radioactive decay of a particular sample or element within a certain period of time. Students of nuclear Physics will come across the term often while studying the subject. However, this concept is also widely used to describe various types of decay processes especially exponential and non-exponential decay.

Apart from physics, the term is used in medical sciences to represent the biological half-life of certain chemicals in the human body or in drugs.



Radioactive displacement law of Fajans and Soddy

The law of radioactive displacements, also known as Fajans's and Soddy's law, in radiochemistry and nuclear physics, is a rule governing the transmutation of elements during radioactive decay. It is named after Frederick Soddy and Kazimierz Fajans, who independently arrived at it at about the same time in 1913.

The law describes which chemical element and isotope is created during the particular type of radioactive decay:

In alpha decay, an element is created with an atomic number less by 2 and a mass number less by four of that of the parent radioisotope, e.g.:

In beta decay, the mass number remains unchanged while the atomic number becomes greater by 1 than that of the parent radioisotope, e.g.:

This corresponds to β^- decay or electron emission, the only form of beta decay which had been observed when Fajans and Soddy proposed their law in 1913. Later, in the 1930s, other forms of beta decay known as β^+ decay (positron emission) and electron capture were discovered, in which the atomic number becomes less by 1 than that of the parent radioisotope, e.g.:

Geiger-Nuttall Rule

The Geiger-Nuttall Rule is a fundamental concept in nuclear chemistry that explains the relationship between the half-life of an α-emitting radioactive isotope and the energy of the emitted α particles. This empirical rule, discovered by Hans Geiger and John Mitchell Nuttall in 1911, provides critical insight into the nature of α decay and the underlying quantum mechanical processes.

At its core, the Geiger-Nuttall Rule states that isotopes emitting high-energy α particles tend to have shorter half-lives, while those emitting lower-energy α particles exhibit longer half-lives. This relationship arises because the emission of an α particle involves quantum tunnelling through the Coulomb barrier created by the positive charges of the nucleus. The height and width of this barrier depend on the charge and size of the nucleus, as well as the energy of the α particle.

Mathematically, the Geiger-Nuttall Rule is expressed as:

$$\log(T_{1/2}) = -aE_{\alpha}^{-1/2} + b$$

Here, $T_{1/2}$ represents the half-life of the radioactive isotope, Eα is the kinetic energy of the emitted α particle, and a and b are constants specific to a family of isotopes. The negative relationship between $\log(T_{1/2})$ and $E\alpha^{-1/2}$ reflects the inverse proportionality between decay rate and particle energy. This rule is rooted in quantum mechanics, where the probability of α particles tunnelling through the Coulomb barrier depends exponentially on their energy. Higher-energy α particles face a lower effective barrier, increasing the likelihood of successful emission and thereby shortening the half-life.

The Geiger-Nuttall Rule has practical applications in nuclear science and engineering. It aids in predicting the decay rates of radioactive isotopes, particularly in the context of natural radioactivity, nuclear power generation, and geochronology. For instance, the decay series of uranium and thorium, essential in radiometric dating techniques, are well-described by this rule. However, the Geiger-Nuttall Rule has its limitations. It is primarily applicable to α decay and does not encompass other decay modes, such as β decay or spontaneous fission. Additionally, the empirical constants a and b vary across different isotopic families, requiring experimental determination for each case.

Isobars, Isotopes, and Isotones

Atoms can be classified in various ways based on the relationships between their atomic number (Z), neutron number (N), and mass number (A). Among these classifications, **isobars**, **isotopes**, and **isotones** are particularly significant in understanding atomic and nuclear structure. These categories provide insights into the similarities and differences in the composition and behavior of atoms, making them essential topics in chemistry and physics.

Isobars

Isobars are atoms of different chemical elements that have the same mass number (A) but differ in their atomic numbers (Z). In other words, while their total number of protons and neutrons remains the same, the distribution between protons and neutrons differs. This distinction leads to differences in their chemical properties since they belong to different elements.

Example:

- Argon-40 ($_{18}^{40}Ar$) and calcium-40 ($_{20}^{40}Ca$) are isobars.

✓ Both have a mass number of 40 (A=40).

✓ Argon has 18 protons and 22 neutrons, while calcium has 20 protons and 20 neutrons.

1. **Chemical Properties**: Isobars have different chemical properties due to differing atomic numbers, which determine the element's identity and electronic configuration.
2. **Physical Properties**: They often exhibit similar nuclear properties, such as mass and nuclear binding energy, but their stability may vary.

Isobars play an important role in nuclear reactions, including radioactive decay. For instance, beta decay often converts one isobar into another by changing a neutron into a proton or vice versa.

Isotopes

Isotopes are atoms of the same element that have the same atomic number (Z) but different mass numbers (A). This means isotopes have the same number of protons but differ in their number of neutrons. Since isotopes belong to the same element, they share identical chemical properties but may differ in their nuclear stability and physical properties.

Example:

Hydrogen isotopes:

Protium ($_{1}^{1}H$): 1 proton, 0 neutrons.

Deuterium ($_{1}^{2}H$): 1 proton, 1 neutron.

Tritium ($_{1}^{3}H$): 1 proton, 2 neutrons.

1. **Chemical Properties**: Isotopes of the same element behave similarly in chemical reactions because they have the same electronic configuration.
2. **Physical Properties**: Isotopes differ in properties such as mass, density, and nuclear stability.

Radioactive Dating: Carbon-14, an isotope of carbon, is used in radiocarbon dating to determine the age of ancient artifacts.

Medical Uses: Isotopes like iodine-131 are used in medical imaging and treatment.

Energy Production: Isotopes like uranium-235 are essential in nuclear reactors.

Isotones

Isotones are atoms that have the same number of neutrons (N) but differ in their atomic numbers (Z) and mass numbers (A). These nuclei belong to different elements, as their proton count is not the same, leading to differing chemical properties.

Example:

Carbon-14 ($_{6}^{14}C$) and nitrogen-15 ($_{7}^{15}N$) are isotones.

Both have 8 neutrons but differ in their number of protons.

Chemical Properties: Isotones belong to different elements and thus have distinct chemical properties.

Nuclear Behavior: Despite chemical differences, isotones are studied to understand neutron-rich or neutron-deficient nuclei and their stability.

Isotones are important in nuclear physics, especially in studying neutron capture reactions and nuclear stability.

Mirror Nuclei and Iso-Diapheres

In nuclear chemistry and physics, certain types of nuclei exhibit unique relationships based on the number of protons and neutrons they contain. These include **mirror nuclei**, which reveal symmetries in nuclear structure, and **iso-diapheres**, which emphasize the balance or imbalance between protons and neutrons. Understanding these concepts provides deeper insights into nuclear forces, stability, and radioactive decay.

Mirror Nuclei

Mirror nuclei are a fascinating pair of atomic nuclei where the number of protons (Z) in one nucleus is equal to the number of neutrons (N) in the other nucleus, and vice versa. These nuclei have the same total number of nucleons (A), which means their mass numbers are identical. However, their atomic numbers differ due to the interchange of protons and neutrons.

For example, consider tritium (${}_1^3H$) and helium-3 (${}_2^3He$). Tritium has 1 proton and 2 neutrons, while helium-3 has 2 protons and 1 neutron. Despite this difference, both nuclei have the same mass number (A=3) because their total number of nucleons is the same.

Mirror nuclei are particularly significant in the study of nuclear forces and symmetries. They illustrate the concept of **isospin symmetry**, which is a theoretical framework used to describe similarities in the behavior of protons and neutrons under the nuclear force. The examination of mirror nuclei helps scientists understand how nuclear forces operate when the roles of protons and neutrons are interchanged.

One important application of mirror nuclei lies in exploring the stability of neutron-rich and proton-rich nuclei. By comparing mirror pairs, researchers can investigate how variations in the neutron-to-proton ratio affect nuclear binding energy and decay processes.

Iso-Diapheres

Iso-diapheres, on the other hand, are nuclei that share the same difference between the number of neutrons and protons. This means that for a pair of iso-diapheres, the value of N−Z remains constant, even though the total number of nucleons (A) may differ. This constant difference provides a way to classify nuclei based on their neutron-to-proton ratio rather than their mass or atomic numbers.

For instance, carbon-14 ($_6^{14}C$) and oxygen-16 ($_8^{16}O$) are examples of iso-diapheres. Carbon-14 has 6 protons and 8 neutrons (N−Z=2), while oxygen-16 has 8 protons and 8 neutrons (N−Z=0). While these nuclei differ in their total number of protons and neutrons, the consistent difference between neutrons and protons offers a unique perspective on their nuclear properties.

Iso-diapheres are particularly useful for studying nuclear stability. The neutron-to-proton ratio is a critical factor in determining whether a nucleus is stable or prone to decay. By examining iso-diapheres, researchers can gain insights into the effects of neutron excess or deficiency on nuclear structure and decay pathways.

Nuclear Isomerism

Nuclear isomerism refers to the phenomenon where a single nucleus exists in different energy states, despite having the same number of protons (Z) and neutrons (N). These states are known as **nuclear isomers** and are characterized by differences in their energy levels and, often, their half-lives. Nuclear isomers can be broadly categorized into the **ground state** and **metastable states**. The ground state is the nucleus's most stable and lowest energy configuration, while metastable states (denoted with "m," e.g., ^{99m}Tc) are higher energy states that may persist for extended periods before decaying.

Types of Nuclear Isomers

Shape Isomers: These occur when a nucleus adopts different shapes, such as spherical or deformed, which correspond to different energy levels.

Spin Isomers: Caused by variations in the spin alignments of protons and neutrons, resulting in distinct energy configurations.

Excited State Isomers: These arise when a nucleus is in an energetically excited state due to nuclear reactions or other processes, temporarily delaying its return to the ground state.

Examples of Nuclear Isomers

Technetium-99m(^{99m}Tc):

A widely used isomer in medical imaging, particularly in diagnostic scans. It emits gamma rays, making it ideal for imaging without significant radiation damage.

Hafnium-178m(^{178m}Hf):

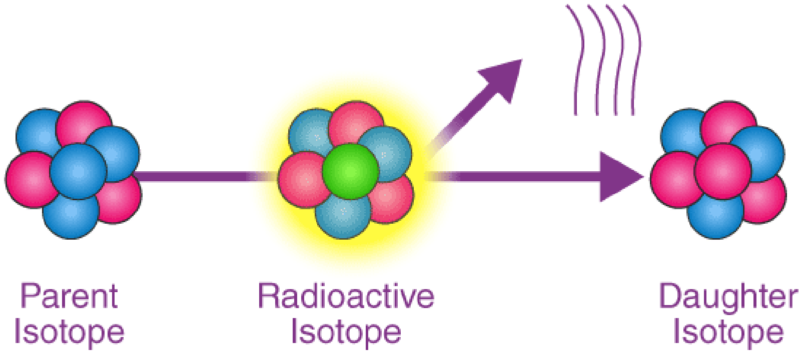
Known for its long-lived metastable state, this isomer is studied for applications in controlled gamma-ray release.

Uranium-236m(^{236m}U):

Formed during specific nuclear reactions, this isomer provides insights into nuclear behavior under high-energy conditions.

Radioactive decay

Radioactivity is the phenomenon exhibited by an atom’s nuclei due to nuclear instability. In 1896, Henry Becquerel discovered this phenomenon. Radioactivity is a process by which the nucleus of an unstable atom loses energy by emitting radiation. A small amount of Uranium compound was wrapped in black paper and put in a drawer containing photographic plates. These plates were later examined, and the results revealed that there had been an exposure. Radioactive Decay is the term introduced for this phenomenon. The elements or isotopes that emit radiation and go through radioactivity are known as radioactive elements.



Magic numbers

Specific numbers of protons or neutrons in an atomic nucleus that result in highly stable configurations. These numbers correspond to fully filled shells of protons or neutrons within the nucleus, analogous to the concept of electron shells in atoms. Nuclei with magic numbers exhibit exceptional stability and lower binding energy compared to other nuclei.

The concept of magic numbers is a cornerstone of the **nuclear shell model**, which explains the arrangement of nucleons (protons and neutrons) in energy levels within the nucleus.

What Are the Magic Numbers?

The experimentally determined magic numbers are: 2,8,20,28,50,82 and these numbers represent the total count of protons or neutrons in a nucleus that form closed nuclear shells. For example:

^{4}He (2 protons and 2 neutrons) and ^{16}O (8 protons and 8 neutrons) are particularly stable because they have magic numbers of both protons and neutrons.

Units in Nuclear Physics: Curie, Rutherford, and Roentgen

In nuclear physics and radiology, specific units are used to quantify different aspects of radiation, such as activity, radiation intensity, and exposure. Some of the commonly used units are **Curie (Ci)**, **Rutherford (Rd)**, and **Roentgen (R)**. These units are important for measuring and understanding radioactive materials and their effects.

1. Curie (Ci)

The **Curie** is a unit of radioactivity that measures the decay rate of radioactive material. It is named after Marie and Pierre Curie, pioneers in the study of radioactivity.

Definition: One Curie (1 Ci) is defined as the amount of a radioactive substance that undergoes 3.7×10^{10} disintegrations per second (or decays per second). This corresponds to the radioactivity of 1 gram of radium-226.

1 Ci=3.7×10^{10} (disintegrations per second)

Use: The Curie unit is primarily used to measure the activity of radioactive isotopes. For example, a sample of radium-226 that has a radioactivity of 1 Ci is undergoing

3.7×10^{10} disintegrations per second.

Relation to SI Units: The SI unit of radioactivity is the **Becquerel (Bq)**, where 1 Bq = 1 disintegration per second.

$1\ \text{Ci} = 3.7 \times 10^{10}\ \text{Bq}$

2. Rutherford (Rd)

The **Rutherford** is a unit of radioactivity used to measure the rate of radioactive decay, named after the physicist Ernest Rutherford.

Definition: One Rutherford (1 Rd) is defined as 1 million disintegrations per second (1,000,000 dps).

$1\ \text{Rd} = 10^6$ disintegrations per second

Use: The Rutherford is commonly used in certain contexts, especially in older literature or in the context of nuclear physics experiments where large amounts of radioactivity are involved.

Relation to Other Units: 1 Rutherford is equivalent to 1 million disintegrations per second, or 10610^6106 disintegrations per second.

$1\ \text{Rd} = 10^6\ \text{dps}$

This is roughly equivalent to 27 microCuries (μCi) in terms of the Curie.

3. Roentgen (R)

The **Roentgen** is a unit of radiation exposure that measures the ionization produced in air by X-rays or gamma rays. It is named after Wilhelm Röntgen, the discoverer of X-rays.

Definition: One Roentgen (1 R) is defined as the amount of X-ray or gamma radiation that produces 2.58×10^{-4} coulombs of charge in 1 kilogram of air (at standard temperature and pressure).

$$1\ \text{R} = 2.58 \times 10^{-4}\ \text{C/kg of air}$$

Use: The Roentgen is used to quantify the amount of ionization caused by radiation in the air, and is particularly useful in radiology and radiological protection.

Relation to Other Units: The Roentgen is mainly used for X-rays and gamma rays. However, its use has become less common in favor of the SI unit **Gray (Gy)** for measuring absorbed dose of radiation in materials, especially for biological tissues.

Nuclear Stability and Neutron-Proton Ratio

Nuclear stability refers to the ability of a nucleus to remain intact without undergoing spontaneous radioactive decay. The stability of a nucleus is influenced by a variety of factors, with the **neutron-to-proton (N/Z) ratio** playing a central role in determining whether a nucleus is stable or unstable. This ratio helps to explain why some nuclei are stable, while others are prone to decay.

The Neutron-Proton Ratio (N/Z)

The **neutron-to-proton ratio (N/Z)** is the ratio of neutrons (N) to protons (Z) in an atomic nucleus. This ratio is crucial because the balance between protons and neutrons affects the forces acting within the nucleus.

Protons are positively charged particles that experience electrostatic repulsion from other protons, making it necessary for the nucleus to have a sufficient number of neutrons to counteract this repulsion.

Neutrons, which are electrically neutral, help to stabilize the nucleus by contributing to the **nuclear force**, a strong force that binds protons and neutrons together.

In light nuclei (small atomic numbers), a 1:1 ratio of protons to neutrons is optimal for stability. As atomic numbers increase, however, more neutrons are needed to balance the increased electrostatic repulsion between protons.

Binding energy

Binding energy is a fundamental concept in nuclear chemistry that plays a pivotal role in determining the stability of atomic nuclei. It is the energy required to break a nucleus into its individual nucleons-protons and neutrons. The greater the binding energy of a nucleus, the more stable it is. Conversely, nuclei with lower binding energies tend to be less stable and may undergo nuclear reactions like fission or fusion to achieve a more stable state.

This concept is central to understanding various processes in nuclear chemistry, including radioactive decay, nuclear fission, nuclear fusion, and the energy production in stars and nuclear reactors. Binding energy is also intimately linked with mass defect, a phenomenon where the mass of a nucleus is less than the sum of the individual masses of its protons and neutrons. Binding energy refers to the energy required to separate a nucleus into its constituent nucleons (protons and neutrons). It is a measure of how strongly the nucleons are bound together by the nuclear force. The stronger the binding force, the more energy is required to separate the nucleons.

The binding energy can be calculated using the mass defect of a nucleus, which is the difference between the mass of a nucleus and the total mass of its individual nucleons. According to Einstein's famous equation:

$E=\Delta m\cdot c^2$

Where:

E is the binding energy of the nucleus,

Δm is the mass defect (the difference between the mass of the nucleus and the sum of the masses of the individual protons and neutrons),

c is the speed of light, which is approximately 3×10^8 m/s.

The mass defect is the result of the conversion of mass into energy when the nucleus is formed. This energy is released as binding energy.

Uses of Isotopes in Various Fields

Isotopes, which are variants of elements that have the same number of protons but different numbers of neutrons, have numerous applications across a variety of fields, ranging from medicine and industry to environmental science and archaeology. Some isotopes are stable, while others are radioactive, making them especially useful in different scientific and technological applications.

1. Medical Applications

Isotopes, particularly radioactive ones, are widely used in medicine for both diagnostic and therapeutic purposes.

Diagnostic Imaging: Radioisotopes are used in nuclear medicine for imaging procedures. One of the most common uses is in positron emission tomography (PET) and single-photon emission computed tomography (SPECT), where isotopes like technetium-99m (Tc-99m) are used to trace and image the function of organs or detect diseases. Tc-99m is ideal for imaging due to its short half-life (6 hours) and its ability to emit gamma rays, which are detectable by medical imaging machines.

Cancer Treatment (Radiotherapy): Certain radioactive isotopes are used in the treatment of cancer. Cobalt-60 (Co-60), for example, is used in external beam radiotherapy to irradiate and destroy cancerous cells. Another example is iodine-131 (I-131), which is used to treat thyroid cancer, as iodine is preferentially absorbed by the thyroid.

Brachytherapy: This involves placing radioactive isotopes directly inside or very close to the tumor. Iridium-192 (Ir-192) and radium-226 (Ra-226) are commonly used in this treatment for cancers such as prostate cancer.

Tracer Studies: Radioisotopes are also used in metabolic studies and to track the flow of substances in biological systems. For example, carbon-14 (C-14) is used to trace the metabolic pathways of carbon-containing molecules in the body.

2. Industrial Applications

Isotopes have a range of uses in industrial applications, particularly for measurement, detection, and material analysis.

Radiography:

Radioactive isotopes are used for industrial radiography to inspect the internal structure of materials, particularly metals and welded joints. Iridium-192 and cobalt-60 are frequently used in this type of non-destructive testing, helping to detect faults such as cracks or defects in the material that would not be visible externally.

Thickness Gauging: Cobalt-60 and iridium-192 are used in gauging devices to measure the thickness of materials in industries like paper, plastics, and steel production. This process helps maintain product consistency and quality.

Tracer Studies in Industry: Stable isotopes are also used in industrial applications to track the flow of materials in pipelines, determine leakage, and study chemical reactions. For instance, sulfur-35 (S-35) can be used to monitor the movement of sulfur compounds in various chemical processes.

Radioactive Dating: In archaeology and geology, carbon-14 (C-14) is used to date organic materials, such as bones, wood, and cloth. The half-life of C-14 is approximately 5,730 years, making it useful for dating objects that are up to around 50,000 years old.

3. Environmental and Agricultural Applications

Isotopes have a variety of uses in environmental and agricultural research, including tracing pollution and improving farming techniques.

Environmental Tracing: Isotopes like tritium (H-3) and carbon-14 (C-14) are used to trace water movement, pollution sources, and chemical pathways in ecosystems. They can be used to track the movement of pollutants, study the effects of climate change, and understand groundwater flow patterns.

Soil Fertility and Water Usage: Stable isotopes such as nitrogen-15 (N-15) and oxygen-18 (O-18) are used to study nutrient cycles, track the movement of water through plants, and understand how fertilizers are absorbed by crops. This helps optimize farming practices, reducing the impact on the environment while improving crop yields.

Pest Control: Carbon-14 isotopes have been used in studies related to pest control by tracking the behavior of insecticides or the movement of pest populations. Isotopes can also help in understanding the ecological impact of pest control methods.

4. Scientific Research

Isotopes are used extensively in scientific research across a wide range of disciplines.

Nuclear Physics: Isotopes play a vital role in nuclear physics experiments. For example, uranium-235 (U-235) and plutonium-239 (Pu-239) are used in nuclear reactors and in the study of nuclear fission. They also help scientists investigate the behavior of materials under nuclear conditions.

Radioactive Tracers: In various chemical and biological research fields, radioactive isotopes like phosphorus-32 (P-32) and sulfur-35 (S-35) are used as tracers to study reaction mechanisms, molecular interactions, and biochemical pathways.

Neutron Activation Analysis: Isotopes are used in neutron activation analysis (NAA), a technique that measures the concentration of elements in a sample by bombarding it with neutrons. The gamma rays emitted by the isotopes in the sample are then analyzed to determine the concentration of elements in the sample. This technique is widely used in the analysis of materials like metals, minerals, and environmental samples.

5. Food and Agriculture

Sterilization and Preservation: Cobalt-60 and cesium-137 (Cs-137) are used in food irradiation to kill bacteria, parasites, and pests, thereby extending shelf life and ensuring food safety. This process is used for fruits, vegetables, and even meat products.

Pest Control and Sterilization: The sterile insect technique uses radioactive isotopes to sterilize male insects (such as fruit flies), which are then released into the wild to reduce pest populations. This method has been successfully used to control agricultural pests without the use of chemical pesticides.

6. Space and Astronomy

Isotopes are also used in space exploration and astronomy to understand the composition of celestial bodies and the processes that occur in outer space.

Cosmic Ray Research: Stable isotopes, like helium-3 (He-3) and neon-21 (Ne-21), are used in cosmic ray research to study the composition of cosmic radiation and the formation of the universe. Isotopes help researchers track the origin and properties of particles in space.

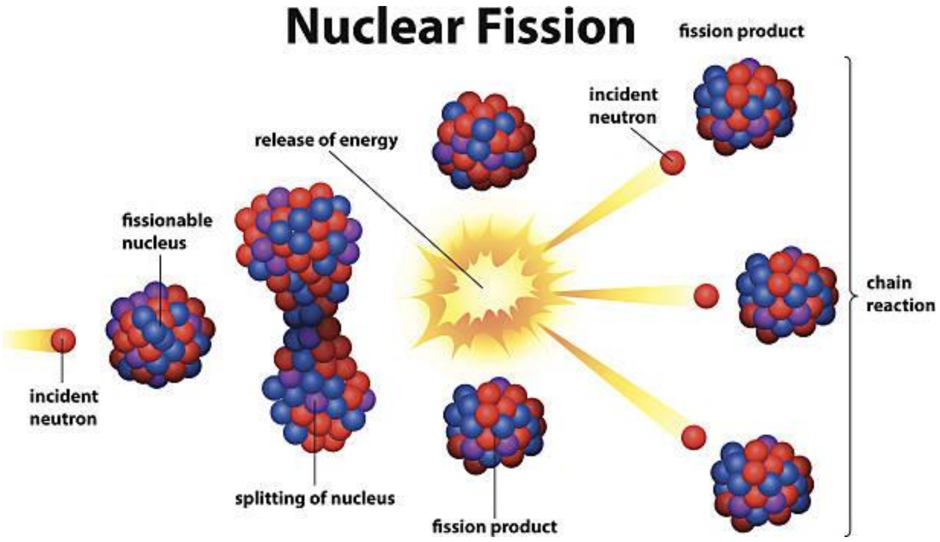
Solar Energy and Solar Flares: Isotopes like carbon-12 and carbon-14 are used to study the composition of stars, including the Sun, and to understand processes like nuclear fusion. These isotopes help scientists study how energy is produced in stars and the dynamics of solar flares.

Nuclear Fusion and Fission

Nuclear fusion and fission are two fundamental processes by which energy is released from the nucleus of an atom. While both are nuclear reactions, they involve vastly different mechanisms and are associated with distinct applications and challenges. These processes are central to understanding the principles of nuclear energy and its utilization in various fields, including power generation and astrophysics.

Nuclear Fission

Nuclear fission is the process by which a heavy atomic nucleus splits into two or more smaller nuclei, accompanied by the release of a large amount of energy. This process is often initiated by the absorption of a neutron.



Mechanism of Fission

Initiation:

✓ A neutron collides with a heavy nucleus, such as uranium-235 (U-235) or plutonium-239 (Pu-239), causing the nucleus to become unstable.

✓ The resulting unstable nucleus splits into two smaller nuclei (fission fragments) and releases additional neutrons.

Chain Reaction:

✓ The released neutrons can further collide with other fissionable nuclei, triggering a self-sustaining chain reaction.

✓ This principle is the basis for nuclear reactors and atomic bombs.

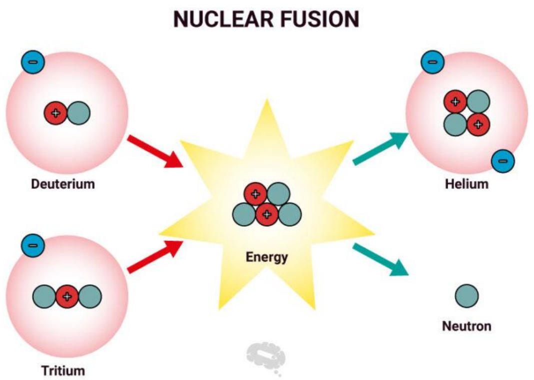
Energy Release:

✓ The energy released in fission comes from the conversion of a small amount of mass into energy, as described by Einstein's equation, $E=mc^2$

✓ A significant portion of this energy appears as kinetic energy of the fragments and neutrons, as well as gamma radiation.

Nuclear Fusion

Nuclear fusion is the process by which two light atomic nuclei combine to form a heavier nucleus, releasing an enormous amount of energy. Fusion is the process that powers the Sun and other stars.



Mechanism of Fusion

Initiation:

- ✓ Two light nuclei, such as isotopes of hydrogen (deuterium, D, and tritium, T), are brought close enough to overcome the electrostatic repulsion between their positively charged protons.
- ✓ This requires extremely high temperatures (millions of degrees) to provide sufficient kinetic energy for the nuclei to collide.

Fusion Reaction:

- ✓ Deuterium and tritium nuclei combine to form a helium nucleus and a high-energy neutron.
- ✓ The reaction releases about 17.6 MeV of energy:

$$^{2}H+^{3}H\rightarrow^{4}He+n+energy$$

Energy Release:

- ✓ Like fission, the energy is released due to the mass difference between the reactants and products, following $E=mc^2$.
- ✓ The energy is primarily in the form of kinetic energy of the products.

Nuclear power plants in india

Tarapur Atomic Power Station (TAPS): India's first nuclear power plant, which began operating in Maharashtra in 1969

Kaiga Atomic Power Plant: Located in Karnataka, this plant has four 220MW PHWR reactors that became operational between 1999 and 2011

Kudankulam Nuclear Power Plant (KKNPP): The largest nuclear power station in India, located in Tamil Nadu's Tirunelveli district

Kakrapar Atomic Power Station (KAPS): Located in Gujarat, near the Tapi, Mandvi, and Surat rivers

Kalpakkam atomic power station: Built entirely in India

Bhimpur: Located in Shivpuri, Madhya Pradesh, with a capacity of 2800 MW

Narora Atomic Power Station (NAPS): Located in Uttar Pradesh

Ionizing radiation is a form of energy. Unlike some other types of energy, such as heat (infrared radiation) or visible light, the human body cannot sense exposure to ionizing radiation. Nonetheless, absorption of ionizing radiation energy by body tissues causes changes to the chemical makeup of living cells. The type and thickness of material needed to make an effective barrier or shield around a source of ionizing radiation varies a great deal depending on the type of ionizing radiation. Beta radiation is a stream of tiny charged particles that can be stopped by a thin layer of plastic, glass, wood, metal and most other common materials. X-rays and Gamma rays are very similar to sunlight in that they are not particles, just electromagnetic waves. While sunlight will pass through only a few materials, such as window glass, X-rays and Gamma rays penetrate easily through most materials. However, even they can be blocked by a sufficient thickness of lead. Ionizing radiation is also similar to other forms of radiation in that the intensity of the radiation exposure decreases very quickly as you move away from the radiation source. Just as moving a short distance closer to or farther from a fireplace causes a large change in how warm you feel; keeping just a few feet away from where someone is handling radioactive material will almost eliminate your exposure.

Disposal of Radioactive Waste and Safety Measures Radioactive waste is an unavoidable byproduct of nuclear energy production, medical applications, and various industrial processes. Its disposal is one of the most critical aspects of nuclear technology, requiring carefully designed strategies to minimize the risks to human health and the environment. Since radioactive isotopes in waste materials can remain hazardous for years or even millennia, their management involves methods that ensure long-term containment and isolation from living organisms.

Types of Radioactive Waste

Radioactive waste is classified based on its level of radioactivity, half-life, and origin, which determines the disposal strategy. Low-level waste (LLW) is the least hazardous, comprising materials like contaminated clothing, tools, and laboratory instruments. These items generally emit low levels of radiation and can often be safely disposed of in shallow burial sites, sometimes after minimal treatment. Intermediate-level waste (ILW), which includes reactor components and filtration resins, contains higher concentrations of radioactivity and often requires shielding during handling. This type of waste demands more robust containment systems, such as engineered repositories designed to prevent leakage.

High-level waste (HLW) represents the most dangerous category and primarily consists of spent nuclear fuel and the byproducts of nuclear reprocessing. It is characterized by intense radioactivity and significant heat generation, necessitating advanced storage and disposal techniques. Additionally, transuranic waste (TRU), which contains elements heavier than uranium like plutonium, poses unique challenges due to its long half-lives and high toxicity. Such waste is primarily a result of nuclear weapons production and is often treated similarly to HLW.

Methods of Waste Disposal

Several methods have been developed to manage radioactive waste, each tailored to the specific type and level of hazard. Near-surface disposal is commonly employed for LLW, where waste is buried in shallow trenches or vaults and covered with layers of soil, clay, and concrete to act as barriers against radiation leakage. While effective for less hazardous materials, this approach is unsuitable for long-lived or highly radioactive waste. For ILW and HLW, deep geological disposal is widely regarded as the most secure method. This involves placing waste in specially constructed repositories located hundreds of meters underground, often in stable rock formations that act as natural barriers against radiation migration. The goal is to ensure the waste remains isolated for thousands of years until its radioactivity diminishes to safe levels. Finland’s Onkalo repository, the world’s first operational deep geological storage facility, exemplifies this approach. By contrast, the United States' Yucca Mountain project has faced significant political and logistical challenges, delaying its implementation. Reprocessing and recycling of spent nuclear fuel provide an alternative to direct disposal. In this process, usable isotopes like uranium-235 and plutonium-239 are extracted from the waste and reused as fuel, reducing the overall volume and radioactivity of the remaining material. However, reprocessing is expensive and has raised concerns about nuclear proliferation due to the potential misuse of separated plutonium. Vitrification is another advanced method for HLW disposal. Here, radioactive waste is immobilized by incorporating it into glass, which is then sealed in robust stainless-steel canisters. This technique not only stabilizes the waste but also significantly reduces the risk of leaching into the environment. For temporary storage, spent fuel rods are often placed in dry casks made of thick steel and concrete, providing safe containment until permanent solutions are available.

Safety Measures in Waste Management

Ensuring the safety of radioactive waste disposal involves multiple layers of precaution and rigorous monitoring. From the initial stage, waste is carefully categorized and treated to minimize its volume and hazard level. Storage facilities are designed with redundant barriers to prevent radiation escape, even under extreme conditions such as earthquakes or flooding. Continuous monitoring of these sites is essential to detect any early signs of material degradation or leakage. Transporting radioactive waste from nuclear plants to disposal facilities is another critical step requiring stringent safety protocols. Specially designed containers shield the waste during transit, while routes are planned to avoid densely populated areas and minimize risks. International cooperation plays a significant role in maintaining safety standards for radioactive waste management. Guidelines established by organizations like the International Atomic Energy Agency (IAEA) ensure that waste disposal practices adhere to globally recognized safety principles. Public engagement is also vital, as gaining the trust and support of local communities can facilitate the implementation of disposal projects.

Challenges and Future Directions Despite advancements in technology, the disposal of radioactive waste remains a complex challenge. Long-lived isotopes in HLW demand solutions that can ensure safety for tens of thousands of years, a scale beyond the lifespan of most human-made structures. Public opposition, high costs, and the risk of accidents add further layers of difficulty. However, ongoing research into innovative methods, such as transmutation of waste into less harmful isotopes and advanced reactor designs that produce minimal waste, offers hope for more sustainable solutions.

UNIT-4

HALOGEN DERIVATIVES

Nomenclature and Classes of Alkyl Halides

Alkyl halides, also known as haloalkanes, are organic compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine, or iodine). These compounds are significant in organic synthesis and industrial applications. Their nomenclature and classification are based on the number of halogen atoms, their position on the carbon chain, and the degree of substitution at the carbon atom bonded to the halogen.

Nomenclature of Alkyl Halides

The naming of alkyl halides follows the International Union of Pure and Applied Chemistry (IUPAC) rules:

Identify the Parent Hydrocarbon: Select the longest continuous carbon chain as the parent hydrocarbon.

Number the Carbon Chain: Number the carbon atoms such that the halogen atom(s) attached to the chain receive the lowest possible numbers.

Prefix with Halogen Names: Use prefixes like *fluoro*-, *chloro*-, *bromo*-, and *iodo*- to indicate the halogen atoms.

Indicate the Position and Quantity: Specify the position of the halogen on the carbon chain using numerical locants. Use prefixes like *di*-, *tri*-, and *tetra*- for multiple halogens.

Alphabetical Order: Arrange the substituent halogens in alphabetical order when naming the compound.

Examples:

CH_3CH_2Br: Bromoethane (common name: ethyl bromide).

$CH_3CH(Cl)CH_3$: 2-Chloropropane (common name: isopropyl chloride).

CCl_4: Tetrachloromethane (common name: carbon tetrachloride).

$CH_2BrCHBrCH_3$: 1,2-Dibromopropane.

Isomerism in Halogen Derivatives

Halogen derivatives of organic compounds exhibit isomerism due to variations in the arrangement of carbon atoms and halogen atoms within their molecular structure. Isomerism in these compounds can be broadly categorized into **structural isomerism** and **stereoisomerism**, each with distinct subtypes.

Structural Isomerism

Structural isomerism arises from differences in the connectivity of atoms within the molecule. The major types observed in halogen derivatives are:

Chain Isomerism:

Occurs when compounds have the same molecular formula but differ in the arrangement of the carbon chain.

Example:

$CH_3CH_2CH_2Cl$ (1-chloropropane).

$CH_3CHClCH_3$ (2-chloropropane).

Position Isomerism:

Arises when the position of the halogen atom differs within the same carbon chain.

Example:

$CH_3CH_2CH_2Cl$ (1-chloropropane).

$CH_3CHClCH_3$ (2-chloropropane).

Functional Group Isomerism:

In rare cases, halogen derivatives can exhibit functional group isomerism when the halogen atom forms a different type of bond (e.g., allylic or vinylic halides).

Example:

CH_3CH_2Cl (ethyl chloride).

$CH_2=CHCl$ (vinyl chloride).

Metamerism:

Observed in compounds with the same molecular formula but different alkyl groups attached to the halogen atom.

Example:

C_2H_5Br (bromoethane).

$CH_3CH_2CH_2Br$ (1-bromopropane).

Stereoisomerism

Stereoisomerism occurs when compounds have the same molecular formula and connectivity of atoms but differ in the spatial arrangement of atoms.

Geometrical Isomerism (Cis-Trans Isomerism):

Found in halogen derivatives of alkenes where restricted rotation around the double bond leads to different spatial arrangements of substituents.

Example:

Cis-1,2-dichloroethene (both Cl atoms on the same side of the double bond).

Trans-1,2-dichloroethene (Cl atoms on opposite sides).

Optical Isomerism:

Observed in halogen derivatives containing a chiral carbon atom (a carbon attached to four different groups).

Example:

2-bromobutane exists as two enantiomers, one dextrorotatory and the other levorotatory.

Examples of Isomerism in Halogen Derivatives

Structural Isomerism in Monohalogenated Alkanes:

For C_3H_7Cl:

1-chloropropane.

2-chloropropane.

Stereoisomerism in Dihalogenated Alkenes:

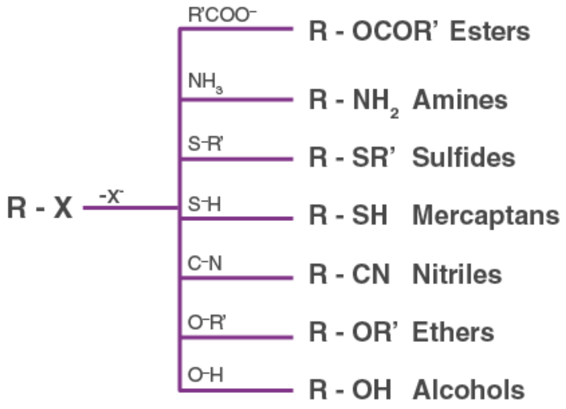
For $C_2H_2Cl_2$:

Cis-1,2-dichloroethene.

Trans-1,2-dichloroethene.

Nucleophilic substitution reaction

Nucleophilic substitution reaction is a class of organic reactions where one nucleophile replaces another. It is very similar to the normal displacement reactions which we see in chemistry, where, a more reactive element replaces a less reactive element from its salt solution. The group which takes electron pair and displaced from the carbon is known as “leaving group” and the molecule on which substitution takes place is known as “substrate”. The leaving group leaves as a neutral molecule or anion.



In nucleophilic substitution reactions, the reactivity or strength of nucleophile is called its nucleophilicity. So, in a nucleophilic substitution reaction, a stronger nucleophile replaces a weaker nucleophile from its compound. It can be illustrated roughly as follows:

$$R{-}LG + Nu^{\ominus} \rightarrow R{-}Nu + LG^{\ominus}$$

Where,

R = Alkyl group

LG = Leaving group (less nucleophilic)

$Nu^{\ominus} \rightarrow$ Stronger nucleophile

Example:

Consider a reaction of methyl bromide with sodium hydroxide, gives sodium bromide as a side product with methanol as the main product.

$$CH_3 - Br + O^{-}H \rightarrow CH_3 - OH + Br^{-}$$

Methyl bromide (Substrate) + Hydroxide ion (Nucleophile) → Methanol (Product) + Bromide ion

Mechanisms of Nucleophilic Substitution

The rate of nucleophilic substitution reactions not only depends on nucleophiles and leaving capacities but also on the mechanism by which the reaction takes place. There are two mechanisms proposed for nucleophilic substation reactions.

SN_2 Mechanism

It is called substitution nucleophilic bimolecular mechanism. It follows 2nd order kinetics and the rate law for a reaction following the SN_2 mechanism is as follows. For SN_2 reaction of the form

$$R-LG+Nu^{\Theta}\rightarrow R-Nu+LG^{\Theta}$$

$$r=K[R-LG][Nu^{\Theta}]$$

$[R-LG]$, $[Nu^{\Theta}]$=concentration of the substrates and nucleophile respectively

From the rate law, it is understood that the rate of SN_2 reaction depends both on the concentration of the substrate and the nucleophile. Therefore, both nucleophilicity of the nucleophile and the leaving capacity of the leaving group increases the rate of the reaction. The mechanism for SN_2 reaction is explained taking $CH_3 - X$ (methyl halide) and some nucleophile

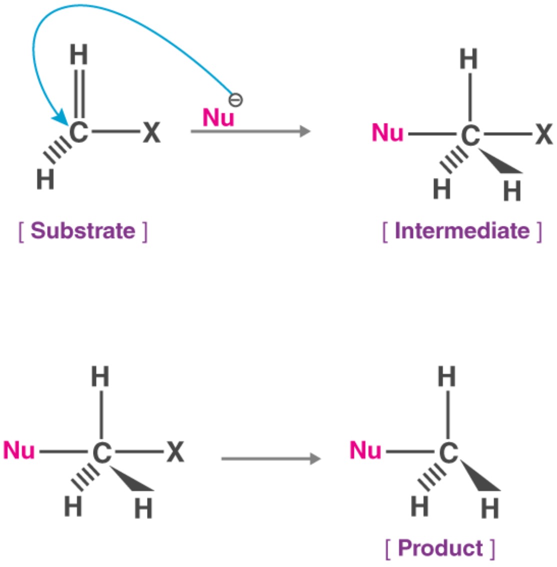
(Nu^{Θ})

as an example.

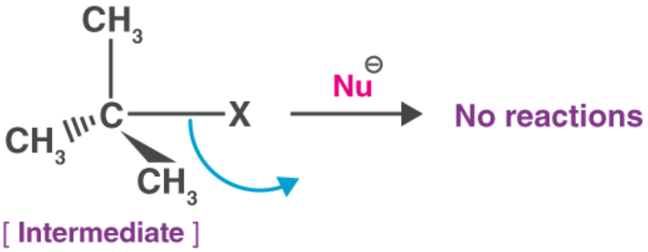
The overall reaction between the two is as follows.

$$CH_3-x+Nu^{\Theta}\rightarrow CH_3-Nu+x^{\Theta}$$

Mechanism:

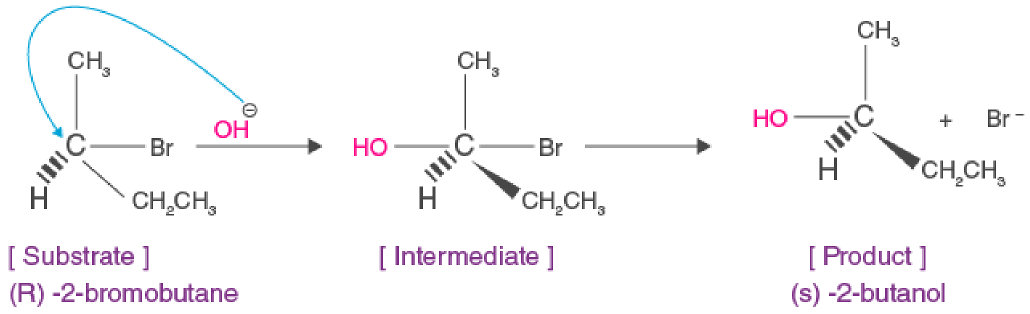


It is a single step process consisting of one intermediate. It proceeds through the backside (of the LG) attack of the incoming nucleophile to avoid repulsions, leading to an intermediate, which is indicated using two dotted lines between carbon – Nu and carbon-X. The two dotted lines in the intermediate indicate that the C – X bond is broken and the C – Nu bond is formed simultaneously. And at the end, C – x bond is completely broken and the c – Nu bond is completed formed. Since it's a backside attack of the nucleophile, the product will always have an inverted configuration wrt the substrate. Therefore, the SN$_2$ mechanism always results in "inversion of configuration". In case of t-butyl of chloride, SN$_2$ mechanism becomes increasingly difficult as the nucleophile will find it difficult to attack from the backside due to the presence of bulky methyl.



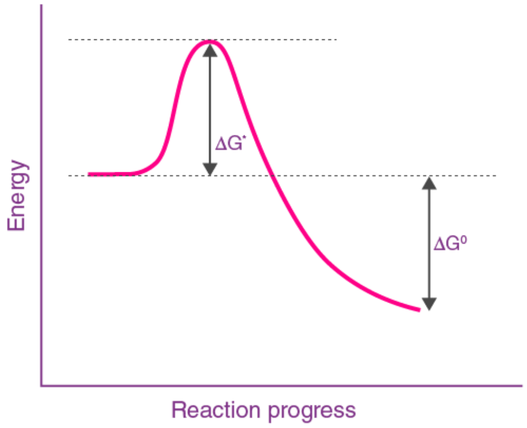
Highly crowded substrates will be less reactive towards the SN_2 mechanism. The order of reactivity of 1°, 2°, 3° halides is as follows. 1° > 2° > 3° (steric hindrance). The rates of SN_2 reactions are enhanced if polar aprotic solvents such as DMF, DMSO, etc are used as reaction mediums.

Example:



S_N2 Transition State

In a transition state of SN2 reaction, a carbon atom and other atoms are in a planar arrangement.



SN_1 Mechanism

It is called unimolecular nucleophilic substitution reaction. For SN_1, mechanism having R – X as substrate and

NuΘ as the incoming nucleophile,

the rate law can be presented as follows. R = k [R – x]

Where

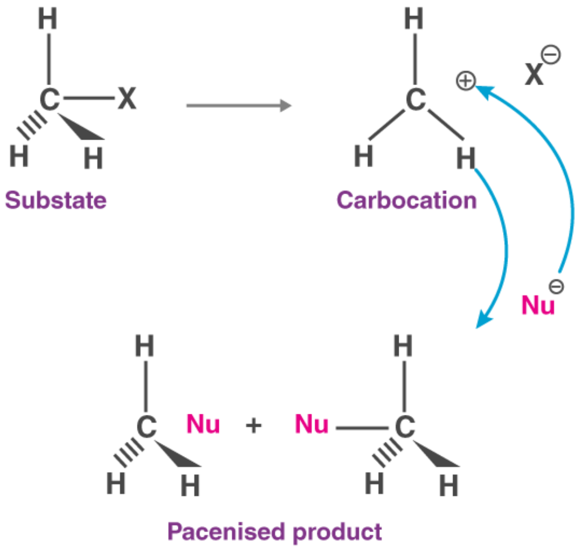
r = rate of SN_1 reaction

k = rate constant

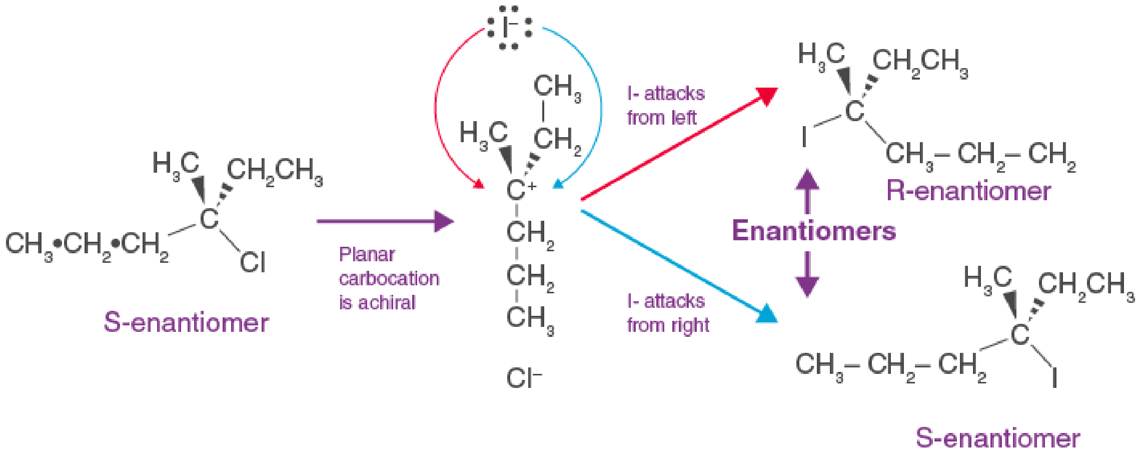
{R – X} = concentration of substrate.

From the above equation, we can see that the rate of SN_1 mechanism depends only on the concentration of the substrate and is independent of the concentration of the incoming nucleophile. Indirectly, the rate depends on leaving capacity of the leaving group but independent of the nucleophilicity of the incoming nucleophile.

Mechanism:



Example: Stereochemistry of SN1 reaction



It is a two-step process, 1st being the breaking of C – X Bond heterolytically to form a carbocation and XΘ and 2nd being the attack of nucleophile onto the carbocation. In a multistep process such as this, the rate-determining step is given by the slowest step and of the two steps above, the formation of the carbocation is the slowest step, and therefore the rate-determining step.

Here, unlike SN$_2$, the incoming nucleophile can attack from both sides (opp and the same side as LG). Therefore, the product will always be a racemized product (50% – 50% enantiomers of the same compound).

For different substrates, the rate of SN$_1$ depends linearly on the stability of carbocation formed. Therefore, the order of reactivity of 1°, 2°, 3° alkyl halides will be

3° > 2° > 1° (stability of carbocation).

Rate is increased when a polar protic solvent is used since it increases the ionisation to form carbocations.

alogen derivatives containing two or more halogen atoms per molecule are widely used in industrial processes, pharmaceuticals, and environmental applications. These compounds, commonly referred to as **di-, tri-, or tetra-halogen derivatives**, exhibit unique chemical and physical properties that make them valuable in diverse fields.

1. Nomenclature

The naming of di-, tri-, and tetra-halogen derivatives follows the IUPAC rules, similar to monohalogen derivatives, with specific prefixes to indicate the number and type of halogen atoms.

Identify the Parent Chain: The longest carbon chain is selected as the parent hydrocarbon.

Positioning of Halogens: Number the carbon atoms in the chain such that the positions of the halogen atoms receive the lowest possible locants.

Prefix for Multiple Halogens: Use prefixes like *di*-, *tri*-, and *tetra*- to indicate the number of identical halogen atoms.

Alphabetical Order for Different Halogens: If multiple types of halogens are present, list them in alphabetical order.

Examples:

CH_2Cl_2: Dichloromethane.

$CBrCl_3$: Bromotrichloromethane.

CF_4: Tetrafluoromethane.

2. Classification

Based on the Number of Halogens:

- ✓ **Dihalogen Derivatives**: Contain two halogen atoms (e.g., CH_2Cl_2).
- ✓ **Trihalogen Derivatives**: Contain three halogen atoms (e.g., $CHCl_3$).
- ✓ **Tetrahalogen Derivatives**: Contain four halogen atoms (e.g., CCl_4).

Based on the Position of Halogens:

✓ **Geminal Dihalides**: Two halogen atoms are attached to the same carbon atom (e.g., CH_2Cl_2).

✓ **Vicinal Dihalides**: Two halogen atoms are attached to adjacent carbon atoms (e.g., $CHClCH_2Cl$).

Isolated Polyhalides: Halogen atoms are separated by other atoms or groups.

Based on the Halogen Type:

✓ Contain identical halogens (e.g., CBr_2Cl_2).

✓ Contain different halogens (e.g., CFClBrI).

3. Preparation

Halogenation of Alkanes:

✓ Reaction of alkanes with halogens (Cl_2, Br_2) under UV light or heat.

✓ Example: $CH_4 + 2Cl_2 \rightarrow CH_2Cl_2 + 2HCl$.

Halogen Exchange Reactions:

✓ Alkyl halides react with halogen salts to form polyhalogen derivatives.

✓ Example: $CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$.

Addition to Alkenes/Alkynes:

✓ Halogens add across double or triple bonds to form vicinal dihalides.

✓ Example: $CH_2{=}CH_2 + Cl_2 \rightarrow CH_2ClCH_2Cl$.

Oxidation of Halogenated Compounds:

✓ Oxidation of mono- or dihalogenated compounds using halogenating agents.

4. Properties

Physical Properties:

✓ **Polarity**: More halogen atoms increase polarity.
✓ **Boiling Points**: Increase with molecular weight and halogen content.
✓ **Density**: Heavier halogens like bromine and iodine increase density.

Chemical Properties:

✓ **Reactivity**:

∗ Vicinal dihalides undergo elimination reactions to form alkenes.
∗ Polyhalogen derivatives can be dehalogenated under certain conditions.

✓ **Hydrolysis**: React with water or alkali to produce alcohols or acids. Example: $CHCl_3 + 3NaOH \rightarrow CHO + 3NaCl$.

5. Applications

Dihalogen Derivatives:

✓ **Dichloromethane (CH_2Cl_2)**: Solvent in paint removers and adhesives.
✓ **Ethylene dichloride (CH_2ClCH_2Cl)**: Used in PVC production.

Trihalogen Derivatives:

✓ **Chloroform ($CHCl_3$)**: Previously used as an anesthetic, now a solvent.
✓ **Bromoform ($CHBr_3$)**: Used in mineral separation and organic synthesis.

Tetrahalogen Derivatives:

✓ **Carbon Tetrachloride (CCl_4)**: Cleaning agent, but its use is restricted due to toxicity.
✓ **Freons (e.g., CF_2Cl_2)**: Refrigerants and propellants (gradually being replaced due to environmental concerns).

Environmental and Safety Considerations

While halogen derivatives are industrially important, they pose environmental risks such as ozone layer depletion (e.g., Freons) and toxicity (e.g., carbon tetrachloride). Safer alternatives and controlled usage are emphasized to mitigate these issues.

Aromatic Halogen Compounds

Aromatic halogen compounds are organic molecules containing one or more halogen atoms (F, Cl, Br, I) attached directly to an aromatic ring. These compounds are widely used in chemical synthesis, pharmaceuticals, and industrial processes due to their unique reactivity and stability.

Structure and Classification

Aromatic halogen compounds can be classified based on the number of halogen atoms and their position relative to each other on the aromatic ring.

Monohalogen Derivatives:

Contain one halogen atom attached to the aromatic ring.

Example: Chlorobenzene (C_6H_5Cl).

Polyhalogen Derivatives:

Contain two or more halogen atoms attached to the aromatic ring.

Examples:

Dichlorobenzene ($C_6H_4Cl_2$).

Trichlorobenzene ($C_6H_3Cl_3$).

Substituted Aromatic Halides:

Aromatic compounds where halogen atoms coexist with other substituents like alkyl groups, nitro groups, or hydroxyl groups.

Example: 2-Chloro-4-nitrotoluene.

Nomenclature

Base Name:

The compound is named as a derivative of benzene.

Halogen Substitution:

Halogen atoms are treated as substituents, and their positions are indicated using numbers or prefixes (ortho-, meta-, para- for disubstituted derivatives).

Priority in Substitution:

When other functional groups are present, the halogen atom is treated as a substituent unless it is part of a higher-priority group.

Examples:

C_6H_5Cl: Chlorobenzene.

$C_6H_4Cl_2$: 1,2-Dichlorobenzene (ortho-dichlorobenzene).

Preparation

Direct Halogenation:

Aromatic compounds react with halogens in the presence of a catalyst (Fe, $FeCl_3$, or $AlCl_3$) to form halogenated products.

Example:

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl \text{ (in the presence of } FeCl_3\text{).}$$

Sandmeyer Reaction:

Aromatic amines are converted to halogen derivatives through diazonium salts.

Example:

$$C_6H_5NH_2 \rightarrow C_6H_5N_2^+Cl^- \rightarrow C_6H_5Cl.$$

Finkelstein Reaction:

Halogen exchange reaction to replace one halogen atom with another.

Example:

$$C_6H_5Cl + NaI \rightarrow C_6H_5I + NaCl.$$

Gattermann Reaction:

Aromatic compounds react with halogen in the presence of copper powder.

Example:

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl \text{ (with Cu as a catalyst).}$$

Properties

Physical Properties:

Boiling and Melting Points: Increase with the number of halogen atoms due to higher molecular weight.

Solubility: Insoluble in water but soluble in organic solvents.

Density: Halogen derivatives are generally denser than water.

Chemical Properties:

Reactivity:

Halogens deactivate the aromatic ring toward electrophilic substitution due to their -I (inductive) effect. However, they direct further substitution to ortho and para positions due to their +M (resonance) effect.

Nucleophilic Substitution: Halogen atoms can be replaced by nucleophiles under suitable conditions.

Example Reactions:

Nitration:

$$C_6H_5Cl + HNO_3 \rightarrow p\text{-}ClC_6H_4NO_2 + o\text{-}ClC_6H_4NO_2.$$

Nucleophilic Substitution:

$$C_6H_5Cl + NaOH \rightarrow C_6H_5OH + NaCl \text{ (at high temperature and pressure).}$$

Applications

Pharmaceutical Industry:

Used in the synthesis of drugs such as antiseptics (chloroxylenol), and antihistamines.

Agrochemicals:

Aromatic halides are used in the production of herbicides, fungicides, and pesticides.

Polymers and Plastics:

Used as intermediates in the production of polymers like PVC.

Dyes and Pigments:

Halogenated aromatic compounds are precursors to synthetic dyes and pigments.

Solvents and Reagents:

Compounds like chlorobenzene and bromobenzene are widely used as solvents in organic synthesis.

Environmental Concerns and Safety

Aromatic halogen compounds, especially polyhalogenated derivatives, pose significant environmental risks due to their persistence and bioaccumulation. Proper handling and disposal are necessary to minimize ecological and health hazards. Examples include polychlorinated biphenyls (PCBs) and dioxins, which are toxic pollutants.

Aryl Alkyl Halides

Aryl alkyl halides are a class of organic compounds in which a halogen atom (F, Cl, Br, or I) is bonded to the carbon atom of an alkyl group that is directly attached to an aromatic ring. These compounds are unique due to the combined reactivity of the aromatic and alkyl halide functionalities.

Structure and Classification

Basic Structure:

A halogen atom is attached to the alkyl chain, which itself is connected to an aromatic ring.

General formula: $Ar–CH_2–X$, where Ar represents the aromatic ring and X is the halogen.

Examples:

Benzyl chloride ($C_6H_5–CH_2Cl$)

Benzyl bromide ($C_6H_5–CH_2Br$)

Benzyl iodide ($C_6H_5–CH_2I$)

Nomenclature

Base Name:

The compound is named as a derivative of the aromatic ring.

Substituent and Position:

The halogen and alkyl group are treated as substituents, and the positions on the ring are numbered if there are multiple substituents.

Examples:

C_6H_5–CH_2Cl Benzyl chloride

$C_6H_4(NO_2)$–CH_2Cl 4-Nitrobenzyl chloride.

Preparation

Halogenation of Toluene:

Toluene reacts with chlorine or bromine in the presence of light or a catalyst to form benzyl halides.

Example: $C_6H_5CH_3+Cl_2 \rightarrow C_6H_5CH_2Cl+HCl$

From Benzyl Alcohol:

Benzyl alcohol reacts with halogenating agents like PCl_3, PCl_5, or $SOCl_2$.

Example: $C_6H_5CH_2OH+SOCl_2 \rightarrow C_6H_5CH_2Cl+SO_2+HCl$

From Aromatic Compounds with Side Chains:

Side chains of aromatic compounds undergo selective halogenation.

Properties

Physical Properties:

State: Benzyl halides are generally colorless liquids or solids.

Boiling and Melting Points: Depend on the halogen atom; heavier halogens result in higher boiling points.

Solubility: Insoluble in water but soluble in organic solvents like ethanol, ether, and chloroform.

Chemical Properties:

Reactivity:

Benzyl halides are highly reactive due to the benzylic position, where the carbon atom is directly attached to the aromatic ring.

Nucleophilic Substitution:

Undergo SN_2 reactions with strong nucleophiles, forming products like benzyl alcohol or ethers.

Example: $C_6H_5CH_2Cl + NaOH \rightarrow C_6H_5CH_2OH + NaCl$

Oxidation:

Benzyl halides can be oxidized to benzoic acid.

Applications

Chemical Synthesis:

Used as intermediates in the production of dyes, perfumes, and resins.

Pharmaceutical Industry:

Serve as precursors in the synthesis of drugs like antihistamines and tranquilizers.

Pesticides and Fungicides:

Benzyl halides are used in the formulation of agricultural chemicals.

Polymers and Plastics:

Employed in the preparation of certain polymers and plastics due to their reactivity.

Laboratory Reagents:

Act as alkylating agents in organic synthesis.

Environmental and Safety Concerns

Aryl alkyl halides, particularly benzyl halides, are toxic and potentially harmful if inhaled or ingested. They may also cause skin and eye irritation. Proper handling, storage, and disposal are essential to minimize risks to health and the environment.

Alcohols

Alcohols are organic compounds characterized by the presence of a hydroxyl group (–OH) attached to a saturated carbon atom. They are versatile in both their chemical reactivity and applications, making them significant in organic chemistry and industrial processes.

Alcohols can be classified, named, prepared, and tested through various systematic methods. Their reactions include conversions, oxidation, and degradation, demonstrating their diverse chemical behavior.

In **nomenclature**, alcohols are named based on the IUPAC system by identifying the longest chain containing the hydroxyl group. The suffix "-ol" is added to the name of the parent alkane, and the position of the hydroxyl group is indicated by a number. For instance, CH_3CH_2OH is ethanol and $CH_3CH(OH)CH_3$ propan-2-ol. When multiple hydroxyl groups are present, prefixes such as di-, tri-, or tetra- are used, as in ethylene glycol $CH_2(OH)CH_2(OH)$. Common names are also frequently used, such as "methyl alcohol" for methanol.

Classification of alcohols is based on the number of alkyl groups attached to the carbon bearing the hydroxyl group. Primary alcohols (1°) have one alkyl group, secondary alcohols (2°) have two, and tertiary alcohols (3°) have three.

Preparation of alcohols can occur through several methods, including:

Hydration of Alkenes: Alkenes react with water in the presence of an acid catalyst to form alcohols, as in the synthesis of ethanol from ethene.

Reduction of Carbonyl Compounds: Aldehydes and ketones can be reduced to alcohols using reducing agents like lithium aluminum hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$).

Hydrolysis of Alkyl Halides: Alkyl halides react with aqueous sodium hydroxide to produce alcohols.

Fermentation: Sugars like glucose are converted into ethanol through fermentation.

The **properties of alcohols** include physical attributes such as higher boiling points due to hydrogen bonding, solubility in water (especially for lower alcohols), and their polar nature. Chemically, they participate in substitution and elimination reactions and can act as acids and bases.

Alcohols are extensively used in various fields. Ethanol is a solvent and fuel, methanol is a precursor to formaldehyde, and polyhydric alcohols like glycerol are used in cosmetics and pharmaceuticals.

In organic conversions, alcohols play a pivotal role in ascending and descending series:

Ascent of Series: A lower alcohol can be converted into a higher alcohol through reactions like Grignard synthesis. For example, methanol can be converted into ethanol by reacting with formaldehyde and Grignard reagents.

Descent of Series: Higher alcohols can be converted into lower alcohols through degradation methods like oxidation to aldehydes and subsequent reduction to a lower alcohol.

Tests for the hydroxyl group involve specific reactions:

Alcohols react with phosphorus halides (PCl_3, PCl_5) or thionyl chloride ($SOCl_2$) to form alkyl halides, releasing identifiable by-products such as HCl.

The Lucas test differentiates primary, secondary, and tertiary alcohols based on their reactivity with zinc chloride and concentrated hydrochloric acid.

Oxidation reactions of alcohols highlight their reactivity. Primary alcohols can be oxidized to aldehydes and carboxylic acids, while secondary alcohols yield ketones. Tertiary alcohols resist oxidation due to the lack of hydrogen on the hydroxyl-bearing carbon.

Oxidation of diols (glycols) using periodic acid (HIO_4) or lead tetraacetate is a significant reaction. These reagents cleave the C–C bond between the hydroxyl groups to produce carbonyl compounds. For example, ethylene glycol reacts with periodic acid to yield formaldehyde:

$$CH_2(OH)CH_2(OH)+HIO_4 \rightarrow 2HCHO+H_2O$$

The versatility of alcohols in reactions and applications demonstrates their importance in both synthetic organic chemistry and industrial processes. Their ability to undergo varied chemical transformations, such as oxidation and nucleophilic substitution, makes them essential intermediates in producing diverse chemical products.

UNIT-5

PHENOLS

phenol, any of a family of organic compounds characterized by a hydroxyl (—OH) group attached to a carbon atom that is part of an aromatic ring. Besides serving as the generic name for the entire family, the term phenol is also the specific name for its simplest member, monohydroxybenzene (C_6H_5OH), also known as benzenol, or carbolic acid.

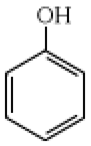
Phenols are similar to alcohols but form stronger hydrogen bonds. Thus, they are more soluble in water than are alcohols and have higher boiling points. Phenols occur either as colourless liquids or white solids at room temperature and may be highly toxic and caustic.

Phenols are widely used in household products and as intermediates for industrial synthesis. For example, phenol itself is used (in low concentrations) as a disinfectant in household cleaners and in mouthwash. Phenol may have been the first surgical antiseptic. In 1865 the British surgeon Joseph Lister used phenol as an antiseptic to sterilize his operating field. With phenol used in this manner, the mortality rate from surgical amputations fell from 45 to 15 percent in Lister’s ward. Phenol is quite toxic, however, and concentrated solutions cause severe but painless burns of the skin and mucous membranes. Less-toxic phenols, such as n-hexylresorcinol, have supplanted phenol itself in cough drops and other antiseptic applications. Butylated hydroxytoluene (BHT) has a much lower toxicity and is a common antioxidant in foods.

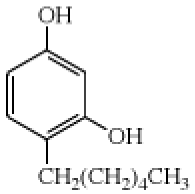
In industry, phenol is used as a starting material to make plastics, explosives such as picric acid, and drugs such as aspirin. The common phenol hydroquinone is the component of photographic developer that reduces exposed silver bromide crystals to black metallic silver. Other substituted phenols are used in the dye industry to make intensely coloured azo dyes. Mixtures of phenols (especially the cresols) are used as components in wood preservatives such as creosote.

Natural sources of phenols

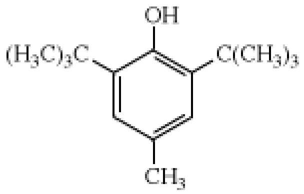
Poison ivy (Toxicodendron radicans) is a natural source of the phenol urushiol—an irritant that causes severe inflammation of the skin. Phenols are common in nature; examples include tyrosine, one of the standard amino acids found in most proteins; epinephrine (adrenaline), a stimulant hormone produced by the adrenal medulla; serotonin, a neurotransmitter in the brain; and urushiol, an irritant secreted by poison ivy to prevent animals from eating its leaves. Many of the more complex phenols used as flavourings and aromas are obtained from essential oils of plants. For example, vanillin, the principal flavouring in vanilla, is isolated from vanilla beans, and methyl salicylate, which has a characteristic minty taste and odour, is isolated from wintergreen. Other phenols obtained from plants include thymol, isolated from thyme, and eugenol, isolated from cloves.



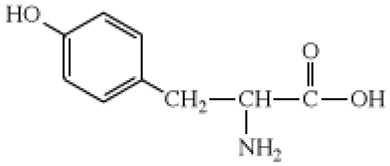
phenol
(hydroxybenzene)



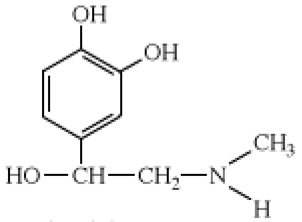
n-hexylresorcinol
4-hexylresorcinol



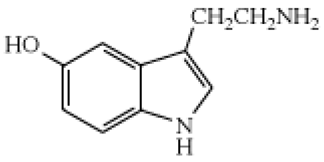
BHT
2,6-di-*t*-butyl-4-methylphenol



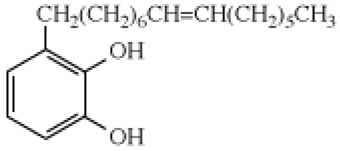
tyrosine



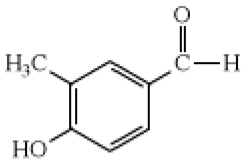
epinephrine
(adrenalin)



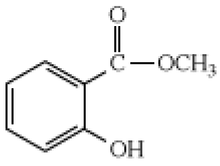
serotonin



urushiol



vanillin

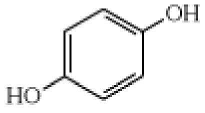


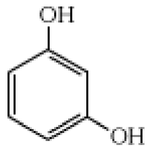
methyl salicylate

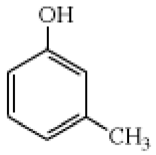
Phenol, the cresols (methylphenols), and other simple alkylated phenols can be obtained from the distillation of coal tar or crude petroleum.

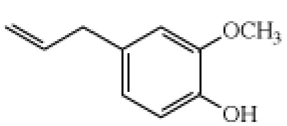
Nomenclature of phenols

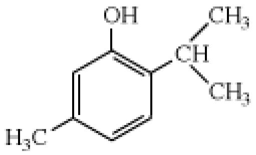
Many phenolic compounds were discovered and used long before chemists were able to determine their structures. Therefore, trivial names (i.e., vanillin, salicylic acid, pyrocatechol, resorcinol, cresol, hydroquinone, and eugenol) are often used for the most common phenolic compounds.


hydroquinone

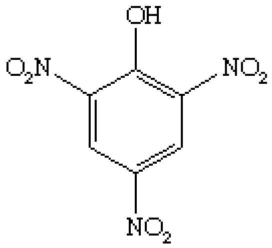

resorcinol

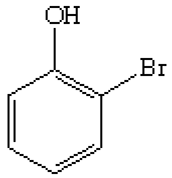

meta-cresol

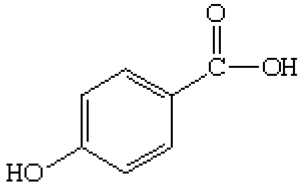

eugenol


thymol

Systematic names are more useful, however, because a systematic name specifies the actual structure of the compound. If the hydroxyl group is the principal functional group of a phenol, the compound can be named as a substituted phenol, with carbon atom 1 bearing the hydroxyl group. For example, the systematic name for thymol is 5-methyl-2-isopropylphenol. Phenols with only one other substituent can be named using either the appropriate numbers or the ortho (1,2), meta (1,3), and para (1,4) system. Compounds with other principal functional groups can be named with the hydroxyl group as a hydroxy substituent. For example, the systematic name for vanillin is 4-hydroxy-3-methoxybenzaldehyde.


2,4,6-trinitrophenol
(picric acid)


2-bromophenol
ortho-bromophenol


4-hydroxybenzoic acid
para-hydroxybenzoic acid

Physical properties of phenols

Similar to alcohols, phenols have hydroxyl groups that can participate in intermolecular hydrogen bonding; in fact, phenols tend to form stronger hydrogen bonds than alcohols. (See chemical bonding: Intermolecular forces for more information about hydrogen bonding.) Hydrogen bonding results in higher melting points and much higher boiling points for phenols than for hydrocarbons with similar molecular weights. For example, phenol (molecular weight [MW] 94, boiling point [bp] 182 °C [359.6 °F]) has a boiling point more than 70 degrees higher than that of toluene ($C_6H_5CH_3$; MW 92, bp 111 °C [231.8 °F]).

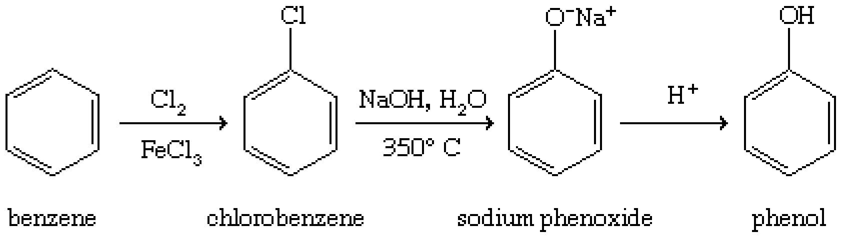
The ability of phenols to form strong hydrogen bonds also enhances their solubility in water. Phenol dissolves to give a 9.3 percent solution in water, compared with a 3.6 percent solution for cyclohexanol in water. The association between water and phenol is unusually strong; when crystalline phenol is left out in a humid environment, it picks up enough water from the air to form liquid droplets.

Synthesis of phenols

Most of the phenol used today is produced from benzene, through either hydrolysis of chlorobenzene or oxidation of isopropylbenzene (cumene).

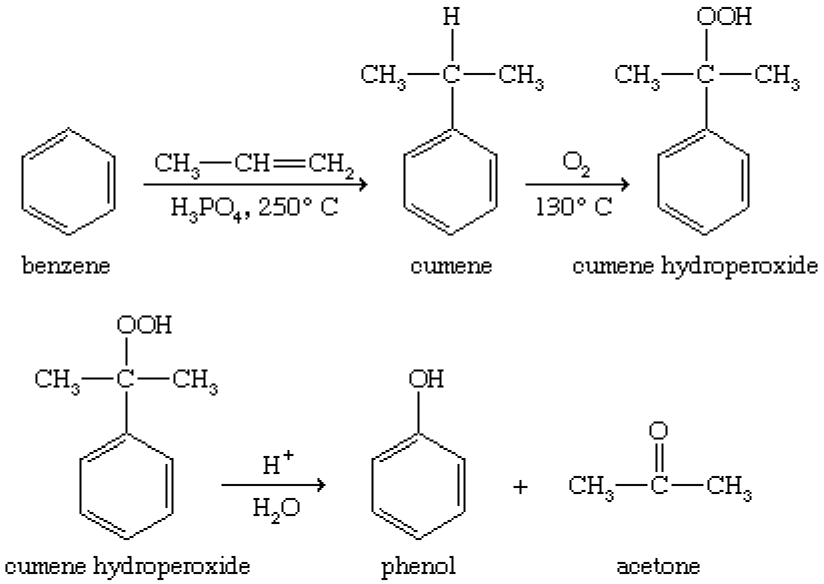
Hydrolysis of chlorobenzene (the Dow process)

Benzene is easily converted to chlorobenzene by a variety of methods, one of which is the Dow process. Chlorobenzene is hydrolyzed by a strong base at high temperatures to give a phenoxide salt, which is acidified to phenol.



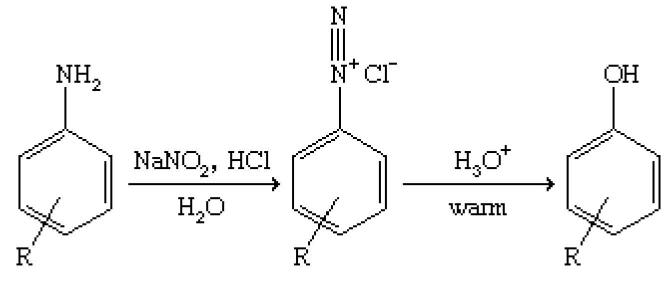
Oxidation of isopropylbenzene

Benzene is converted to isopropylbenzene (cumene) by treatment with propylene and an acidic catalyst. Oxidation yields a hydroperoxide (cumene hydroperoxide), which undergoes acid-catalyzed rearrangement to phenol and acetone. Although this process seems more complicated than the Dow process, it is advantageous because it produces two valuable industrial products: phenol and acetone.



General synthesis of phenols

To make more-complicated phenolic compounds, a more general synthesis is needed. The cumene hydroperoxide reaction is fairly specific to phenol itself. The Dow process is somewhat more general, but the stringent conditions required often lead to low yields, and they may destroy any other functional groups on the molecule. A milder, more general reaction is the diazotization of an arylamine (a derivative of aniline, $C_6H_5NH_2$) to give a diazonium salt, which hydrolyzes to a phenol. Most functional groups can survive this technique, as long as they are stable in the presence of dilute acid.

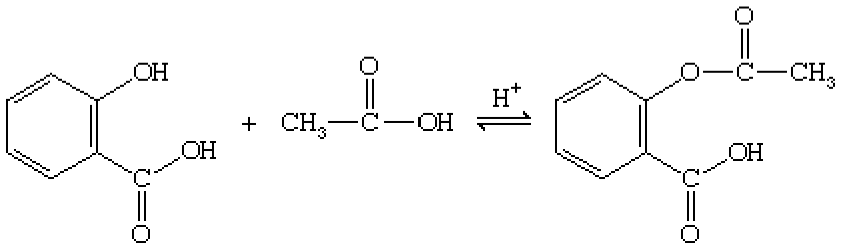


an arylamine a diazonium salt a phenol

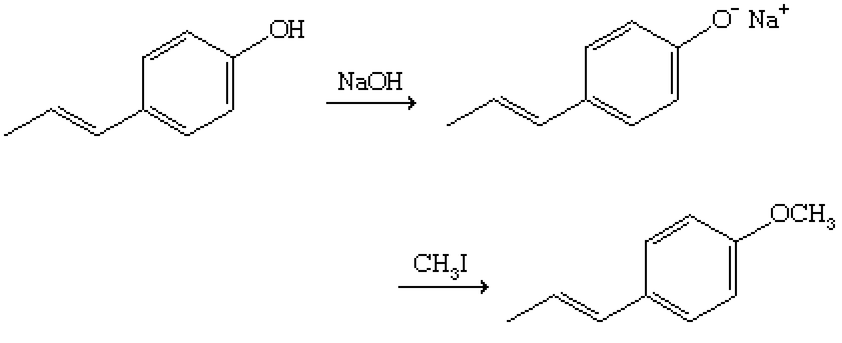
R = alkyl group or functional group at any position

Reactions of phenols

Much of the chemistry of phenols is like that of alcohols. For example, phenols react with acids to give esters, and phenoxide ions (ArO^-) can be good nucleophiles in Williamson ether synthesis.



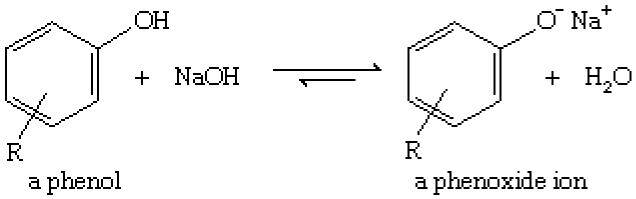
salicylic acid acetic acid acetylsalicylic acid (aspirin)



anethole
(licorice flavouring)

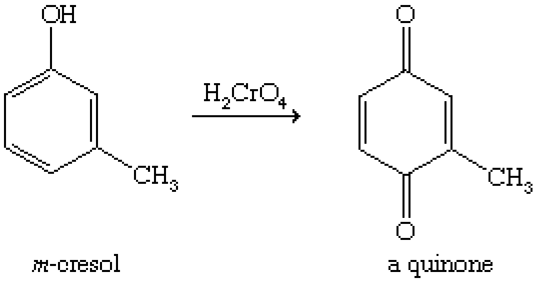
Acidity of phenols

Although phenols are often considered simply as aromatic alcohols, they do have somewhat different properties. The most obvious difference is the enhanced acidity of phenols. Phenols are not as acidic as carboxylic acids, but they are much more acidic than aliphatic alcohols, and they are more acidic than water. Unlike simple alcohols, most phenols are completely deprotonated by sodium hydroxide (NaOH).

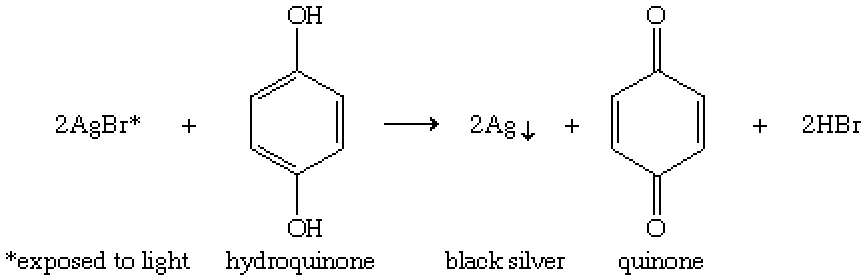


Oxidation

Like other alcohols, phenols undergo oxidation, but they give different types of products from those seen with aliphatic alcohols. For example, chromic acid oxidizes most phenols to conjugated 1,4-diketones called quinones. In the presence of oxygen in the air, many phenols slowly oxidize to give dark mixtures containing quinones.

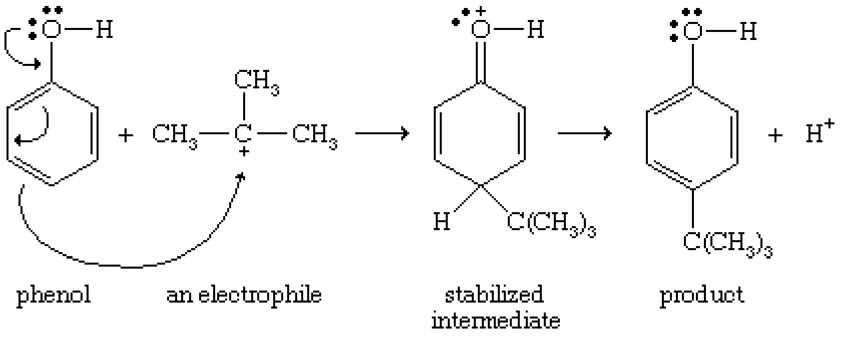


Hydroquinone (1,4-benzenediol) is a particularly easy compound to oxidize, because it has two hydroxyl groups in the proper relationship to give up hydrogen atoms to form a quinone. Hydroquinone is used in developing photographic film by reducing activated (exposed to light) silver bromide (AgBr) to black metallic silver (Ag↓). Unexposed grains of silver bromide react more slowly than the exposed grains.

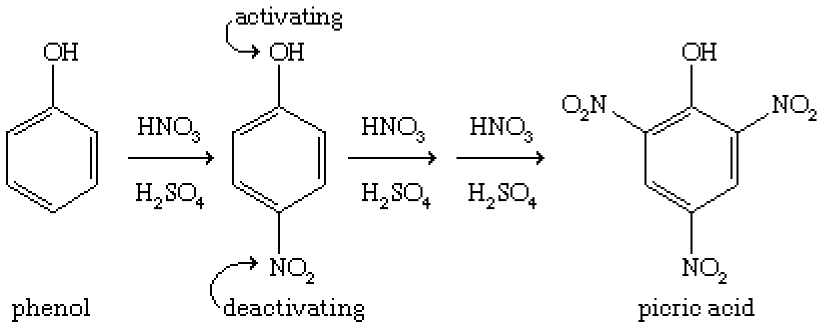


Electrophilic aromatic substitution

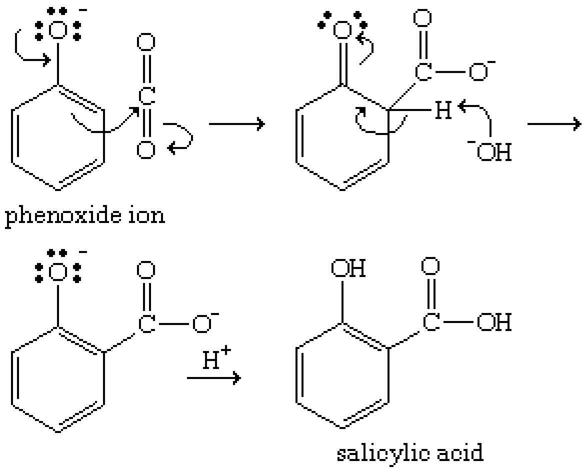
Phenols are highly reactive toward electrophilic aromatic substitution, because the nonbonding electrons on oxygen stabilize the intermediate cation. This stabilization is most effective for attack at the ortho or para position of the ring; therefore, the hydroxyl group of a phenol is considered to be activating (i.e., its presence causes the aromatic ring to be more reactive than benzene) and ortho- or para-directing.



Picric acid (2,4,6-trinitrophenol) is an important explosive that was used in World War I. An effective explosive needs a high proportion of oxidizing groups such as nitro groups. Nitro groups are strongly deactivating (i.e., make the aromatic ring less reactive), however, and it is often difficult to add a second or third nitro group to an aromatic compound. Three nitro groups are more easily substituted onto phenol, because the strong activation of the hydroxyl group helps to counteract the deactivation of the first and second nitro groups.

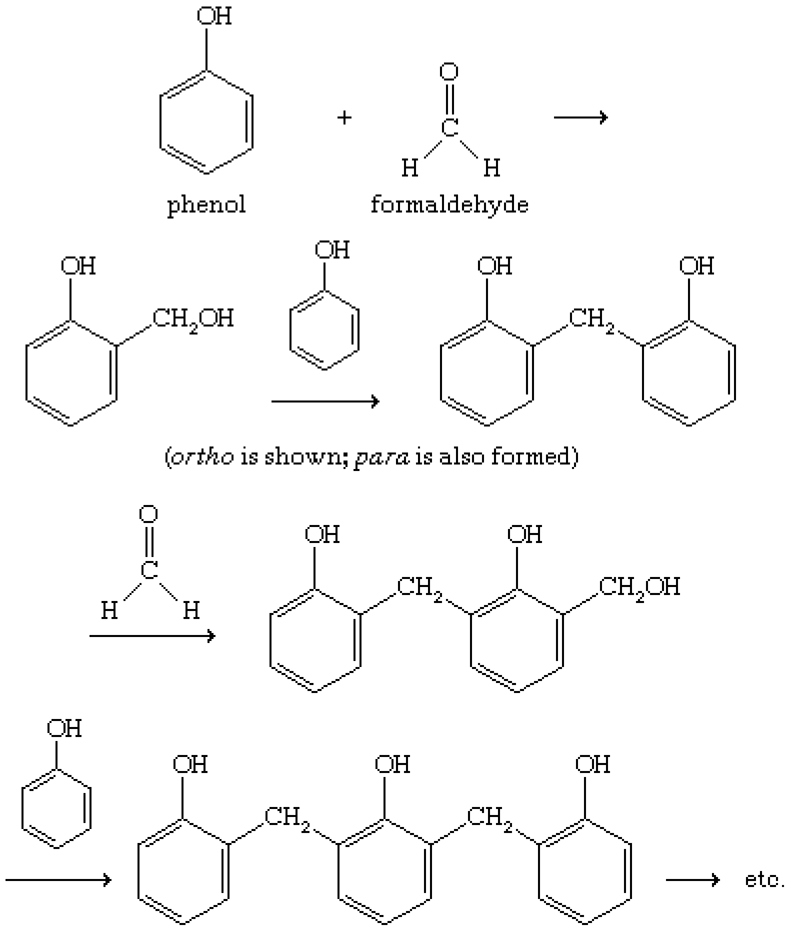


Phenoxide ions, generated by treating a phenol with sodium hydroxide, are so strongly activated that they undergo electrophilic aromatic substitution even with very weak electrophiles such as carbon dioxide (CO_2). This reaction is used commercially to make salicylic acid for conversion to aspirin and methyl salicylate.



Formation of phenol-formaldehyde resins

Phenolic resins account for a large portion of phenol production. Under the trade name Bakelite, a phenol-formaldehyde resin was one of the earliest plastics, invented by American industrial chemist Leo Baekeland and patented in 1909. Phenol-formaldehyde resins are inexpensive, heat-resistant, and waterproof, though somewhat brittle. The polymerization of phenol with formaldehyde involves electrophilic aromatic substitution at the ortho and para positions of phenol (probably somewhat randomly), followed by cross-linking of the polymeric chains.



Preparation of Phenols

Phenols can be synthesized through various methods, including:

From Aryl Halides (Dow Process): Chlorobenzene is reacted with sodium hydroxide at high temperature and pressure to produce sodium phenoxide, which is then acidified to yield phenol.

$$C_6H_5Cl+2NaOH \rightarrow C_6H_5ONa+NaCl$$

$$C_6H_5ONa+HCl \rightarrow C_6H_5OH+NaCl$$

From Benzene Sulfonic Acid: Benzene sulfonic acid is fused with sodium hydroxide to produce sodium phenoxide, which is acidified to form phenol.

Hydrolysis of Diazonium Salts: Benzene diazonium chloride, formed from aniline, undergoes hydrolysis in the presence of dilute acids to yield phenol.

$$C_6H_5N_2Cl+H_2O\rightarrow C_6H_5OH+N_2+HCl$$

Industrial Preparation: Phenol is industrially prepared from cumene. Cumene hydroperoxide, formed by the oxidation of cumene, is treated with acid to yield phenol and acetone.

Acidic Character of Phenols

Phenols are weak acids, capable of donating a proton (H^+) from the hydroxyl group to form a phenoxide ion (C_6H_5O). Their acidity is greater than that of alcohols but less than that of carboxylic acids. This is due to the resonance stabilization of the phenoxide ion, where the negative charge is delocalized over the aromatic ring.

The reaction with bases highlights this acidic nature:

$$C_6H_5OH+NaOH\rightarrow C_6H_5ONa+H_2O$$

Phenols do not react with weaker bases such as sodium bicarbonate, distinguishing them from stronger acids like carboxylic acids.

Effect of Substituents on Acidity

The acidity of phenols is significantly influenced by substituents on the benzene ring:

Electron-Withdrawing Groups (EWGs): Substituents like nitro (NO_2), cyanide (CN), and halogens increase the acidity of phenols. These groups stabilize the negative charge on the phenoxide ion through inductive and resonance effects. For example, p-nitrophenol is more acidic than phenol.

Electron-Donating Groups (EDGs): Substituents such as alkyl groups, hydroxyl (OH), and methoxy (OCH_3) decrease the acidity of phenols. These groups destabilize the phenoxide ion by donating electron density to the aromatic ring. For example, p-cresol (methyl-substituted phenol) is less acidic than phenol.

The position of the substituent (ortho, meta, or para) also plays a role in modulating the acidity due to steric and resonance effects.

Phenols are versatile compounds with applications in the production of resins, dyes, antiseptics, and pharmaceuticals. Understanding their preparation, properties, and acidic behavior is essential for utilizing them effectively in chemical reactions and industrial processes.

Fries Rearrangement

The Fries rearrangement is a reaction in which an aryl ester is converted into hydroxyaryl ketones (ortho and para products) using aluminum chloride ($AlCl_3$) as a catalyst.

$$C_6H_5COOR \rightarrow o\text{-}OH\text{-}C_6H_4COR + p\text{-}OH\text{-}C_6H_4COR$$

This reaction is useful for synthesizing aromatic hydroxy ketones, which are intermediates in dye and pharmaceutical industries.

Claisen Rearrangement

The Claisen rearrangement involves the rearrangement of allyl phenyl ethers to form ortho-allyl phenols. It occurs when allyl phenyl ether is heated:

$$C_6H_5OCH_2CH{=}CH_2 \rightarrow o\text{-}CH_2CH{=}CH_2\text{-}C_6H_4OH$$

This reaction is an example of a [3,3]-sigmatropic rearrangement and is commonly used in organic synthesis.

Electrophilic Substitution Reactions

Phenols are highly reactive towards electrophilic substitution reactions due to the electron-donating nature of the hydroxyl group, which activates the benzene ring.

Nitration: Phenol reacts with dilute nitric acid to form ortho- and para-nitrophenols. Using concentrated nitric acid produces 2,4,6-trinitrophenol (picric acid).

$$C_6H_5OH+HNO_3 \rightarrow o\text{-}NO_2\text{-}C_6H_4OH+p\text{-}NO_2\text{-}C_6H_4OH$$

Halogenation: Bromination of phenol in water yields 2,4,6-tribromophenol due to the activating effect of the hydroxyl group.

$$C_6H_5OH+3Br_2 \rightarrow C_6H_2Br_3OH+3HBr$$

Sulfonation: Phenol reacts with concentrated sulfuric acid to form ortho- and para-phenol sulfonic acids.

Reimer-Tiemann Reaction

The Reimer-Tiemann reaction is used to form ortho-hydroxybenzaldehyde from phenol. This reaction involves the use of chloroform and aqueous sodium hydroxide:

$$C_6H_5OH+CHCl_3+NaOH \rightarrow o\text{-}HO\text{-}C_6H_4CHO+NaCl+H_2O$$

This reaction is widely applied in the synthesis of salicylaldehyde.

Kolbe-Schmitt Reaction

In the Kolbe-Schmitt reaction, phenol reacts with carbon dioxide under pressure and heat in the presence of sodium hydroxide to form salicylic acid.

$$C_6H_5OH+NaOH \rightarrow C_6H_4OH\text{-}COONa \rightarrow C_6H_4OH\text{-}COOH$$

This reaction is crucial in the industrial production of aspirin and other pharmaceuticals.

Gattermann Synthesis

The Gattermann synthesis introduces a formyl group (−CHO) into the benzene ring of phenol using hydrogen cyanide (HCN) and hydrogen chloride in the presence of aluminum chloride or zinc chloride as a catalyst.

Liebermann Reaction

In this reaction, phenol reacts with sodium nitrite and concentrated sulfuric acid to form a deep blue or green compound that changes to red upon dilution with water. This reaction serves as a qualitative test for phenol.

Nitro Reaction

Phenols react with concentrated nitric acid to form trinitrophenol (picric acid), a yellow crystalline compound used in explosives and dyes.

Phthalein Reaction

The phthalein reaction involves the condensation of phenol with phthalic anhydride in the presence of concentrated sulfuric acid to form phenolphthalein. This compound is widely used as an acid-base indicator.

Phenols exhibit remarkable reactivity and versatility due to their unique structure. These reactions and their applications are fundamental to synthetic organic chemistry, particularly in producing pharmaceuticals, dyes, and industrial chemicals.

Resorcinol

Resorcinol, also known as m-dihydroxybenzene, is an aromatic compound featuring two hydroxyl groups attached to a benzene ring in the meta position. Its versatile reactivity makes it a valuable compound in organic chemistry, industrial applications, and medicine.

Preparation:

From Benzene Sulfonic Acid:

Resorcinol is commonly prepared by fusing benzene disulfonic acid with sodium hydroxide under high temperatures.

$$C_6H_4(SO_3H)_2+2NaOH \rightarrow C_6H_4(OH)_2+Na_2SO_3$$

This method is widely used due to its efficiency in producing resorcinol on a commercial scale.

From Phenol Derivatives:

Phenol derivatives, such as m-hydroxybenzaldehyde or m-nitrophenol, can be reduced or oxidized respectively to yield resorcinol.

Properties:

Physical Properties:

Appearance: Colorless or faintly pink crystalline solid.

Solubility: Highly soluble in water, alcohol, and ether.

Melting Point: ~110 °C.

Chemical Properties:

Electrophilic Substitution: Resorcinol undergoes typical electrophilic substitution reactions, such as halogenation and nitration, to yield mono- or polysubstituted products.

Oxidation: Oxidizing agents convert resorcinol into various quinone derivatives.

Uses:

Industrial Applications:

Resorcinol is used in the manufacture of adhesives, dyes (e.g., fluorescein), and resins.

Medical Applications:

It serves as an antiseptic, disinfectant, and a component in skin ointments.

Other Uses:

Utilized in tanning, photographic chemicals, and as an intermediate in organic synthesis.

Quinol (Hydroquinone)

Quinol, or hydroquinone (p-dihydroxybenzene), is an aromatic compound where two hydroxyl groups occupy para positions on the benzene ring. It is well-known for its strong reducing properties and widespread applications in industry and medicine.

Preparation:

From Aniline:

Aniline is oxidized to p-benzoquinone using an oxidizing agent like potassium dichromate. The quinone is then reduced to quinol:

$$C_6H_5NH_2 \rightarrow C_6H_4(O)_2 \rightarrow C_6H_4(OH)_2$$

From Phenol:

Phenol is oxidized directly using potassium permanganate or hydrogen peroxide to form quinol.

Properties:

Physical Properties:

Appearance: White crystalline solid with a slight phenolic odor.

Solubility: Soluble in water and alcohol.

Melting Point: ~172 °C.

Chemical Properties:

Reducing Agent: Quinol can easily reduce oxidizing agents due to its reversible oxidation to p-benzoquinone.

Electrophilic Substitution: The hydroxyl groups activate the benzene ring towards reactions like halogenation, sulfonation, and nitration.

Uses:

Photography: Widely used as a developer in photographic films.

Industry: Acts as an antioxidant in the rubber and polymer industries.

Cosmetics: Used in skin-lightening creams to reduce hyperpigmentation.

Synthesis: Employed in the production of dyes, herbicides, and pharmaceuticals.

Picric Acid (2,4,6-Trinitrophenol)

Picric acid is a yellow crystalline compound derived from phenol. It is highly nitrated and exhibits explosive properties, making it both valuable and hazardous. It is one of the oldest known explosives and has diverse applications in dyes and analytical chemistry.

Preparation:

From Phenol:

Phenol is treated with concentrated nitric acid in the presence of sulfuric acid, which acts as a dehydrating catalyst.

$$C_6H_5OH+3HNO_3 \rightarrow C_6H_2(NO_2)3OH+3H_2O$$

From Chlorobenzene:

Chlorobenzene is converted to phenol, which is subsequently nitrated to form picric acid.

Properties:

Physical Properties:

Appearance: Yellow crystalline solid.

Solubility: Slightly soluble in cold water but highly soluble in hot water.

Melting Point: ~122.5 °C.

Chemical Properties:

Acidic Nature: The hydroxyl group in picric acid enhances its acidity, making it a stronger acid than phenol. It reacts with bases to form picrate salts.

Explosive Nature: When dry, picric acid is highly explosive due to the presence of nitro groups.

Complex Formation: Picric acid forms stable complexes with various metals and organic compounds.

Uses:

Explosives: Picric acid is a key component in military explosives due to its high detonation power.

Dye Industry: Used to dye silk and wool, imparting a bright yellow color.

Analytical Reagent: Acts as a test reagent for metals and alkaloids.

Medicine (Historical): Previously used as an antiseptic and in burn treatments, though its use is now limited due to toxicity concerns.

AROMATIC ALCOHOLS

Aromatic alcohols are organic compounds that feature one or more hydroxyl groups (−OH) attached to an aromatic ring or a side chain connected to an aromatic ring. Their structure combines the reactivity of alcohols with the stability and delocalized electron system of the aromatic nucleus, leading to a diverse range of chemical behavior and applications.

Nomenclature of Aromatic Alcohols

Aromatic alcohols are named following IUPAC conventions:

Phenols are alcohols where the hydroxyl group is directly attached to the benzene ring (e.g., phenol, cresol).

Benzyl Alcohols have a hydroxyl group attached to a side chain containing a benzene ring. The simplest example is benzyl alcohol ($C_6H_5CH_2OH$).

Substituents on the aromatic ring are denoted with prefixes like ortho (o−), meta (m−), or para (p−) or numerically (e.g., 2-hydroxybenzyl alcohol).

Benzyl Alcohol

Structure: Benzyl alcohol consists of a benzene ring attached to a single hydroxymethyl group ($-CH_2OH$). Its formula is $C_6H_5CH_2OH$

Methods of Preparation

Hydrolysis of Benzyl Chloride:

Benzyl chloride reacts with water in the presence of a base to produce benzyl alcohol.

$$C_6H_5CH_2Cl+H_2O \rightarrow NaOH C_6H_5CH_2OH+HCl$$

Reduction of Benzaldehyde:

Benzyl alcohol is formed by the catalytic hydrogenation or reduction of benzaldehyde using reducing agents like sodium borohydride (NaBH4):

$$C_6H_5CHO+2[H]\rightarrow C_6H_5CH_2OH$$

Grignard Synthesis:

Benzyl alcohol can be synthesized by reacting benzyl magnesium halide (C_6H_5MgX) with formaldehyde, followed by hydrolysis:

$$C_6H_5MgX+HCHO\rightarrow C_6H_5CH_2OMgX$$

$$C_6H_5CH_2OMgX+H_2O\rightarrow C_6H_5CH_2OH+Mg(OH)X$$

Hydrolysis Reaction of Benzaldehyde

Benzaldehyde undergoes hydrolysis under basic conditions to yield benzyl alcohol and a salt of benzoic acid via the Cannizzaro reaction:

$$2C_6H_5CHO+NaOH\rightarrow C_6H_5CH_2OH+C_6H_5COONa_2$$

Cannizzaro Reaction

The Cannizzaro reaction involves the disproportionation of non-enolizable aldehydes (e.g., benzaldehyde) in the presence of a strong base to produce a mixture of an alcohol and a carboxylic acid salt.

Physical Properties

Appearance: Benzyl alcohol is a colorless liquid with a mild, pleasant aroma.

Boiling Point: 205 °C.

Solubility: Slightly soluble in water but readily soluble in organic solvents such as alcohol and ether.

Polarity: Exhibits hydrogen bonding due to the hydroxyl group, affecting its boiling point and solubility.

Chemical Reactions

Reaction with Sodium:

Benzyl alcohol reacts with sodium metal to form benzyl alkoxide and hydrogen gas:

$$2C_6H_5CH_2OH+2Na \rightarrow 2C_6H_5CH_2ONa+H_2$$

Reaction with Phosphorus Pentachloride (PCl_5):

Benzyl alcohol reacts with PCl_5 to form benzyl chloride:

$$C_6H_5CH_2OH+PCl_5 \rightarrow C_6H_5CH_2Cl+POCl_3+HCl$$

Reaction with Thionyl Chloride ($SOCl_2$):

Thionyl chloride converts benzyl alcohol into benzyl chloride:

$$C_6H_5CH_2OH+SOCl_2 \rightarrow C_6H_5CH_2Cl+SO_2+HCl$$

Reaction with Acetic Anhydride:

The reaction of benzyl alcohol with acetic anhydride involves esterification, where the hydroxyl group (−OH) of benzyl alcohol reacts with acetic anhydride to form an ester, benzyl acetate, along with acetic acid as a byproduct. The process can be represented as:

$$C_6H_5CH_2OH+(CH_3CO)_2O \rightarrow C_6H_5CH_2OCOCH_3+CH_3COOH$$

Mechanism of the Reaction:

Nucleophilic Attack: The hydroxyl group of benzyl alcohol acts as a nucleophile and attacks one of the carbonyl carbons in acetic anhydride.

Intermediate Formation: This forms a tetrahedral intermediate where the oxygen of the hydroxyl group bonds with the carbonyl carbon.

Elimination: The intermediate rearranges, releasing a molecule of acetic acid (CH_3COOH) and forming the ester product benzyl acetate ($C_6H_5CH_2OCOCH_3$). This reaction is typically carried out under mild heating or in the presence of a catalyst, such as a trace amount of acid, to enhance the rate of reaction. Benzyl acetate is a fragrant ester commonly used in perfumes and flavoring agents.

Reaction with Hydrogen Iodide (HI):

Benzyl alcohol reacts with HI to produce toluene:

$$C_6H_5CH_2OH + HI \rightarrow C_6H_5CH_3 + H_2O$$

Oxidation:
Benzyl alcohol oxidizes to benzaldehyde using mild oxidizing agents like chromium compounds.

Electrophilic Substitution on Benzene Ring:

The benzene ring in benzyl alcohol undergoes typical electrophilic substitutions such as halogenation, sulfonation, and nitration, facilitated by the activating hydroxymethyl group.

Uses of Benzyl Alcohol

Industry: Used as a solvent for inks, paints, and coatings.

Pharmaceuticals: An ingredient in injectable drugs and ointments.

Perfume Industry: Acts as a fixative in perfumes and scents.

Laboratory Reagent: Serves as a precursor in organic synthesis.

Thiols

Thiols, also known as mercaptans, are sulfur analogs of alcohols where the hydroxyl group (−OH) is replaced with a sulfhydryl group (−SH). The presence of sulfur imparts unique properties to these compounds, such as a strong and often unpleasant odor. Thiols play vital roles in biological systems, industrial processes, and chemical synthesis.

Nomenclature

IUPAC System:

In the IUPAC system, thiols are named by adding the suffix **-thiol** to the name of the parent alkane. The carbon chain is numbered such that the −SH group gets the lowest possible number.

Example: Methanethiol (CH_3SH), Ethanethiol (CH_3CH_2SH).

Common Names: In common nomenclature, thiols are named by adding the word "mercaptan" to the name of the alkyl group.

Example: Methyl mercaptan, Ethyl mercaptan.

Aromatic Thiols:

For aromatic thiols, the −SH group attached to an aromatic ring is denoted by the name **thiophenol**. Substituents on the ring are specified using standard naming conventions.

Example: 2-Methylthiophenol.

Preparation of Thiols

From Alkyl Halides:

Alkyl halides react with sodium hydrosulfide (NaSH) to yield thiols via nucleophilic substitution:

$$R\text{-}X + NaSH \rightarrow R\text{-}SH + NaX$$

Hydrolysis of Thioesters:

Thioesters undergo hydrolysis to form thiols:

$$R\text{-}SCOR' + H_2O \rightarrow R\text{-}SH + R'\text{-}COOH$$

Reduction of Disulfides:

Disulfides can be reduced to thiols using reducing agents such as zinc and hydrochloric acid:

$$R\text{-}S\text{-}S\text{-}R + 2[H] \rightarrow 2R\text{-}SH$$

Reaction of Grignard Reagents with Sulfur:

Grignard reagents react with elemental sulfur, followed by acid hydrolysis, to produce thiols:

$$R\text{-}MgX + S \rightarrow R\text{-}S\text{-}MgX$$

From Alcohols:

Alcohols can be converted to thiols by replacing the oxygen atom with sulfur using reagents like P_4S_{10}

$$R\text{-}OH + P_4S_{10} \rightarrow R\text{-}SH + H_2O$$

Properties of Thiols

Physical Properties:

Odor: Thiols have a strong, characteristic odor often described as foul or skunky.

Boiling Point: Lower than corresponding alcohols due to weaker hydrogen bonding.

Solubility: Lower solubility in water compared to alcohols but soluble in organic solvents.

Chemical Properties:

Acidity: Thiols are more acidic than alcohols, with pKa values around 10-11. They readily form thiolate ions (R-S) in the presence of bases:

$$\text{R-SH}+\text{NaOH}\rightarrow\text{R-SNa}+\text{H}_2\text{O}$$

Oxidation: Thiols oxidize to form disulfides (R-S-S-R):

$$2\text{R-SH}+[\text{O}]\rightarrow\text{R-S-S-R}+\text{H}_2\text{O}$$

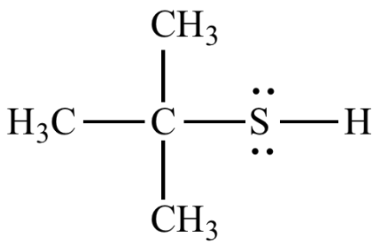
Reaction with Alkyl Halides: Thiols react with alkyl halides to form thioethers:

$$\text{R-SH}+\text{R'-X}\rightarrow\text{R-S-R'}+\text{HX}$$

Reaction with Metal Ions: Thiols form metal thiolates with heavy metals such as mercury and lead, which are often insoluble:

$$2\text{R-SH}+\text{HgCl}_2\rightarrow(\text{R-S})_2\text{Hg}+2\text{HCl}_2$$

Structure of Thiols



The sulfur atom in thiols is sp^3-hybridized, with two lone pairs of electrons and a single bond to the carbon atom. The −SH group has a bent structure similar to that of water, with a bond angle of approximately 90-100°. The sulfur-hydrogen bond is weaker and longer than the oxygen-hydrogen bond in alcohols, which influences the reactivity and acidity of thiols.