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TIRUNELVELI – 627012

OPEN AND DISTANCE LEARING(ODL) PROGRAMMES

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

M.Sc. CHEMSITY
COURSE MATERIALS
GENERAL CHEMISTRY IV
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UNIT-I

THERMO DYNAMICS I

Thermodynamics is the branch of science that deals with energy, heat, work, and the changes they bring in a system. A system refers to the specific part of the universe chosen for study, while the surroundings include everything outside the system that can interact with it. The system is separated from its surroundings by a boundary, which can be real or imaginary. Systems can be classified into three types: open systems, which exchange both matter and energy with the surroundings; closed systems, which exchange only energy but not matter; and isolated systems, which do not exchange either energy or matter. The state of a system is defined by properties such as temperature, pressure, volume, and composition, while state functions are properties that depend only on the current state of the system, not on the path taken to reach that state. Thermodynamic properties can also be categorized as extensive properties, which depend on the amount of substance (such as mass and volume), and intensive properties, which are independent of the amount of substance (such as temperature and pressure). A system is said to be in thermodynamic equilibrium when it is in mechanical, thermal, and chemical equilibrium, meaning there are no unbalanced forces, no temperature differences, and no net chemical reactions. Thermodynamic processes include isothermal processes (constant temperature), adiabatic processes (no heat exchange), isobaric processes (constant pressure), and isochoric processes (constant volume). Processes can be reversible, where changes occur infinitely slowly and the system remains in equilibrium, or irreversible, where they proceed rapidly with energy dissipation. The First Law of Thermodynamics, also known as the law of energy conservation, states that energy cannot be created or destroyed but only transferred or transformed, mathematically represented as ΔU=q+w\Delta U = q + wΔU=q+w, where ΔU\Delta UΔU is the change in internal energy, qqq is heat added to the system, and www is work done on or by the system. These fundamental concepts form the basis for understanding energy transformations in physical and chemical systems.

Thermodynamics classifies variables and processes to understand how energy and matter behave in different systems. Intensive variables are properties that do not depend on the amount of substance present, such as temperature, pressure, and density. In contrast, extensive variables depend on the system's size or amount of matter, such as mass, volume, and total energy.

Thermodynamic properties can also be categorized into state functions and path functions. State functions depend only on the system's current state and are independent of the path taken to reach that state; examples include enthalpy, entropy, internal energy, and Gibbs free energy. Path functions, on the other hand, depend on the process or pathway taken and include heat (qqq) and work (www).

Thermodynamic systems are classified based on their interaction with the surroundings. An isolated system does not exchange either energy or matter with its surroundings, like an insulated thermos. A closed system exchanges energy but not matter, such as a sealed container that allows heat transfer. An open system allows both energy and matter exchange, like an uncovered boiling pot of water.

Thermodynamic processes describe how a system changes from one state to another. An isothermal process occurs at constant temperature ($\Delta T= 0$), while an adiabatic process occurs without heat exchange ($q=0$). An isobaric process happens at constant pressure ($\Delta P=0$), and an isochoric process takes place at constant volume ($\Delta V=0$). A cyclic process returns a system to its initial state after a series of transformations. In a reversible process, changes occur infinitely slowly, allowing the system to maintain equilibrium at every stage, whereas an irreversible process occurs quickly with energy dissipation, often resulting in entropy increase. Understanding these concepts helps in analyzing energy transformations in physical and chemical systems.

First law of thermodynamics

The First Law of Thermodynamics, also known as the Law of Energy Conservation, states that energy cannot be created or destroyed; it can only be transferred or transformed from one form to another. Mathematically, it is expressed as:

$$\mathbf{\Delta U=q+w}$$

where ΔU represents the change in internal energy of the system, q is the heat added to or removed from the system, and www is the work done on or by the system.

This law implies that any energy gained by a system must come from its surroundings, and vice versa. For example, in a gas expansion process, if heat is added to the system, its internal energy increases, or it does work on the surroundings by expanding. Similarly, if heat is removed or work is done on the system, its internal energy decreases.

The First Law applies to different types of thermodynamic processes:

Isothermal Process ($\Delta T=0$): The internal energy remains constant ($\Delta U=0$), so heat transfer is equal to work done ($q=-wq$).

Adiabatic Process ($q=0$): No heat is exchanged, so the change in internal energy is solely due to work done ($\Delta U=w$).

Isobaric Process ($\Delta P=0$): The pressure remains constant, and heat transfer changes both internal energy and work done.

Isochoric Process ($\Delta V=0$): The volume remains constant, so no work is done ($w=0$), and the change in internal energy is only due to heat ($\Delta U=q$).

The First Law of Thermodynamics is fundamental in understanding energy conservation in various systems, from engines and refrigerators to biological processes and chemical reactions.

Thermodynamics, heat, work, and internal energy are fundamental concepts that describe energy transformations within a system. These quantities help in understanding how energy is transferred and conserved in physical and chemical processes.

Heat (q):

Heat is a form of energy transfer that occurs due to a temperature difference between a system and its surroundings. It always flows from a higher-temperature region to a lower-temperature region until thermal equilibrium is reached. Heat transfer can occur through conduction, convection, or radiation. The significance of heat lies in its ability to change a system’s internal energy, affecting phase transitions, chemical reactions, and physical properties of materials.

Work (w):

Work is the energy transferred when a force is applied to a system, causing movement or volume change. In thermodynamics, work is often associated with pressure-volume (PV) work, where expansion or compression of gases takes place. The work done by or on a system is mathematically expressed as:

$$\mathbf{w = -P\Delta V}$$

where P is the external pressure and ΔV is the change in volume. Work is significant in mechanical and thermal processes, such as engines, turbines, and compressors, where energy conversion occurs.

Internal Energy (E or U):

Internal energy is the total energy contained within a system, including kinetic and potential energy at the molecular level. It accounts for translational, rotational, and vibrational motion of molecules as well as intermolecular interactions. The First Law of Thermodynamics expresses the change in internal energy as:

$$\Delta U = q + w$$

where qqq is heat added to the system and www is work done on the system. Internal energy plays a crucial role in determining thermodynamic stability, chemical equilibrium, and phase changes.

Together, heat, work, and internal energy define how energy flows and transforms in a system, providing the foundation for thermodynamic analysis in physics, chemistry, and engineering applications.

Enthalpy (H) and Energy Calculations for Expansion of Gases

Enthalpy (H):

Enthalpy (H) is a thermodynamic property that represents the total heat content of a system. It is defined as:

$$H = U + PV$$

where U is internal energy, P is pressure, and V is volume. Enthalpy is useful for analyzing heat changes in constant-pressure processes, such as chemical reactions and phase transitions. The change in enthalpy (ΔH) is given by:

$$\Delta H = \Delta U + P\Delta V$$

For ideal gases, if pressure remains constant, the heat absorbed or released by the system is equal to the enthalpy change:

$$qp = \Delta H$$

Calculation of q,w,U,H for Expansion of Gases

Gas expansion can be classified into reversible and irreversible processes, and it can occur under isothermal or adiabatic conditions.

1. Isothermal Expansion of an Ideal Gas

In an isothermal process (T= constant), the internal energy of an ideal gas does not change ($\Delta U=0$), so:

$$\mathbf{q= -w}$$

For reversible expansion, the work done by the gas is:

$$w= -nRT\ln Vi/Vf$$

where:

n = number of moles

R = gas constant

T = temperature

Vi/Vf = initial and final volumes

Since q=−wq, the heat absorbed by the system is also given by:

$$q= nRT\ln Vi/Vf$$

For irreversible expansion against constant external pressure (Pext), work is given by:

$w=-Pext\Delta V$

Since $\Delta U=0$, the heat exchanged is:

$q=Pext(Vf-Vi)$

2. Adiabatic Expansion of an Ideal Gas

In an adiabatic process (q=0), no heat exchange occurs, so the change in internal energy is equal to the work done:

$\Delta U=w$

For reversible adiabatic expansion, the work done is given by:

$w=nR(Ti-Tf)/\gamma-1$

where $\gamma=Cp/Cv$ (heat capacity ratio).

For irreversible adiabatic expansion, if the gas expands against a constant external pressure, the work done is:

$w=-Pext(Vf-Vi)$

Since q=0, the change in internal energy is given by:

$\Delta U=-Pext(Vf-Vi)$

The enthalpy change (ΔH\Delta HΔH) for an adiabatic process is:

$\Delta H=nCp(Tf-Ti)$

where CpC is the heat capacity at constant pressure.

Expansion of Real Gases

For real gases, deviations from ideal behavior occur due to intermolecular interactions. The van der Waals equation is used instead of the ideal gas law:

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

where:

a accounts for intermolecular attraction

b accounts for the finite volume of gas molecules

For real gases, additional factors such as Joule-Thomson expansion and non-ideal compressibility effects must be considered in work and heat calculations.

Relation Between Heat Capacities (Cp & Cv)

Heat capacity is the amount of heat required to raise the temperature of a substance by one degree. There are two types of heat capacities for gases:

- Heat capacity at constant volume (Cv): The heat required to raise the temperature of a gas while keeping volume constant.

- Heat capacity at constant pressure (Cp): The heat required to raise the temperature of a gas while keeping pressure constant.

The relation between these two is given by:

$$Cp - Cv = R$$

where R is the universal gas constant.

This equation is derived from the first law of thermodynamics:

$$dU = dq - PdV$$

For an ideal gas:

$$dU = nCvdT$$

and from enthalpy definition:

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

For a process at constant pressure:

$$dH = nCpdT$$

Using the ideal gas equation ($PV=nRTPV$), differentiating gives $PdV+VdP= nRdT$.

$$nCpdT = nCvdT + nRdT$$

which simplifies to:

$$Cp - Cv = R$$

This equation shows that at constant pressure, a gas absorbs more heat than at constant volume because part of the energy goes into doing work on the surroundings.

Joule-Thomson Effect and Inversion Temperature

The Joule-Thomson effect describes the temperature change of a real gas when it expands adiabatically (without heat exchange) through a porous plug or a throttling valve at constant enthalpy.

The Joule-Thomson coefficient (μJT) is defined as:

$$\mu JT=(\partial T/\partial P)H$$

If $\mu JT> 0$, the gas cools upon expansion (e.g., CO_2, N_2).

If $\mu JT<0$, the gas heats up upon expansion (e.g., H_2, He).

If $\mu JT=0$, the temperature remains unchanged, which occurs at the inversion temperature.

Inversion Temperature (Ti)

The inversion temperature is the temperature at which the Joule-Thomson coefficient changes sign. It is given by:

$$Ti=2aRb$$

where a and b are van der Waals constants.

For $T> Ti$, the gas warms upon expansion.

For $T< Ti$, the gas cools upon expansion.

The Joule-Thomson effect is widely used in liquefaction of gases such as in cryogenic applications, where gases like oxygen, nitrogen, and helium are cooled and converted into liquid states.

Thermochemistry

Thermochemistry is the branch of thermodynamics that deals with the study of heat changes occurring during chemical reactions. It provides insights into the energy transformations that take place when reactants convert into products.

Fundamental Concepts in Thermochemistry

1. System and Surroundings

The system refers to the part of the universe under study (e.g., a chemical reaction in a container).

The surroundings include everything outside the system.

The system and surroundings together form the universe.

2. Types of Systems

Open System: Exchanges both matter and energy with surroundings.

Closed System: Exchanges only energy, not matter.

Isolated System: No exchange of matter or energy.

3. Types of Reactions Based on Heat Changes

Exothermic Reactions: Release heat to the surroundings ($\Delta H < 0$). Example: Combustion of fuels.

Endothermic Reactions: Absorb heat from the surroundings ($\Delta H > 0$). Example: Photosynthesis.

4. First Law of Thermodynamics

The total energy of an isolated system remains constant.

Mathematically, it is expressed as:

$$\Delta U=q+w$$

where:

ΔU = Change in internal energy

q = Heat absorbed or released

w = Work done on or by the system

5. Enthalpy (H)

Enthalpy is the total heat content of a system, defined as:

$$H=U+ PV$$

The change in enthalpy (ΔH) at constant pressure is:

$$\Delta H=qp$$

where qp is the heat absorbed or released at constant pressure.

Important Thermochemical Laws

1. Hess's Law of Constant Heat Summation

The enthalpy change for a reaction is the same, whether it occurs in one step or multiple steps.

$$\Delta H_{overall}=\sum \Delta H_{steps}$$

2. Kirchhoff's Law

Describes how enthalpy changes with temperature:

$$dH/dT=Cp$$

Where Cp is the heat capacity at constant pressure.

Standard Enthalpy Changes

1. Standard Enthalpy of Formation (ΔHf°)

Heat change when 1 mole of a compound is formed from its elements in their standard states.

Example: Formation of water

$$H_2(g)+1/2\ O_2(g)\rightarrow H_2O(l)\ \Delta Hf^\circ=-285.8\ kJ/mol$$

Standard Enthalpy of Combustion ($\Delta Hc\ ^\circ$)

Heat change when 1 mole of a substance completely burns in oxygen.

Example: Combustion of methane

$$CH_4(g)+2O_2(g)\rightarrow CO_2(g)+2H_2O(l)\ \Delta Hc^\circ=-890.3\ kJ/mol$$

Standard Enthalpy of Neutralization ($\Delta Hneu\ ^\circ$)

Heat change when 1 mole of water forms from an acid-base reaction.

Example:

$$HCl(aq)+NaOH(aq)\rightarrow NaCl(aq)+H_2O(l)\ \Delta Hneu^\circ=-57.1\ kJ/mol$$

Applications of Thermochemistry

Fuel Efficiency: Helps in determining the energy content of fuels.

Industrial Processes: Used in designing energy-efficient chemical processes.

Food Industry: Determines calorific values of foods.

Environmental Science: Helps in studying heat absorption and release in atmospheric processes.

Heats of Reactions and Standard States

Heat of reaction refers to the amount of heat energy absorbed or released during a chemical reaction at constant pressure. It is represented by enthalpy change (ΔH\Delta HΔH) and depends on the nature of the reactants, products, and conditions under which the reaction occurs.

Standard States

A standard state is a reference state of a substance used to calculate thermodynamic properties. The standard state conditions are:

Pressure: 1 atm (101.3 kPa)

Temperature: 298 K (25°C)

Concentration (for solutions): 1 M

Physical state: The most stable form of the substance at standard conditions (e.g., O_2 is a gas, H_2O is a liquid).

The enthalpy change of a reaction under standard conditions is called standard enthalpy change (ΔH ∘).

Types of Heats of Reaction and Their Applications

1. Standard Enthalpy of Formation (ΔHf ∘)

The heat change when 1 mole of a compound is formed from its elements in their standard states.

Example: Formation of water

$$H_2(g)+12O_2(g)\rightarrow H_2O(l)\Delta Hf\circ=-285.8\ \text{kJ/mol}H\_2(g)$$

Application: Used to determine the stability of compounds.

2. Standard Enthalpy of Combustion (ΔHc°)

The heat released when 1 mole of a substance completely burns in oxygen.

Example: Combustion of methane

$$CH_4(g)+2O_2(g)\rightarrow CO_2(g)+2H_2O(l)\Delta Hc^\circ=-890.3\ \text{kJ/mol}$$

Application: Used to evaluate fuel efficiency.

3. Standard Enthalpy of Neutralization ($\Delta Hneu^\circ$)

The heat change when an acid and a base react to form 1 mole of water.

Example:

$$HCl(aq)+NaOH(aq)\rightarrow NaCl(aq)+H_2O(l)\Delta Hneu^\circ=-57.1\ \text{kJ/mol}$$

Application: Used in calculating energy changes in titrations and industrial acid-base reactions.

4. Standard Enthalpy of Solution ($\Delta Hsol^\circ$)

The heat change when 1 mole of a substance dissolves in a large amount of solvent.

Example: Dissolution of NaCl in water.

Application: Used in pharmaceutical and chemical industries to understand solubility and energy release during dissolution.

5. Standard Enthalpy of Fusion ($\Delta Hfus^\circ$)

The heat required to convert 1 mole of a solid to liquid at constant pressure.

Example: Melting of ice

$$H_2O(s)\rightarrow H_2O(l)\Delta Hfus^\circ=6.01\ \text{kJ/mol}$$

Application: Important in phase transition studies and material science.

6. Standard Enthalpy of Vaporization ($\Delta Hvap^\circ$)

The heat required to convert 1 mole of a liquid into vapor at constant pressure.

Example:

$$H_2O(l) \rightarrow H_2O(g) \Delta H_{vap}^{\circ} = 40.79 \text{ kJ/mol}$$

Application: Used in distillation and refining processes.

7. Standard Enthalpy of Sublimation (ΔH_{sub}°)

The heat required to convert 1 mole of a solid directly into vapor without passing through the liquid phase.

Example: Sublimation of dry ice (CO_2)

Application: Used in freeze-drying of foods and pharmaceuticals.

8. Standard Enthalpy of Atomization (ΔH_{atm}°)

The heat required to convert 1 mole of a substance into its individual gaseous atoms.

Example: Breaking O_2 into individual oxygen atoms.

Application: Important in bond energy calculations and metallurgy.

Applications of Heats of Reactions

Industrial Processes: Helps in designing energy-efficient chemical reactions (e.g., manufacturing ammonia via the Haber process).

Environmental Science: Used to study heat balance in the atmosphere and global warming.

Energy Production: Essential in evaluating fuels, explosives, and alternative energy sources.

Material Science: Helps in understanding phase transitions, alloy formation, and thermal stability of materials.

Effect of Temperature and Pressure on Enthalpy of Reactions

The enthalpy change (ΔH\Delta HΔH) of a reaction can be influenced by changes in temperature and pressure. These effects are described by Kirchhoff's equations and the principles of thermodynamics.

Effect of Temperature on Enthalpy of Reactions: Kirchhoff's Equations

Kirchhoff’s equation describes how the enthalpy change of a reaction varies with temperature. It is based on the relationship between enthalpy and heat capacity (CpC_pCp). The equation is:

$$d(\Delta H)dT= \Delta Cp$$

where:

ΔH = enthalpy change of the reaction

T = temperature

ΔCp = difference in heat capacities (Cp) of products and reactants

Integrated Kirchhoff’s Equation

For reactions occurring between two temperatures (T1-T2):

$$\Delta HT2=\Delta HT1+\int T1T2\Delta CpdT$$

If ΔCp is constant:

$$\Delta HT2=\Delta HT1+\Delta Cp(T2-T1)$$

This equation indicates that if the heat capacity of the products is greater than that of the reactants ($\Delta Cp>0$), enthalpy increases with temperature. Conversely, if $\Delta Cp<0$, enthalpy decreases with temperature.

Example: Application of Kirchhoff’s Law

For the combustion of carbon:

$$C(s)+O_2(g)\rightarrow CO_2(g)\Delta H298K=-393.5\text{ kJ/mol}$$

If ΔCp for the reaction is known, Kirchhoff’s equation can be used to calculate ΔH\Delta HΔH at a different temperature, such as 500 K.

Effect of Pressure on Enthalpy of Reactions

The dependence of enthalpy on pressure is given by:

$$(dP/dH)T=V-T(dT/dV)P$$

For solids and liquids, the change in enthalpy with pressure is negligible because they are incompressible (i.e., volume does not change significantly with pressure).

For gases, enthalpy depends on pressure only if there is a change in the number of moles of gas during the reaction.

If $\Delta ng=0$ (no net change in gaseous moles), enthalpy remains constant with pressure.

If $\Delta ng>0$ (more gas molecules in products), increasing pressure shifts equilibrium towards reactants (Le Chatelier's principle), potentially affecting ΔH\Delta HΔH.

If $\Delta ng< 0$ (fewer gas molecules in products), increasing pressure shifts equilibrium towards products.

Hess's Law and Its Applications

Hess's Law: Definition

Hess's Law, also known as the Law of Constant Heat Summation, states that the total enthalpy change of a reaction is the same, regardless of the pathway taken, provided the initial and final states remain unchanged.

Mathematically, if a reaction occurs in multiple steps, the sum of the enthalpy changes for each step equals the total enthalpy change of the overall reaction:

$$\Delta H_{overall}=\sum \Delta H_{steps}$$

This principle follows from the first law of thermodynamics, which states that energy is conserved. Since enthalpy is a state function, its change depends only on the initial and final states, not on the reaction path.

Applications of Hess's Law

1. Determination of Enthalpy Changes for Complex Reactions

Hess's law allows the calculation of enthalpy changes (ΔH) for reactions that are difficult to measure experimentally by breaking them into simpler known reactions.

Example: Formation of Carbon Dioxide

The direct combustion of carbon to CO_2:

$$C(s)+O_2(g)\rightarrow CO_2(g)\Delta H=-393.5\ kJ/mol$$

However, if carbon is first converted to CO and then to CO_2, the enthalpy changes are:

$$C(s)+1/2O_2(g)\rightarrow CO(g)\Delta H=-110.5\ kJ/mol$$

By Hess's law, summing these two reactions gives the total enthalpy change:

$$\Delta H=(-110.5)+(-283.0)=-393.5\ kJ/mol$$

This confirms the direct enthalpy change using an indirect path.

2. Calculation of Standard Enthalpy of Formation ($\Delta Hf\ ^\circ$)

The enthalpy change for the formation of a compound from its elements in their standard states can be determined using Hess's law.

Example: Enthalpy of Formation of Methane (CH_4)

$$C(s)+2H_2(g)\rightarrow CH_4(g)\Delta Hf^\circ$$

Since direct measurement is difficult, we use known enthalpy changes:

$$C(s)+O_2(g)\rightarrow CO_2(g)\quad \Delta H=-393.5\ kJ/mol$$
$$H_2(g)+1/2O_2(g)\rightarrow H_2O(l)\quad \Delta H=-285.8\ kJ/mol$$
$$CH_4(g)+2O_2(g)\rightarrow CO_2(g)+2H_2O(l)\quad \Delta H=-890.3\ kJ/mol$$

By rearranging and applying Hess's law, the enthalpy of formation for methane can be determined.

3. Calculation of Bond Enthalpies

Hess's law helps determine bond dissociation enthalpies by using enthalpy changes of known reactions.

Example: Bond Energy of O_2

$$O_2(g) \rightarrow 2O(g) \Delta H=?$$

Using combustion data and Hess's law, we can derive the bond energy.

4. Calculation of Lattice Energy

Hess's law is used in Born-Haber cycles to determine the lattice energy of ionic compounds by summing various energy steps.

Example: Formation of NaCl

$$Na(s)+1/2\ Cl_2(g) \rightarrow NaCl(s) \qquad \Delta H=?$$

By using ionization energy, electron affinity, and enthalpy of sublimation, the lattice energy can be determined indirectly.

Determination of Bond Energy

Definition of Bond Energy

Bond energy (also called bond dissociation enthalpy) is the amount of energy required to break one mole of a specific chemical bond in a gaseous state. It is measured in kilojoules per mole (kJ/mol) and provides insight into the strength and stability of chemical bonds.

The bond dissociation energy for a homolytic bond cleavage (where each atom retains one electron) is given by:

$$X-Y \rightarrow X\cdot+Y\cdot \Delta H=\text{Bond Energy}$$

Methods for Determining Bond Energy

1. Using Hess's Law

Hess's law states that the total enthalpy change of a reaction is independent of the pathway taken. Bond energies can be determined using this principle by analyzing known enthalpy changes of reactions.

Example: Calculation of O-H Bond Energy in Water

The reaction:

$$H_2O(g) \rightarrow 2H(g) + O(g)H_2O(g)$$

Given:

- Enthalpy of formation of water:

$$H_2O(g) \rightarrow 2H(g) + O(g)$$

Bond energy of H-H = 436 kJ/mol

Bond energy of O=O = 498 kJ/mol

Using Hess's Law, we can solve for the O-H bond energy.

2. Using Average Bond Energies

Since bond energies vary slightly depending on the molecular environment, average bond energies are calculated by considering multiple molecules.

Example: CH_4 (Methane)

$$CH_4(g) \rightarrow C(g) + 4H(g)$$

The experimental enthalpy change is measured, and since methane has four identical C-H bonds, the average bond energy per bond is:

$$\text{C-H Bond Energy} = \Delta H_{\text{total}}/4$$

3. Born-Haber Cycle for Ionic Compounds

In ionic compounds, bond energy is often related to lattice energy and determined using the Born-Haber cycle. This involves calculating ionization energy, electron affinity, and enthalpy changes during formation.

Example: NaCl Formation

$$Na(s) + 1/2Cl_2(g) \rightarrow NaCl(s)$$

By applying Hess's Law to sublimation energy, ionization energy, and electron affinity, the Na-Cl bond energy can be derived.

Factors Affecting Bond Energy

1. Bond Order: Higher bond order (single, double, triple) increases bond energy.

2. Bond Length: Shorter bonds are stronger and have higher bond energy.
3. Electronegativity Difference: Polar bonds tend to have higher bond energy.
4. Resonance and Delocalization: Delocalized bonds have lower bond energy.

Applications of Bond Energy

- Predicting reaction enthalpies using bond energy values.
- Understanding molecular stability and chemical reactivity.
- Explaining combustion reactions and biochemical processes.

Measurement of Heat of Reaction

The heat of reaction (enthalpy change, ΔH) is the amount of heat released or absorbed during a chemical reaction at constant pressure. It is measured in kilojoules per mole (kJ/mol) and can be determined experimentally using calorimetry or calculated using thermodynamic equations.

Methods for Measuring Heat of Reaction

1. Calorimetry

Calorimetry is the most common experimental method for measuring the heat of reaction. It involves using a calorimeter, which is an insulated system that prevents heat loss to the surroundings.

- Principle: The heat absorbed or released in a reaction is transferred to a known amount of substance (usually water), and the temperature change is measured.
- Formula Used:

$$q= mCp\Delta T$$

where:

q = heat exchanged (J or kJ)

m = mass of the substance (g)

Cp = specific heat capacity (J/g·°C)

ΔT = temperature change (°C or K)

Types of Calorimeters:

1. Bomb Calorimeter (Constant Volume)

Used for combustion reactions (e.g., measuring the heat of combustion of fuels).

A sample is placed in a strong metal bomb, ignited in excess oxygen, and the heat released is absorbed by surrounding water.

2. Coffee Cup Calorimeter (Constant Pressure)

Used for reactions occurring in solutions (e.g., neutralization, dissolution).

The reaction takes place in a styrofoam cup with a thermometer measuring the temperature change of the solution.

2. Hess's Law Approach

Hess's Law states that the total enthalpy change of a reaction is the sum of the enthalpy changes of individual steps leading to the overall reaction.

If direct measurement is difficult, enthalpy of formation or bond energies can be used to calculate ΔH.

Example:

$$\Delta H_{\text{reaction}} = \sum \Delta H_{\text{products}} - \sum \Delta H_{\text{reactants}}$$

3. Using Bond Energy Values

The heat of reaction can be estimated using bond dissociation energies (BDE).

Formula:

$$\Delta H = \sum_{\text{Bond Energies (Reactants)}} - \sum_{\text{Bond Energies (Products)}}$$

This approach is useful for gas-phase reactions but less accurate for solutions or solid-state reactions.

Applications of Measuring Heat of Reaction

- Determining reaction feasibility (Exothermic or Endothermic).
- Industrial applications (Designing energy-efficient processes).

- Biochemical studies (Measuring metabolic heat changes).
- Environmental studies (Heat released from combustion fuels).

Heat of reaction measurement is crucial in thermodynamics and chemical engineering, helping predict reaction behavior, energy efficiency, and safety considerations in various chemical processes.

Determination of Calorific Value of Food and Fuels

The calorific value is the amount of heat energy released when a substance undergoes complete combustion. It is measured in kilojoules per gram (kJ/g) or kilocalories per gram (kcal/g). This value is crucial for determining the energy content of fuels and food items, which helps in energy management, diet planning, and fuel efficiency assessments.

Methods for Determining Calorific Value

1. Bomb Calorimeter Method (For Fuels & Food)

A sample of fuel or food is placed in a bomb calorimeter, which is a sealed container surrounded by water.

The sample is ignited in the presence of excess oxygen.

The heat released during combustion is transferred to the surrounding water, and the temperature rise is recorded.

The calorific value is calculated using:

$$\text{Calorific Value} = \text{Heat absorbed by water}/\text{Mass of Sample}$$

$$q = {}_{m}Cp\Delta T$$

where:

q = heat released (J or kJ)

m = mass of water (g)

Cp = specific heat capacity of water (J/g·°C)

ΔT = temperature change (°C)

Dulong’s Formula (For Fuels)

Used to estimate the calorific value of solid and liquid fuels based on their elemental composition:

$$CV=(8080C+34500(H-O/8)+2240S)\ kJ/kg$$

where:

C,H,O,S = percentage of Carbon, Hydrogen, Oxygen, and Sulfur in fuel.

Zeroth Law of Thermodynamics

The Zeroth Law of Thermodynamics states that:

"If two systems are each in thermal equilibrium with a third system, then they are in thermal equilibrium with each other."

Concept & Significance

- This law establishes the concept of temperature and thermal equilibrium.
- It forms the basis for designing thermometers and temperature measurement scales.

Example:

Suppose body A is in thermal equilibrium with body B, and body B is in thermal equilibrium with body C. Then, body A and body C must also be in thermal equilibrium. This means they all have the same temperature.

The Zeroth Law is fundamental in thermodynamics, ensuring that temperature can be used as a reliable property to compare thermal states of different systems.

Absolute Temperature Scale

The absolute temperature scale is a thermodynamic temperature scale that starts from absolute zero, the lowest possible temperature where all molecular motion theoretically stops. The two most commonly used absolute temperature scales are:

1. Kelvin Scale (K) – Used in scientific and engineering calculations.
2. Rankine Scale (°R) – Used in thermodynamic calculations in some engineering fields, especially in the U.S.

Kelvin Scale (SI Unit of Temperature)

The Kelvin (K) is the SI unit of temperature, defined so that absolute zero is 0 K.

It is related to the Celsius scale by:

$$T(K)=T(°C)+273.15$$

Water freezes at 273.15 K and boils at 373.15 K under standard conditions.

Rankine Scale (°R)

The Rankine scale is mainly used in engineering applications in the U.S.

It is related to the Fahrenheit scale as:

$$T(°R)=T(°F)+459.67$$

Absolute zero in this scale is 0°R.

Significance of Absolute Temperature Scale

It eliminates negative temperatures in thermodynamic calculations.

It is used in thermodynamic laws, such as the ideal gas law:

$$PV= nRT$$

The Kelvin scale provides a universal reference for scientific studies and engineering application.

UNIT-II

THERMO DYNAMICS II

Second Law of Thermodynamics

The Second Law of Thermodynamics states that the entropy of an isolated system always increases over time, meaning that natural processes tend to move towards a state of greater disorder or randomness. This law establishes the concept of irreversibility in natural processes and sets limits on the efficiency of heat engines.

Statements of the Second Law

There are two widely used formulations of the Second Law:

1. Kelvin-Planck Statement (Heat Engine Statement)

It is impossible to construct a heat engine that operates in a cyclic process and converts all the heat energy into work without any loss.

This implies that some energy will always be lost as waste heat in any practical heat engine.

2. Clausius Statement (Refrigeration Statement)

It is impossible to construct a device that transfers heat from a colder body to a hotter body without external work being done.

This means that heat cannot flow spontaneously from a cold region to a hot region, requiring external energy input (e.g., refrigerators, air conditioners).

Concept of Entropy (S)

Entropy is a measure of disorder or randomness in a system.

The Second Law states that for any spontaneous process, the total entropy of the system and its surroundings always increases:

$$\Delta S_{universe}=\Delta S_{system}+\Delta S_{surroundings}>0$$

In a reversible process, entropy remains constant, while in an irreversible process, entropy increases.

Applications of the Second Law

1. Heat Engines – Limits the efficiency of engines such as steam turbines and car engines.
2. Refrigerators & Heat Pumps – Explains why external work is required to transfer heat from cold to hot.
3. Energy Degradation – Demonstrates that energy transformations always result in some unusable energy (waste heat).
4. Natural Spontaneous Processes – Explains why ice melts, gases expand, and chemical reactions proceed in a certain direction.

The Second Law of Thermodynamics is fundamental in physics, chemistry, and engineering, governing how energy is transferred and used in real-world systems.

Limitations of the First Law of Thermodynamics

The First Law of Thermodynamics states that energy can neither be created nor destroyed, only converted from one form to another. It is mathematically expressed as:

$$\Delta U=Q-W$$

where ΔU is the change in internal energy, Q is the heat added to the system, and W is the work done by the system.

However, the First Law has several limitations:

1. No Direction of Processes

The First Law only accounts for energy conservation but does not specify whether a process is spontaneous or reversible.

Example: It does not explain why heat naturally flows from a hot object to a cold object, not vice versa.

2. No Explanation of Efficiency

It does not impose limits on the efficiency of heat engines or other energy conversions.

Example: While energy is conserved, it does not tell us how much useful work can be extracted from a given process.

3. No Consideration of Entropy

The First Law does not discuss entropy (S), which governs disorder and irreversibility.

Example: A gas expands freely in a vacuum, but the law does not explain why the process is irreversible.

4. Cannot Distinguish Between Possible and Impossible Processes

The First Law allows processes that do not actually occur in nature.

Example: It suggests that 100% efficient machines (perpetual motion machines of the second kind) could exist, which violates the Second Law of Thermodynamics.

5. Does Not Address Spontaneity

It does not tell us whether a reaction or process will occur spontaneously without external energy.

Example: The First Law alone cannot explain why a chemical reaction happens in one direction but not in reverse.

Spontaneity and Randomness in Thermodynamics

Spontaneity

Spontaneity in thermodynamics refers to the ability of a process to occur on its own without any external influence. A spontaneous process moves in a preferred direction naturally and is irreversible without external energy.

Example: Ice melts at room temperature without any external intervention.

Criteria for Spontaneity:

A process is spontaneous if the total entropy (S) of the universe increases:

$$\Delta S_{universe}=\Delta S_{system}+\Delta S_{surroundings}>0$$

A process is also spontaneous if the Gibbs free energy change (ΔG) is negative:

$$\Delta G = \Delta H - T\Delta S < 0$$

where ΔH is enthalpy change, T is temperature, and ΔS is entropy change.

Types of Spontaneous Processes:

1. Exergonic Processes ($\Delta G < 0$) – Occur spontaneously (e.g., combustion, rusting).
2. Endergonic Processes ($\Delta G > 0$) – Do not occur spontaneously and require energy input.

Randomness (Entropy, S)

Randomness in thermodynamics is measured by entropy (S), which represents the degree of disorder in a system. A highly disordered system has higher entropy.

Example: Gas molecules in a container move randomly, leading to high entropy.

Entropy Change (ΔS):

If $\Delta S > 0$, the system becomes more disordered (spontaneous).

If $\Delta S < 0$, the system becomes more ordered (non-spontaneous).

Relationship Between Spontaneity and Randomness

A process is more likely to be spontaneous if it increases disorder ($\Delta S > 0$).

For a process to be spontaneous at all temperatures, ΔS must be positive, or ΔG must be negative.

Carnot's Cycle

Carnot's Cycle is a theoretical thermodynamic cycle that defines the maximum possible efficiency of a heat engine operating between two temperatures. It was developed by Sadi Carnot in 1824 and is considered the most efficient cycle for converting heat into work.

Stages of Carnot's Cycle

The Carnot cycle consists of four reversible processes operating between a hot reservoir (T_1) and a cold reservoir (T_2):

1. **Isothermal Expansion (A → B)**

The gas expands **slowly** while absorbing heat **(Q_1)** from the hot reservoir at **constant temperature (T_1)**.

Since temperature is constant, **internal energy (ΔU) does not change**, and the heat input is completely converted into work.

Work done:

$$W=nRT1lnV1/V2$$

2. **Adiabatic Expansion (B → C)**

The gas expands **without heat exchange** ($Q = 0$), causing the temperature to drop from **T_1 to T_2**.

The gas continues to do **work**, but now at the expense of **internal energy (U)**, leading to a temperature decrease.

3. **Isothermal Compression (C → D)**

The gas is compressed **slowly** at the lower temperature **T_2**, releasing heat **(Q_2)** to the cold reservoir.

Since temperature remains constant, work is done **on** the gas, and heat is expelled.

4. **Adiabatic Compression (D → A)**

The gas is compressed **without heat exchange**, increasing the temperature from **T_2 back to T_1**.

The cycle returns to its initial state, completing one full operation.

Efficiency of Carnot's Cycle

The Carnot efficiency (**η**) is the maximum efficiency a heat engine can achieve:

$$\eta=1-T2/T1$$

where:

T_1 = Temperature of the hot reservoir (in Kelvin)

T_2 = Temperature of the cold reservoir (in Kelvin)

Significance of Carnot's Cycle

- Defines the upper limit of efficiency for any real heat engine.
- Shows that efficiency increases as the temperature difference (T_1 - T_2) increases.
- Demonstrates that no real engine can be 100% efficient, as some heat is always lost to the cold reservoir.

Concept of Entropy

Entropy is a fundamental concept in thermodynamics that measures the degree of disorder or randomness in a system. It is denoted by S and plays a crucial role in determining the direction of spontaneous processes.

Definition of Entropy

Entropy is defined as the measure of energy dispersion in a system or the unavailability of energy for doing useful work. Mathematically, for a reversible process, the change in entropy (ΔS) is given by:

$$\Delta S=dQrev/T$$

where:

dQ_{nev} = Heat absorbed or released in a reversible process

T = Absolute temperature in Kelvin

Entropy and the Second Law of Thermodynamics

The Second Law states that for any spontaneous process, the total entropy of the universe always increases:

$$\Delta S_{universe}=\Delta S_{system}+\Delta S_{surroundings}>0$$

This implies:

Reversible processes: Entropy remains constant ($\Delta S = 0$)

Irreversible (spontaneous) processes: Entropy increases ($\Delta S > 0$)

Physical Interpretation of Entropy

1. Entropy as Disorder

- A highly ordered system (e.g., a solid) has low entropy.
- A disordered system (e.g., a gas) has high entropy.
- Melting of ice or evaporation of water increases entropy.

2. Entropy as Energy Dispersal

Heat naturally flows from hot to cold because it spreads energy more uniformly, increasing entropy.

3. Entropy and Probability

Entropy is linked to the number of ways particles can be arranged. More possible arrangements mean higher entropy.

Entropy in Real-Life Examples

- Mixing of gases: When two gases are mixed, they spread out, increasing entropy.
- Dissolution of salt in water: The ions disperse, increasing randomness and entropy.
- Burning of fuel: A highly ordered solid fuel converts into gaseous products, increasing entropy.

Entropy Change for Reversible and Irreversible Processes

Entropy (S) is a measure of the disorder in a system. The change in entropy (ΔS) depends on whether a process is reversible or irreversible.

1. Entropy Change in a Reversible Process

A reversible process is an idealized process that occurs infinitely slowly and can be reversed without leaving any effect on the surroundings. The entropy change for a reversible process is given by:

$$\Delta S = \int dQrev/T$$

For a system undergoing a reversible process between two states A and B:

$$\Delta S = Qrev/T$$

where:

Q_{nev} = Heat absorbed or released in a reversible process

T = Absolute temperature in Kelvin

Example: Melting of ice at 0°C under equilibrium conditions is a reversible process.

For an isothermal expansion of an ideal gas:

$$\Delta S = nR\ln Vi/Vf$$

where n is the number of moles, R is the gas constant, and Vf/Vi is the final/initial volume ratio.

2. Entropy Change in an Irreversible Process

An irreversible process occurs spontaneously and cannot be reversed without external intervention. Examples include heat transfer, spontaneous expansion, and frictional processes.

For an irreversible process, the entropy change of the system remains the same as in the reversible case, but the entropy change of the universe increases:

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

In spontaneous processes, the entropy of the surroundings increases because heat is dissipated.

Example: Free expansion of a gas in a vacuum is an irreversible process, leading to an entropy increase.

For an irreversible heat transfer, the entropy change of the system is:

$$\Delta S > Qirr/T$$

where Q_{nev} is replaced by Q_{nirr}, meaning the process is no longer reversible.

Entropy of Mixing

Entropy of mixing refers to the increase in entropy when two or more different substances (usually gases or liquids) are mixed without any chemical reaction. This entropy change occurs due to the increased randomness and distribution of molecules in the final mixture compared to the separate components.

1. Expression for Entropy of Mixing

For an ideal gas mixture, the entropy change upon mixing is given by:

$$\Delta S_{mix} = -nR\sum x_i \ln x_i$$

where:

n = Total number of moles in the system

R = Universal gas constant

x_i = Mole fraction of component i

For a binary mixture of two ideal gases A and B:

$$\Delta S_{mix} = -nR(x_A \ln x_A + x_B \ln x_B)$$

where x_A and x_B are the mole fractions of gases A and B.

2. Explanation

Before mixing, each gas has its own defined volume and occupies specific regions.

After mixing, the molecules are randomly distributed, leading to an increase in disorder.

Since entropy is a measure of disorder, entropy increases upon mixing.

3. Entropy of Mixing in Liquids and Solutions

For ideal liquid solutions, a similar formula applies. However, in real solutions, deviations occur due to intermolecular interactions. If the interactions are strong, the entropy of mixing may be lower than expected for an ideal solution.

4. Special Cases

For identical gases: No entropy change occurs since the molecular arrangement remains unchanged.

For non-ideal solutions: Additional factors like enthalpic interactions must be considered.

5. Significance of Entropy of Mixing

It explains why gases spontaneously mix without requiring external energy.

It plays a key role in chemical thermodynamics, affecting phase behavior and solution stability.

It contributes to the Gibbs free energy of mixing, influencing spontaneity in mixing processes.

Calculation of Entropy Changes of an Ideal Gas and a van der Waals Gas with Changes in Temperature

Entropy is a thermodynamic quantity that measures the disorder of a system. For gases, entropy changes occur due to variations in temperature, volume, and pressure. Here, we derive entropy changes for ideal gases and van der Waals gases due to temperature changes.

1. Entropy Change of an Ideal Gas with Temperature Change

For an ideal gas, entropy depends only on temperature and volume (or pressure). The differential form of entropy change is:

$$dS=dqrev/T$$

For a temperature change at constant volume, heat transfer is given by:

$$dqrev= C_VdT$$

Thus, the entropy change from T_1 to T_2 at constant volume is:

$$\Delta S=\int T1T2\ CVdT/T$$

Similarly, at constant pressure, using CPC instead of CVC

$$\Delta S=CPln\ T2/T1$$

Where:

CP = Heat capacity at constant pressure

CV = Heat capacity at constant volume

These equations show that entropy increases with temperature because molecular disorder increases.

2. Entropy Change for a van der Waals Gas with Temperature Change

The van der Waals equation modifies the ideal gas law to include intermolecular interactions and finite molecular volume:

$$(P+a/V2)(V-b)=RT$$

where:

- a accounts for attractive forces
- b accounts for molecular volume

For a van der Waals gas, entropy change with temperature at constant volume is:

$$\Delta S=\int T1T2CV/TdT$$

Since CV is different from that of an ideal gas due to molecular interactions, it includes an additional correction term:

$$\Delta S=CVvdWlnT2/T1$$

=CVideal+f(a,b), a function that depends on the van der Waals constants a and b.

Key Differences Between Ideal and van der Waals Gas Entropy Change

1. For ideal gases, entropy change depends only on temperature.
2. For van der Waals gases, entropy change is influenced by intermolecular forces and molecular volume.
3. The van der Waals correction reduces the entropy compared to an ideal gas, as attractive forces restrict randomness.

Volume and Pressure, Entropy, and Disorder

Volume and Pressure

- **In Thermodynamics**: According to Boyle's Law, for a given mass of gas at constant temperature, the product of pressure and volume is constant (PV=constant). This means that if the volume of a gas decreases, its pressure increases, and vice versa. For example, when you squeeze a balloon (reducing its volume), the air inside exerts more pressure on the balloon's walls.
- **In Fluid Mechanics**: Volume and pressure are also crucial. For incompressible fluids like water, changes in volume are minimal, but pressure variations play a significant role in fluid flow and force calculations. In a hydraulic system, pressure applied to a small volume of fluid can transmit force to a larger volume, enabling the lifting of heavy objects.

Entropy and Disorder

- **In Thermodynamics**: Entropy is a measure of the randomness or disorder of a system. The Second Law of Thermodynamics states that in any natural process, the total entropy of an isolated system will always increase over time. For example, when ice melts into water, the molecules move more freely, and the system becomes more disordered, leading to an increase in entropy.

- **In Information Theory**: Entropy is used to quantify the amount of uncertainty or information content in a message or data set. Higher entropy means more uncertainty or randomness in the information. For example, a coin toss has an entropy of 1 bit because there are two equally likely outcomes (heads or tails). If you have a message with more unpredictable symbols, it has higher entropy and conveys more information.

Free Energy and Work Functions

Free Energy

Free energy is a thermodynamic property that helps determine the maximum amount of work that can be extracted from a system at constant temperature and pressure. There are two main types of free energy:

1. Helmholtz Free Energy (A):

Definition: The Helmholtz free energy is defined as $A=U-TS$, where U is the internal energy, T is the temperature, and S is the entropy.

Use: It is useful for systems at constant temperature and volume. The change in Helmholtz free energy (ΔA) represents the maximum reversible work done by the system at constant temperature.

2. Gibbs Free Energy (G):

Definition: The Gibbs free energy is defined as $G=H-TS$, where H is the enthalpy, T is the temperature, and S is the entropy. It can also be written as $G=U+PV-TS$, where P is the pressure and V is the volume.

Use: It is particularly useful for systems at constant temperature and pressure. The change in Gibbs free energy (ΔG) indicates the maximum non-volume expansion work that can be done by the system. A negative ΔG indicates a spontaneous process, while a positive ΔG indicates a non-spontaneous process.

Work Functions

In thermodynamics, work functions are related to the free energy and describe the maximum amount of work that can be done by a system under specific conditions:

1. Maximum Work at Constant Temperature and Volume:

For a system at constant temperature and volume, the maximum reversible work done by the system is given by the negative change in Helmholtz free energy: $W\text{max}=-\Delta A$.

2. Maximum Work at Constant Temperature and Pressure:

For a system at constant temperature and pressure, the maximum reversible work done by the system, excluding work done against the atmosphere, is given by the negative change in Gibbs free energy: $W\text{max}=-\Delta G$

The need for free energy functions arises from several practical and theoretical considerations in thermodynamics and related fields. Here are the key reasons why free energy functions, such as Helmholtz free energy (A) and Gibbs free energy (G), are essential:

1. Predicting Spontaneity of Processes

Gibbs Free Energy (G): The change in Gibbs free energy (ΔG) is a crucial indicator of the spontaneity of a process at constant temperature and pressure. If $\Delta G<0$, the process is spontaneous; if $\Delta G>0$, the process is non-spontaneous; and if $\Delta G=0$, the system is at equilibrium.

Helmholtz Free Energy (A): Similarly, the change in Helmholtz free energy (ΔA) helps determine the spontaneity of a process at constant temperature and volume.

2. Maximizing Work Output

Gibbs Free Energy: The maximum non-volume expansion work that can be extracted from a system at constant temperature and pressure is given by $-\Delta G$. This is particularly important in practical applications such as chemical reactions, batteries, and fuel cells, where the goal is to maximize the useful work output.

Helmholtz Free Energy: The maximum work that can be extracted from a system at constant temperature and volume is given by $-\Delta A$. This is relevant in systems where volume changes are negligible or controlled.

3. Understanding Equilibrium Conditions

Gibbs Free Energy: At equilibrium, $\Delta G=0$. This condition helps in determining the equilibrium state of a system, which is crucial for understanding phase transitions, chemical equilibria, and other equilibrium phenomena.

Helmholtz Free Energy: Similarly, at equilibrium, $\Delta A=0$, providing insights into systems where volume is constant.

4. Simplifying Complex Systems

Gibbs Free Energy: By combining enthalpy (H) and entropy (S) into a single function ($G=H-TS$), Gibbs free energy simplifies the analysis of systems where both heat transfer and work are involved. This is particularly useful in chemical engineering, materials science, and biochemistry.

Helmholtz Free Energy: Combining internal energy (U) and entropy ($A=U-TS$) simplifies the analysis of systems where volume changes are not significant.

5. Thermodynamic Cycles and Engines

Gibbs Free Energy: In thermodynamic cycles (e.g., Carnot cycle, Rankine cycle), the Gibbs free energy helps in evaluating the efficiency and work output of engines and refrigerators. It provides a clear measure of the useful work that can be extracted from a system.

Helmholtz Free Energy: In systems where volume is constant, such as some types of heat engines or in the analysis of phase transitions, Helmholtz free energy is a valuable tool.

6. Biological and Chemical Systems

Gibbs Free Energy: In biochemistry, the Gibbs free energy is used to understand metabolic pathways, enzyme kinetics, and the spontaneity of biochemical reactions. It helps in determining the direction of reactions and the energy changes involved.

Helmholtz Free Energy: In systems where volume changes are minimal, such as in some biological cells, Helmholtz free energy provides insights into the thermodynamic behavior of the system.

7. Material Science and Phase Transitions

Gibbs Free Energy: In material science, the Gibbs free energy is used to study phase transitions, such as melting, freezing, and vaporization. It helps in predicting the stability of different phases and the conditions under which phase transitions occur.

Helmholtz Free Energy: Similarly, Helmholtz free energy is used in the study of phase transitions in systems where volume changes are not significant.

Gibbs Free Energy

Definition

Gibbs free energy (G) is a thermodynamic potential that measures the maximum amount of reversible work that can be done by a system at constant temperature and pressure. It is defined as:

$G=H-TS$

where:

G is the Gibbs free energy,

H is the enthalpy of the system,

T is the absolute temperature,

S is the entropy of the system.

Significance

The Gibbs free energy is crucial for determining the spontaneity of a process under constant temperature and pressure conditions. The change in Gibbs free energy (ΔG) for a process is given by:

$\Delta G=\Delta H-T\Delta S$

where:

ΔH is the change in enthalpy,

ΔS is the change in entropy.

The spontaneity of a process can be determined as follows:

If $\Delta G<0$, the process is spontaneous.

If $\Delta G>0$, the process is non-spontaneous.

If $\Delta G=0$, the system is at equilibrium.

Applications

1. **Chemical Reactions**:

Gibbs free energy is used to predict the direction and feasibility of chemical reactions. For example, in a reaction where ΔG is negative, the reaction will proceed spontaneously in the forward direction.

2. **Phase Transitions**:

It helps in understanding phase transitions such as melting, freezing, and vaporization. The equilibrium between phases occurs when $\Delta G=0$.

3. **Electrochemical Cells**:

In electrochemistry, the Gibbs free energy change is related to the cell potential (E) by the equation: $\Delta G=-nFE$ where n is the number of moles of electrons transferred, and F is the Faraday constant.

4. **Biological Systems**:

In biochemistry, Gibbs free energy is used to study metabolic pathways and enzyme-catalyzed reactions. It helps in understanding the energy changes and the spontaneity of biochemical processes.

5. **Thermodynamic Cycles**:

In engineering, Gibbs free energy is used to analyze the efficiency of thermodynamic cycles, such as the Carnot cycle, Rankine cycle, and Brayton cycle.

Standard Gibbs Free Energy of Formation ($\Delta Gf\circ$)

The standard Gibbs free energy of formation ($\Delta Gf\circ$) is the change in Gibbs free energy when one mole of a substance is formed from its elements in their standard states. It is used to calculate the Gibbs free energy change for a reaction:

$\Delta G\circ=\sum\Delta Gf\circ(\text{products})-\sum\Delta Gf\circ(\text{reactants})$

Temperature Dependence

The Gibbs free energy change is temperature-dependent. The relationship between ΔG, ΔH, and ΔS shows how temperature affects the spontaneity of a process:

$\Delta G=\Delta H-T\Delta S$

If ΔH is negative and ΔS is positive, ΔG will be negative at all temperatures, indicating a spontaneous process.

If ΔH is positive and ΔS is negative, ΔG will be positive at all temperatures, indicating a non-spontaneous process.

If ΔH and ΔS have opposite signs, the spontaneity depends on the temperature.

Helmholtz Free Energy

Definition

Helmholtz free energy (A) is a thermodynamic potential that measures the useful work obtainable from a closed thermodynamic system at a constant temperature and volume. It is defined as:

$A=U-TS$

where:

A is the Helmholtz free energy,

U is the internal energy of the system,

T is the absolute temperature,

S is the entropy of the system.

Significance

1. **Work Function**: Helmholtz free energy is often referred to as the "work function" because it represents the maximum amount of work that can be done by a system at constant temperature and volume. For a reversible isothermal process, the change in Helmholtz free energy (ΔA) is equal to the maximum work done by the system:
2. $\Delta A=W\text{max}$

3. **Equilibrium and Spontaneity**: The Helmholtz free energy is used to determine the equilibrium state and the spontaneity of processes. At equilibrium, $\Delta A=0$. For a spontaneous process, $\Delta A<0$, indicating that the system will move towards a state of lower Helmholtz free energy.

4. **Statistical Mechanics**: In statistical mechanics, the Helmholtz free energy is closely related to the partition function (Z). It is given by:

$$A=-kT\ln Z$$

where k is the Boltzmann constant and T is the temperature. This relationship makes Helmholtz free energy a fundamental quantity in statistical physics.

Applications

1. **Equation of State**: The Helmholtz free energy is used to describe pure fluids with great precision, particularly in industrial applications such as refrigerants.
2. **Auto-Encoders**: In machine learning, the Helmholtz free energy is used in auto-encoders to calculate the total cost of the original code and the rebuilt code.
3. **Phase Transitions**: It helps in understanding phase transitions in systems where volume changes are minimal or controlled.

Derivation

The Helmholtz free energy can be derived from the first and second laws of thermodynamics. For a closed system at constant temperature and volume, the change in Helmholtz free energy is given by:

$dA=dU-TdS$

Using the first law of thermodynamics ($dU=\delta Q-\delta W$) and the second law ($\delta Q=TdS$), we get:

$dA=-PdV-SdT$

For a process at constant temperature and volume, $dV=0$ and $dT=0$, so:

$dA=0$

This indicates that the Helmholtz free energy is minimized at equilibrium

Variation of Gibbs Free Energy and Helmholtz Free Energy with Temperature, Pressure, and Volume

Gibbs Free Energy (G)

Variation with Temperature and Pressure:

Temperature: The Gibbs free energy (G) is defined as $G=H-TS$, where H is the enthalpy, T is the temperature, and S is the entropy. The change in Gibbs free energy (ΔG) is given by $\Delta G=\Delta H-T\Delta S$. The spontaneity of a process depends on the signs of ΔH and ΔS:

- If ΔH is negative and ΔS is positive, ΔG is negative at all temperatures, indicating a spontaneous process.
- If ΔH is positive and ΔS is negative, ΔG is positive at all temperatures, indicating a non-spontaneous process.
- If ΔH and ΔS have opposite signs, the spontaneity depends on the temperature.

Pressure: For processes at constant temperature and pressure, the Gibbs free energy is the most relevant thermodynamic potential. The Gibbs free energy change (ΔG) is directly related to the work done by the system at constant pressure.

Criteria for Spontaneity:

A process is spontaneous if $\Delta G<0$.

A process is non-spontaneous if $\Delta G>0$.

A process is at equilibrium if $\Delta G=0$.

Helmholtz Free Energy (A)

Variation with Temperature and Volume:

Temperature: The Helmholtz free energy (A) is defined as $A=U-TS$, where U is the internal energy, T is the temperature, and S is the entropy. The change in Helmholtz free energy (ΔA) is given by $\Delta A=\Delta U-T\Delta S$. Similar to Gibbs free energy, the spontaneity of a process depends on the signs of ΔU and ΔS:

If ΔU is negative and ΔS is positive, ΔA is negative at all temperatures, indicating a spontaneous process.

If ΔU is positive and ΔS is negative, ΔA is positive at all temperatures, indicating a non-spontaneous process.

If ΔU and ΔS have opposite signs, the spontaneity depends on the temperature.

Volume: For processes at constant temperature and volume, the Helmholtz free energy is the most relevant thermodynamic potential. The Helmholtz free energy change (ΔA) is directly related to the work done by the system at constant volume.

Criteria for Spontaneity:

A process is spontaneous if $\Delta A<0$.

A process is non-spontaneous if $\Delta A>0$.

A process is at equilibrium if $\Delta A=0$

Gibbs-Helmholtz Equation – Derivation and Applications

1. Introduction to the Gibbs-Helmholtz Equation

The Gibbs-Helmholtz equation is a fundamental thermodynamic equation that relates the Gibbs free energy (**G**) of a system to temperature (**T**) and enthalpy (**H**). It is used to determine how Gibbs free energy changes with temperature and is crucial for understanding spontaneity, equilibrium, and reaction feasibility.

The equation is expressed as:

$$(\partial(GT)\partial T)P=-H/T2$$

where:

G = Gibbs free energy

H = Enthalpy

T = Temperature in Kelvin

P = Constant pressure

2. Derivation of the Gibbs-Helmholtz Equation

From the definition of Gibbs free energy:

$G=H-TS$

Differentiating both sides with respect to temperature (**T**) at constant pressure (**P**):

$dG/dT=dH/dT-S-TdS/dT$

Using the thermodynamic relation:

$$(\partial G/\partial T)P=-S$$

And the enthalpy definition:

$$dH/dT=CP$$

where **CP** is the heat capacity at constant pressure, we get:

$$d(G/T)dT=-H/T2$$

which is the **Gibbs-Helmholtz equation**.

3. Applications of the Gibbs-Helmholtz Equation

Determining Temperature Dependence of Gibbs Free Energy

The equation helps evaluate how Gibbs free energy changes with temperature. It predicts how reactions shift at different temperatures.

Predicting Spontaneity of Chemical Reactions

- If **$G < 0$**, the reaction is spontaneous.
- If **$G > 0$**, the reaction is non-spontaneous.
- The equation helps analyze these changes under varying temperatures.

Van't Hoff Equation and Equilibrium Constant

The Gibbs-Helmholtz equation is used to derive the **Van’t Hoff equation**, which explains the temperature dependence of the equilibrium constant (**K**).

Phase Transitions

It helps in understanding phase equilibria, such as melting, boiling, and sublimation.

Electrochemical Cells

The equation is used to determine the temperature dependence of cell potentials in electrochemical reactions.

Thermodynamic Efficiency of Engines

It is used in evaluating energy transformations in thermodynamic cycles, such as in fuel cells and heat engines.

Maxwell Relationships

1. Introduction to Maxwell Relations

Maxwell relationships are a set of four important thermodynamic equations derived from the fundamental thermodynamic potentials. They provide a convenient way to express the interdependence between thermodynamic variables such as pressure (**P**), volume (**V**), temperature (**T**), and entropy (**S**). These relations are particularly useful in solving complex thermodynamic problems without directly measuring entropy changes.

2. Derivation of Maxwell's Relations

Maxwell's equations are derived from the four thermodynamic potentials:

Internal Energy (U):

$dU=TdS-PdV$

Enthalpy (H):

$dH=TdS+VdP$

Helmholtz Free Energy (F or A):

$dF=-SdT-PdV$

Gibbs Free Energy (G):

$dG=-SdT+VdP$

Since these functions are state functions, their second-order mixed partial derivatives must be equal, leading to the **four Maxwell relations**:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

3. Applications of Maxwell Relations

1. Determining Entropy and Internal Energy Changes

Maxwell's equations help express entropy (**S**) in terms of measurable variables like pressure (**P**) and volume (**V**), which are easier to measure.

2. Heat Capacity Relations

Maxwell relations are used to derive equations that connect heat capacities at constant pressure (**CP**) and constant volume (**CV**).

3. Joule-Thomson Coefficient

The Maxwell relations help derive the **Joule-Thomson coefficient**, which explains the cooling or heating of gases during expansion.

4. Thermodynamic Stability

The relations provide insight into phase transitions and conditions for stability in thermodynamic systems.

5. Calculation of Work and Free Energy

They simplify the calculation of thermodynamic potentials, making it easier to determine work done in various processes.

Thermodynamic Equations of State

1. Introduction

Thermodynamic equations of state describe the relationships between different thermodynamic variables such as pressure (**P**), volume (**V**), temperature (**T**), and internal energy (**U**) for a given system. These equations help define the behavior of gases, liquids, and solids under different thermodynamic conditions.

2. Types of Equations of State

(a) Ideal Gas Equation of State

One of the simplest and most fundamental equations of state is the **ideal gas law**, given by:

$PV=nRT$

where:

P = Pressure

V = Volume

n = Number of moles of gas

R = Universal gas constant (8.314 J/mol·K)

T = Temperature in Kelvin

This equation assumes that gas molecules do not interact and have negligible volume, which is valid for low-pressure and high-temperature conditions.

(b) Real Gas Equations of State

For real gases, the **ideal gas law** does not accurately describe behavior due to intermolecular interactions and finite molecular size. Several improved equations are used, such as:

1. Van der Waals Equation:

$(P+aV2)(V-b)=RT$

where:

a = Measure of attractive forces between molecules

b = Volume occupied by gas molecules

This equation corrects for molecular interactions and finite molecular volume.

2. Redlich-Kwong Equation:

$$P = \frac{RT}{V-b} - \frac{a}{T^{1/2}V(V+b)}$$

This equation further improves the accuracy of predictions for real gases by modifying temperature dependence.

3. Peng-Robinson Equation:

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)+b(V-b)}$$

This is widely used in engineering applications, especially for hydrocarbon gases.

(c) Thermodynamic Relationships

Other thermodynamic equations describe state functions and their relationships, including:

1. First Law of Thermodynamics:

$$dU=TdS-PdV$$

This equation expresses the change in internal energy (**U**) as a function of heat (**T dS**) and work (**-P dV**).

2. Gibbs Free Energy Equation:

$$dG=VdP-SdT$$

This equation relates the change in **Gibbs free energy (G)** to pressure and temperature variations.

3. Helmholtz Free Energy Equation:

$$dF=-SdT-PdV$$

This equation is useful in systems where temperature and volume are controlled.

3. Applications of Equations of State

Gas and vapor calculations in chemistry and engineering

Phase equilibrium analysis (e.g., predicting phase changes in substances)

Thermodynamic property estimation in real-world processes

Fluid dynamics and heat transfer studies

Thermodynamics of Mixing of Ideal Gases

The thermodynamics of mixing deals with the changes in thermodynamic properties when two or more ideal gases are mixed. For an **ideal gas mixture**, the gases do not interact with each other except through elastic collisions, and their behavior follows the **ideal gas law**. The mixing process occurs spontaneously due to entropy increase, without any heat exchange or work done.

2. Assumptions for Ideal Gas Mixing

The gases obey the **ideal gas law** ($PV=nRT$).

No chemical reactions occur between the gases.

The gases do not exert intermolecular forces on each other.

Mixing is **spontaneous** and occurs without energy input.

3. Changes in Thermodynamic Properties During Mixing

(a) Change in Volume

If the gases mix at constant pressure, the total volume of the mixture is simply the sum of the individual gas volumes before mixing:

$$V_{mix}=V_1+V_2+\cdots+V_n$$

However, if mixing occurs at constant volume, pressure changes according to Dalton’s Law of Partial Pressures.

(b) Change in Internal Energy (ΔU)

For ideal gases, the internal energy **U** depends only on temperature. Since mixing does not change temperature, there is **no change in internal energy**:

$$\Delta U_{mix}=0$$

(c) Change in Enthalpy (ΔH)

Similarly, for an ideal gas, enthalpy **H** is a function of temperature and remains unchanged during mixing:

$$\Delta H_{mix}=0$$

(d) Change in Entropy (ΔS)

The most significant thermodynamic change during mixing is the **increase in entropy** due to increased randomness. The entropy change for mixing of two ideal gases at constant temperature and pressure is given by:

$$\Delta S_{\text{mix}} = -R\sum_{i=1}^{n} n_i \ln X_i$$

where:

ni= number of moles of component iii

Xi= mole fraction of component iii in the final mixture

R = universal gas constant

Since the mole fractions are always less than one (Xi<1), the entropy change is **always positive**, meaning that mixing is spontaneous.

(e) Change in Gibbs Free Energy (ΔG\Delta GΔG)

The Gibbs free energy change for mixing at constant temperature and pressure is given by:

$$\Delta G_{\text{mix}} = RT\sum_{i=1}^{n} n_i \ln X_i$$

Since lnXi is always negative, ΔGmix is **always negative**, confirming that mixing of ideal gases is a spontaneous process.

Ellingham Diagram

The Ellingham diagram is a graphical representation that shows how the free energy of formation of metal oxides and other compounds changes with temperature. It is widely used in metallurgy to predict the ease of reducing metal oxides and to determine the best reducing agents for metal extraction. The diagram provides a clear way to understand the thermodynamic feasibility of oxidation and reduction reactions.

Applications of the Ellingham Diagram

(a) Predicting Feasibility of Reduction Reactions

The position of a metal oxide on the Ellingham diagram helps determine how easily it can be reduced. A metal oxide placed higher in the diagram is more difficult to reduce, whereas those lower in the diagram are easier to reduce.

(b) Determining Suitable Reducing Agents

The diagram helps select the most effective reducing agent for extracting metals from their ores. If the free energy of formation of a reducing agent's oxide is lower than that of the metal oxide, then the reducing agent can successfully remove oxygen and extract the metal. For example, carbon is commonly used to reduce iron ore in steelmaking.

(c) Metallurgical Extraction Processes

Metallurgists use the Ellingham diagram to optimize extraction processes in industries such as iron, aluminum, and copper production. It helps determine the best temperature and conditions for reduction reactions, improving efficiency and reducing energy costs.

(d) Predicting Stability of Oxides

The stability of metal oxides can be determined using the diagram. Metals that form oxides with very low free energy values are more stable and difficult to reduce. For example, aluminum oxide is extremely stable and requires electrolysis rather than carbon reduction for metal extraction.

(e) Effect of Temperature on Reduction

As temperature increases, the free energy of formation for oxides changes. Some oxides become easier to reduce at high temperatures, while others remain stable. This helps in deciding at what temperature a particular reduction process should be carried out for maximum efficiency.

Third Law of Thermodynamics

The Third Law of Thermodynamics states that as a system approaches absolute zero (0 K), the entropy of a perfect crystalline substance approaches a constant minimum, typically zero. This principle helps in understanding the behavior of substances at extremely low temperatures and is crucial for calculating absolute entropy values.

Nernst Heat Theorem

Nernst Heat Theorem, a key foundation of the Third Law, states that the change in entropy (ΔS) for a reaction or phase transition approaches zero as the temperature approaches absolute zero. This means that at extremely low temperatures, processes involving energy exchange occur with almost no entropy change.

3. Implications of the Third Law

(a) Absolute Zero is Unattainable

Since entropy approaches a minimum value but never reaches absolute zero, it is practically impossible to cool any system to exactly 0 K.

(b) Determination of Absolute Entropies

Using the Third Law, the absolute entropy of substances can be calculated, which is useful in thermodynamic calculations for predicting reaction spontaneity.

(c) Behavior of Materials at Low Temperatures

The Third Law explains why chemical and physical processes slow down significantly at very low temperatures, as energy and entropy changes become negligible.

(d) Implications in Cryogenics and Superconductivity

The law plays a vital role in low-temperature physics, influencing the study of superconductors, Bose-Einstein condensates, and cryogenic systems.

Applications of the Third Law of Thermodynamics

The Third Law of Thermodynamics is widely used in thermodynamic calculations, especially for determining entropy values at very low temperatures. One of its key applications is the **evaluation of absolute entropies from heat capacity measurements**.

1. Evaluation of Absolute Entropies from Heat Capacity Measurements

The Third Law allows the determination of absolute entropy values for substances by integrating heat capacity (Cp) data from absolute zero (0 K) to a given temperature. Since the entropy of a perfect crystal at 0 K is assumed to be zero, the entropy at any higher temperature can be found using heat capacity measurements.

The heat capacity (cp) of a substance is measured over a range of temperatures.

The entropy change is then calculated by integrating Cp/T over the temperature range.

This method provides reliable absolute entropy values, which are crucial for thermodynamic calculations.

2. Significance of Absolute Entropy Evaluation

Thermodynamic Data for Chemical Reactions: Absolute entropy values help in calculating entropy changes (ΔS\Delta SΔS) for reactions, which are used in Gibbs free energy equations to predict reaction spontaneity.

Understanding Phase Transitions: By analyzing entropy variations, phase transition behaviors like melting, boiling, and sublimation can be studied more precisely.

Material Science and Low-Temperature Studies: Absolute entropy values are crucial in studying properties of materials at extremely low temperatures, such as superconductors and quantum materials.

Environmental and Industrial Applications: Accurate entropy values help in optimizing energy conversion processes in industrial applications, such as power generation and refrigeration.

Exceptions to the Third Law of Thermodynamics

The Third Law of Thermodynamics states that the entropy of a perfect crystal at absolute zero (0 K) is exactly zero. However, there are some exceptions where substances do not follow this rule due to residual entropy, quantum effects, or structural irregularities.

1. Residual Entropy

Certain substances, even in their crystalline form, retain some entropy at absolute zero due to disorder in their atomic or molecular arrangement. This disorder prevents them from reaching a true zero-entropy state.

Example: Ice (H_2O at 0 K) Water molecules in ice can have multiple orientations due to hydrogen bonding, leading to residual entropy. Even at 0 K, the hydrogen atoms do not settle into a single unique arrangement.

Example: Carbon Monoxide (CO) In solid CO, the carbon and oxygen atoms can occupy different lattice positions randomly, preventing a perfect crystalline structure.

2. Glasses and Amorphous Solids

Glasses and amorphous solids do not form a well-ordered crystalline structure, even at very low temperatures. Instead of achieving a single minimum-energy state, these materials exhibit a "frozen disorder," leading to nonzero entropy at absolute zero.

Example: Silica (SiO_2) Glass Unlike crystalline quartz, silica glass remains disordered at low temperatures and retains entropy.

3. Magnetic and Spin Systems

Some materials, particularly magnetic substances, may not reach a perfectly ordered state even at absolute zero due to quantum mechanical effects.

Example: Spin Glasses and Frustrated Magnets Certain magnetic materials exhibit a phenomenon called "spin frustration," where their atomic spins cannot align in a single lowest-energy configuration. This leads to residual entropy.

Example: Superparamagnetic Materials In some cases, atomic spins fluctuate even near absolute zero, preventing complete entropy reduction.

4. Isotopic Disorder

If a crystal contains atoms of different isotopes (e.g., different masses of the same element), the arrangement of these isotopes may introduce disorder, preventing entropy from reaching zero.

Example: Solid Helium (^3He and ^4He mixtures) Helium does not solidify easily at low temperatures due to quantum mechanical effects. When helium is in a mixed isotope state, it exhibits residual entropy.

5. Quantum Effects in Superfluid and Superconducting Systems

Certain quantum mechanical phenomena, such as superfluidity and superconductivity, can lead to deviations from the Third Law.

Example: Helium-4 Superfluidity Liquid helium-4 remains a fluid even at absolute zero and does not crystallize under normal pressure. Since entropy is associated with phase transitions, helium-4 in the superfluid state does not reach a well-defined zero-entropy condition.

UNIT-III

GENERAL CHARACTERISTICS OF D-BLOCK ELEMENTS

TRANSITION ELEMENTS

What are Transition elements?

The elements lying between s and p-block of periodic table that constitute a large block of elements are called transition elements. These elements have partly field (n-1) d orbital. Since last electron fill into d-orbital, so they are called transition elements or d-block elements. They show transitional behavior.

Transition elements or d-block elements

They are classified into four series 3d, 4d, 5d and 6d series or I, II, III and IV series. Each series has ten (10) elements while 6d series has at present only one element namely Actinium (Z=89). The elements of IB group, Cu, Ag and Au should not be included in d-block because of their filled d-orbital and Zn, Cd, Hg are also have filled d-orbitals except their formation of complex. These elements are much differ from the properties of next of the elements due to the periodic classification. These elements show a wide application such as in heavy industries paint industries, catalytic use, building materials, jewellery items and coins. Biologically active compounds such as hemoglobin, myoglobin, blue proteins, synthetic, oxygen carriers, vitamin B_{12} contain different transition elements. The elements of group IIIB, IVB, VB, VIB, VIIB, VIII, IB, IIB (3-12) belong to this block.

Position of elements in periodic table

These d-block elements are placed into four series of ten elements in each, which are kept in 4th period (3d series); 5th period (4d series) 6th period (5d series) and 7th period (6d series incomplete series).

4th 5th 6th 7th

Period – first transition series (Sc-Zn, Z= 21-30)

Per – second transition series (Y-Cd, Z= 39-47)

General characteristic of d- block elements:

(i) All transition metals are hard except for group 11 (copper family) and have high melting and boiling point. Nearly ten transition elements have melting point above 2000˚C and three elements Ta, W and Re have melting points above 3000˚C.(ii) They are hard, strong refractory and electropositive. (iii) The transition elements all have high densities. Os and Ir have densities of the order of 23g/cm^3.

(iv) Most of the transition elements are malleable and ductile. (v) Most of the transition metals are good electrical conductors. (vi) Most of element's form-coloured compounds of every colour of the rainbow. (vii) They form alloy with other metals. (viii) These elements form well known coordination complexes. (ix) Transition metals exhibit several oxidation states. (x) Most of the transition metals and compounds are used as catalyst.

The general properties of d-block elements of all the series (3d, 4d, 5d ,6d are not so different because of their electronic configuration. Which includes the number of electrons in d-orbital are generally same only vary in number in s- orbital it is invariably 0, 1 or 2. important physical properties of the elements are discussed below and the data are given in table -A.

Properties

Electronic configuration of Transition Series Elements:

The electronic configuration of 4d and 5d series are given for comparison with 3d series. The outermost electronic configuration (valence shell) of the series can be represented by $3d^{1-10}4s^{1-2}$ (table-1.1). First two electrons go into 4s-orbital due to their low energy state compared to 3d-orbital. The rest electron enters into 3d- orbital. Since the filling of electron takes places from 1 to 10 in d-orbitals, these are called 3d series, 4d series, 5d series and 6d series. There are certain exception in configuration of Cr (Z=24) and Mo (Z=42). The expected configuration of Cr (Z=24) atom is $[Ar]^{18}$ $3d^4$ $4s^2$ but

actual configuration as Cr (Z=24) $[Ar]^{18}$ $3d^5$ $4s^1$. This can be explained on fact that these two orbitals have close energy separation thus giving rise to six nearly same energy state and extra stable configuration is observed for both Cr and Mo as given above. In table 1.1,1.2 and 1.3 two type electronic distribution are given one is predicated and another is observed. Observed is actual electronic configuration found by experiments. The irregularities found in observed configuration from predicated i.e. Cr, Cu, Mo, Pd, Ag, and Au are explained on the basis of half field completely field d-orbitals are relatively more stable than other d-orbital. On the basis of this concept, it is however not easy to explain the irregularities found in other elements. Since one has to consider net effect of so many other factors such as (i) nuclear- electronic attraction
(ii) shielding of one electron by several other electrons, (iii) interelectronic repulsive forces, (iv) exchange energy forces, etc. All these forces play an important part together in determining the final stability of an electronic distribution of an atom. It is not easy to explain configuration of Nb, Ru, Rh and tungsten unlike chromium ($3d^5$ $4s^1$) and molybdenum ($4d^5$ $5s^1$) should have idealised the configuration $4f^{14}$ $5d^4$ $6s^2$.

Melting and Boiling points: The d-block elements have very high melting and boiling points and melts above 900 c. Due to completely filled d-orbital elements like Zn, Cd, and Hg do not form covalent compound. The formation of covalend bond present in rest elements as it also accounts of the having incomplete d- orbital.

Atomic and ionic radii:

These points may be noted from the data of table. (i) As it is clear from the table- A that the atomic and ionic radii show a gradual decrease in their values in any period. This is due to increase in nuclear charges try to pull the electron clouds toward itself that is attraction of electrons towards nucleus increases. This increase in attraction leads to decrease in radii values across each period. There are however few exceptions, the atomic radii of the elements from chromium to copper are very close to one another. This is explained as further the addition of extra electrons screen the outer electron very effectively from the nuclear charge thus screening effect increase considerably due to increase in atomic number and hence there is a marginable increase in effective nuclear charge. Thus results a small change in atomic radii of the middle elements in any period.

(ii) In any particular series, the atomic radius attains the minimum value for elements of 8th group (that is 8,9 and 10) and increases again towards the end of the series. This is explained in terms of increase force of repulsion among the added electrons which dominate to the attractive forces due to increased nuclear charge and results in expansion of electron cloud.

On descending in the group, principal quantum number ‘n’ increases and atomic size is therefore is expected to increase from top to bottom but the increase are not same for all the members. The difference in radius of second and third series elements is very small as compared to first and second series members. This is due to lanthanide contraction here the inclusion of 14 lanthanide elements between La and Hf.

2. Density: The transition elements show a high density compared to alkali and alkaline earth metals. Due to smaller size and increased nuclear charge and poor screening effect by the orbitals the electron is attached more strongly towards the nucleus this results a decrease in atomic volume of transition metals and there is an increase in density. It can be also seen a trend of table that densities increases from period 4 to 6 elements the osmium and iridium with highest values ($23 g/cm^3$) and then decreases in a group there is also an increase in density of elements. Thus, increase in densities is due to small radii and closed packed structure of the elements. The densities of the second series are nearly two times those of the second series elements due to the atomic masses because twice those of the first series elements. This is one of the peculiar properties of transition element that the element exists in different stable oxidation state. Change in oxidation state usually shown a unit change of Fe^{3+} and Fe^{2+} as compared to non–metals usually changed by two units. After calcium (atomic no. 20 the electronic configuration $1s^2$, 2s2, 2p6, 3s2, 3p6, 4s2) the next ten elements will have the electronic configuration started with filling of 3d orbital from one to ten. This prevails exception in the case of Cr and Cu, due to extra stability of their half filed or completely filled configuration, these two electrons prefer to shift their one 4s electron to 3d orbital. Therefore, the first element of 1st transition series have an oxidation number (+II) when two 4s electron are engaged in bonding and (+III) when addition of one 3d electron is involved in bonding. Thus, from titanium to chromium a regular change in oxidation state takes place with a correlation between electronic structure and minimum and maximum oxidation states. Further the highest oxidation state of these elements, all of the s and d electrons are used in bonding. After the $3d^5$ configuration the tendency to show higher oxidation state decreases among the rest elements. Fe has a maximum (+VI) oxidation state and ruthenium and rhodium the often two elements of their group contain oxidation state (+VIII) due to their larger size.

(b) Mn^{2+} ($3d^5$ $4s^0$) is more stable than Mn^{3+} ($3d^4$ $4s^0$) because of presence of $3d^5$ orbital in Mn^{2+}.

(c) Ag^+ ($4d^{10}$ $5s^0$) is more stable than Ag^{2+}($4d^9$ $5s^0$) due to presence of d^{10} orbital. (iii)Transition element can form ionic bond in their lower oxidation state and covalent bond in higher oxidation state. The acidic nature of metal- oxygen and metal-chloride bond increases with increasing oxidation state.

Ionization Energy: There is a considerable increase ionization energy value from left to right in first series (table) due to effective attraction of nuclear charge on the outer electrons. A perusal of table 3 and 4 showed higher value of ionization energies of third series than first and second series. It can be explained based on poor shielding of outer most electron due to presence of 4f orbital in the third series elements. The outermost electrons are more exposed nuclear charge and therefore it in enhance the ionization energy of third series elements. Copper has a stable completely filled configuration (table1.3) shows +1 by losing one electron from 4s orbital whereas Zn show only one oxidation state (+II) reveals that 3d shell is completely filled. Folloing point may be noted from data of table (i) There is an increase in number of oxidation state in going from left to right in a period, however the elements towards middle of the series have more oxidation states than those towards the end of the series. The increase in number of oxidation states in proceeding left to right in a period is due to readily availability of s and d electrons for binding maximum number of oxidation state is reached somewhere in the middle of the series. (ii) The relative stabilities of various oxidation state shown by given oxidation state can be explained on the basis of stability of d^0, d^5 and d^{10} electronic configuration. For example (a) Ti^4 ($3d^0$ $4s^0$) is more stable than Ti^{3+} ($3d^0$

$4s^0$) because of presence of d^0 orbital in Ti^{4+} ion.

3. Magnetic properties: The substances when placed in a magnetic field show a decrease or increase in in magnetic field of strength. If the external magnetic field is larger than applied field the substance is called paramagnetic. Diamagnetic substance repelled by magnetic filled of strength.

The transition metal compounds are generally paramagnetic in nature due to having unpaired electrons in their d- orbitals. Fe, Co and Ni are ferromagnetic in nature due to large number of unpaired electrons. In these element alignments occur when these materials are magnetized and behave as a permanent magnet.

The magnetic propertied shown by majority of compounds of transition metals. This arises due to spin of electrons and orbital motion, which produce a spin moment and orbital moment respectively. Therefore, an interaction of spin magnetic moment and orbital magnetic moment continues to produce magnetic properties in an atom ion or molecules. The unit of magnetic moment expressed is called Bohr magneton (BM). For an electron it is given by:

$$\mu_B = eh/4\pi mc$$

where e=charge on electron, h=planks constant, c=velocity of light and m=mass of the electron Magnetic moment of a single electron is given by:

$$\mu_s = \sqrt{4S+1}$$

Where, S=total spin quantum number of unpaired electrons. thus, for a single electron μ_S is given by:

$$\mu_S = \ = \sqrt{4x1/2 + 1} = \sqrt{3} = 1.73 \text{ BM}$$

Magnetic moment for an atom or ion or molecules containing more than one unpaired electron (n) can be calculated as:

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

$$\text{for } n=1,\ \mu_S = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM for } n=2$$

$$\mu_S = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \text{ BM}$$

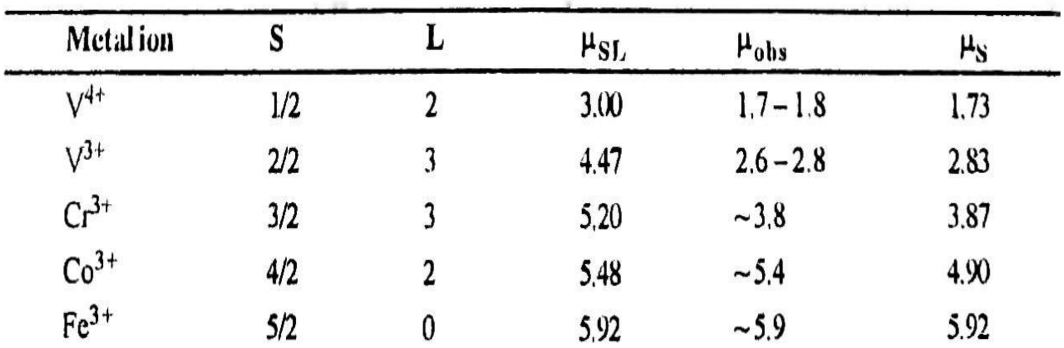
It is observed that the experimental value for magnetic moment is found to be more than the spin only value due to orbital motion contribution of the electron. This is given by the expression:

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

where L=total orbital angular momentum.

The observed and calculated values of magnetic moments for first transition series elements are given in the following table 1.7

Table 1.4 Magnetic moments of first transition series metal ions



Metal ion	S	L	μ_{SL}	μ_{obs}	μ_S
V^{4+}	1/2	2	3.00	1.7 – 1.8	1.73
V^{3+}	2/2	3	4.47	2.6 – 2.8	2.83
Cr^{3+}	3/2	3	5.20	~3.8	3.87
Co^{3+}	4/2	2	5.48	~5.4	4.90
Fe^{3+}	5/2	0	5.92	~5.9	5.92

4. Colour: Transition metal compound is coloured in contrast to s and p block elements. Properties of these and differentiate to main group element due to absorption of radiations in visible region of the spectrum, the transmitted light is coloured with the complementary colour, the light absorbed. Absorption of radiation takes place due to electronic transition caused by changes in electronic energy. This is also called electronic spectra. The transition elements compounds show various colour depend upon the oxidation states and nature of ligand surround the metal ion. Thus, an aqueous solution of titanium (III) compound is blue green colour. This compound absorbs light at 493 nm corresponds to blue green with complementary colour of reddish violet colour. The copper compounds appear reddish blue as it absorbs red region. The various colours are given in table of first transition series elements.

Metal ions which contain completely filled d- orbital like $m^{2+,}$ $Hg^{2+,}$ Cu^{+} etc are normally white for example $ZnCl_2$ is white.

Catalytic properties of transition metal: Transition metals play an important role in catalytic activities for the several commercial syntheses of various organic as well as inorganic compounds, hydrogenation of unsaturated compounds, nickel is used as catalyst. In Haber process of synthesis of ammonia, iron and molybdenum are used as catalyst. Manganese dioxide and vanadium pentoxide are used to catalyze the decomposition of H2O2 and SO2 to get O2 and SO3 respectively. Other metals like chromium, platinum etc. are also used in different chemical reaction.

Formation of complex Compounds:

The transition elements have unique property to form complex salts due to presence of vacant d-orbital to accept electron from Lewis bases, groups which are capable to donate a pair of electrons. These groups are called ligands. The number of ligands coordinated to metal is called the coordination number of metal ion. The ligand may be neutral groups as NH3 and ion as Cl^- or CN^- etc. $(Fe\ (CN)6)^{4-}$and $(Fe\ (CN)6)^{3-}$complex compounds are formed by donation of six pairs of electrons from CN^- to Fe^{2+} and Fe^{+3} respectively.

$[Ni\ (CN)4]^{2-}$and $[Ni\ (Cl)4)^{2-}$ complex compounds are formed by the gain of four pairs of electrons from CN^- and Cl^- ions. Various other transition metals also form complex compounds with N, O, F and S atoms as donor.

5. Reactivity: The reactivity towards other groups is found less for the transition metal's high ionization potential and smaller size. Thus, they have tendency to remain un reactive. Elements like platinum and gold do not react with air and are called noble metals.

Binary compounds of the first transition series

The element with only one other element combines to form binary compound. These are the simplest type of compound formed by transition element with a variety of non-metals like oxygen nitrogen phosphorous halogens and carbon to form binary compounds. In lower oxidation state metals form simple salts and show electropositive character whereas in higher oxidation state oxides are formed and metal show more electropositive character.

Oxides: Oxides of the elements of first transition series shown by general formula as MO, M2O3, MO2, M2O5 and MO3.Their stability increases from scandium to zinc. It indicates that the elements from starting in the 3d series attain stable state to reduce electrons and this show their strong reducing nature. In these elements Cr (II) and V(II) oxides are strong reducing agent, copper and zinc do not show +3 oxidation state.

The oxides are basic in the low oxidation state and basic in high oxidation state of the metal involved. Therefore, basicity decreases from left to right in the first series of elements. Amphoteric oxides are formed by the intermediate oxidation state of metal the basic and amphoteric oxides when dissolved in acid forming hexaaquo complex ions [(M (H2O] $^{n+}$.

MO type oxides in which each M^{2+} metal ions and each O^{2-} ion is surrounded by six M^{2+} ion have a NaCl type crystal structure.

Iron form non-stochiometric oxides in which ratio of metal to oxygen is not a whole number.

All oxides are very stable and are insoluble in water or aqueous acid except NO_2 dissolves in acid to give NO^{2+} ions. Chromium trioxide is soluble in water converting dichromate ion.

$$2CrO_3+H_2O= H_2CrO_7$$

It is a strong oxidizing agent and oxidizes many organic compounds the acid base character of the first transition series oxides in different oxidation state are given in the following table.

1.5. Complexes with Relative stability of oxidation state: Tendency of the elements to form complex compounds is directly related to their oxidation reduction potential. Further the oxidation state of the elements is stabilised in accordance with its electronic configuration. Such configuration, d^0, d^5, and d^{10} possess more stable oxidation state.

From left to right in 3d series stability of +2 oxidation state will increase from Sc to Zn. Thus, lower elements in +2 oxidation state e. g. V and Cr show powerful reducing nature while Cu and Zn do not behave as reducing agents.

It is observed that from Sc to Cu, the stability of +3 oxidation state decreases. That is why +3 oxidation state of Sc is very stable, Ti is also oxidized to Ti^{3+} and is also oxidized toTi^{4+}. Mn^{2+} is also unstable, whereas Fe^{3+} is a state of stable oxidation state. Following point may be noted-

(i) stability of complex compounds decreases with increase atomic number of central transition metal atom.

(ii) Transition metal in high oxidation state form stable complexes with the small highly electronegative and basic ligands like F^-, Cl^-, NH_3, IO_6^{5-}, TeO_6^{6-}, etc. While these metal in low oxidation state (e.g. +1, 0, -1) give stable complexes with pi acid ligand like CO, CN^-, PCl_3, C_6H_6 etc. The complex compound formed by transition metal atoms in low oxidation states contain $L \rightleftharpoons M$ coordination bond.

(iii) When transition metal form complexes with same ligand in different oxidation states, the complex compound having the metal in higher oxidation state is more stable e,g, $[Co^{3+}(NH_3)_6]^{3+}$ is more stable than $[Co^{2+}(NH_3)_6]^{2}$. Greater stability is due to the fact the metal cations having higher charge has greater power to attract the lone pair of electrons on the ligand. In other words, we can say that since the metal cation with high charge is smaller in size, it can attract the lone pair of electrons of the ligend more strongly and hance can give more stable complex ion.

1.6. Coordination number (C.N.) and geometry of complexes formed by the transition series elements-

First transition elements show 0 to 12 coordination number but greater than 8 is not isolated and very rare. These compounds are formed by reaction of their respective metal salts and species like NH3, H2O etc, containing the lone pair electrons, called ligands are Lewis bases. The bonding between metal and ligands are explained by Werner's coordination theory suggesting two types valency, primary and secondary valency. Now the term primary valency is called oxidation state of metal ion and secondary valency termed as coordination number.

Thus, the coordination number is the number of ligands which surround the metal in a specific arrangement in space this specific arrangement of ligands around metal ion adopt a definite shape to have a minimum electrostatic repulsion and maximum stability. This definite shape is termed as geometry of complex compound. For example, in the compound $[Co (NH_3)_6] Cl_2$, metal ion Co^{2+} is surrounded by six ammonia molecules, formed the coordination compound and of coordination number six and octahedral geometry. Metals Cu, Ag and Au form complexes with coordination two and adopt a linear geometry. The examples of such coordination compounds are $[CuCl_2]$, $[Ag (NH_3)_2]^+$, $[Ag (CN)_2]^-$ and $[Au (CN)_2]^-$. In such cases all the complexes are linear and involved completely filled d- orbital(d^{10}) metal atom. Complexes with coordination number three are not very common. Examples are: $[Hg I_3]^-$, adopt a planar geometry having coordination three. Other complexes which show coordination three are $K_2[(CN)_3]. H_2O$, $Sc [N (Si Me_3)_2]_3$

Complex compound with coordination number four can isolated for number of metals, these are usually adopted tetrahedral and square planar geometry. Although both the complexes have same coordination number four, but adopt different geometry because of steric and electronic factor. A tetrahedral geometry is more favored due to steric effect makes maximum distance between ligands and minimum repulsion. This can be also explained on the basis of strength of ligand and formation of hybrid orbitals of central metal atoms, Ni involves 4s and 4p orbital in Ni $(C_{l4})_4$ whereas 3d and 4s in $[Ni (CN)_4]^{2-}$ complexes adopt a tetrahedral and square planar geometry respectively Other complexes of square planar geometry are $[Cu (NH4)]^{2+}$ and $[Ni (Py)_4]$; Py=pyridine, $[Ni (NH)_4]^{2+}$ etc.

Complexes with coordination number one relatively rare. Examples of five coordinated complexes are $[Cu (Cl)_5]^{3-}$, $[Cu (Br)_5]^{3-}$, $[FeCO)_5]$ and $[Cd (Cl)_5]$. Five coordinated complexes adopt a trigonal bipyramidal or square pyramidal geometry. These complexes are not very stable. This can be prepared on the basis of the formation of a dimer of MoCl5 of coordination number six bridging by chlorine atom between two Mo metals.

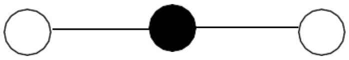
The most common coordination of transition metal complexes is six, which adopt a regular or distorted octahedral geometry. Tetragonally distorted structure is obtained for ligands surround metal atom results of elongating or contraction of the octahedral geometry. Examples of octahedral complexes formed by transition metals are;

$[Fe(F_6)]^{3-}$, $[Co (H_2O)_6]^{2+}$, $[Ni (H_2O)_6]^{3+}$, $K_3[Fe (CN_6)]$, $[Cr (NH)_6]^{3+}$,

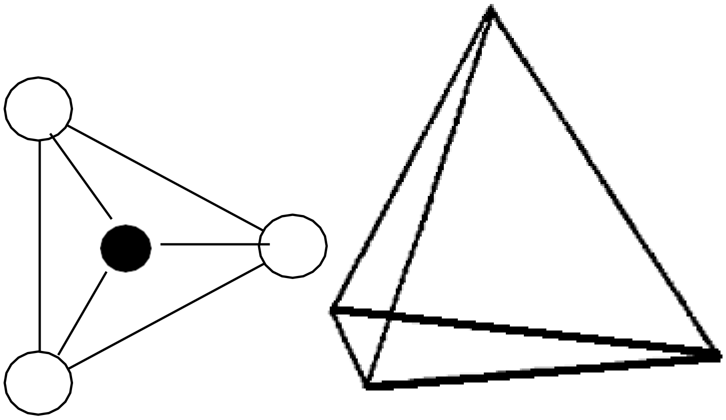
$[Mn (CN)_6]^{3-}$, and $[Sc(F)_6]^{3-}$ etc. The geometry of various complexes in several CN numbers are shown below.

For example-

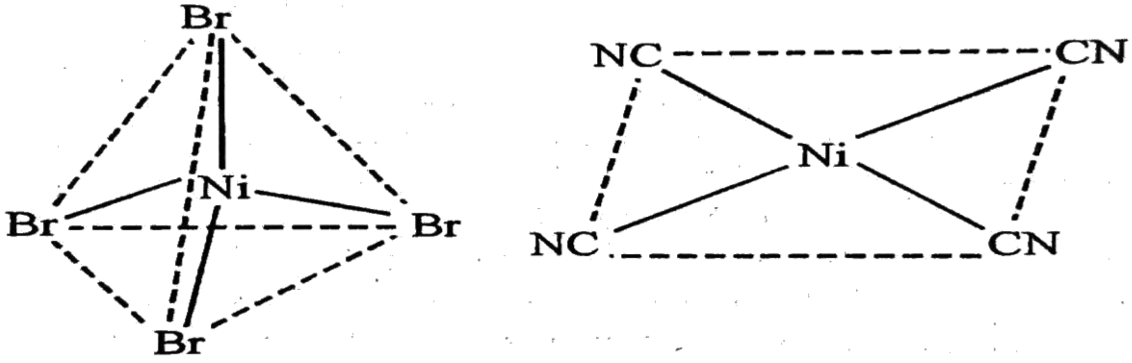
(i) CN=2 linear geometry, example- CuCl $^-$, [Au$_2$ (CN)]$^-$ and$_2$[Ag (CN)]$^-$ $_2$



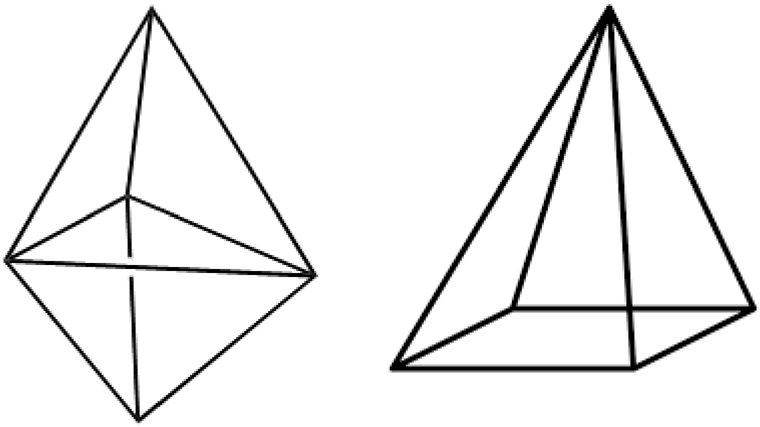
(iii) CN=3 geometry planar and pyramidal, example- K_2 [Cu $(CN)_3$] H_2O and HgI_3^-



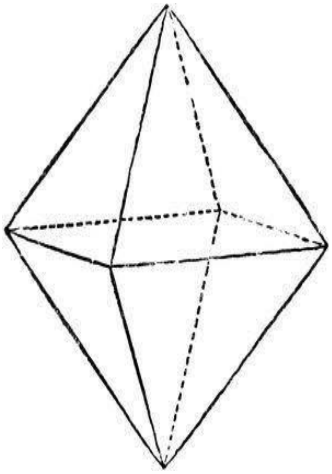
(iv) CN=4 geometry square planar and tetrahedral, given in above figure 1.0 example- Ni $(CN)^{2-}$ and $NiCl^{2-}$ and $NiBr^{2-}$



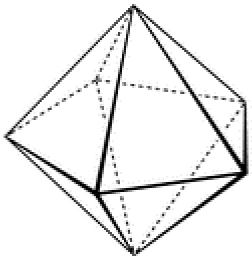
(v) CN=5 trigonal bipyramidal and square pyramidal, example- $[CuCl5]^{3-}$, Fe (CO)5 and $Ni(Et_3P)_2Br_3$

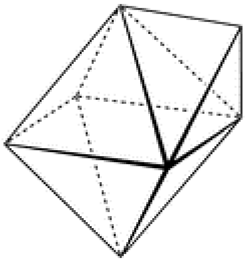


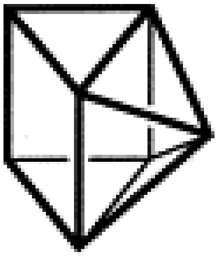
(vi) CN=6 octahedral geometry given in above figure 1.1 example- $K_4[Fe(CN)_6]$, $[Co(NH_3)_6]^{3+}$



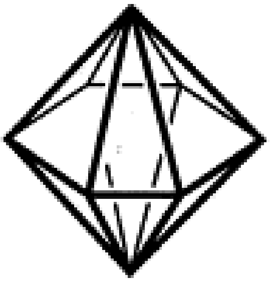
(vii) CN=7 pentagonal bipyramidal, capped octahedron and capped trigonal prism, example- $[Zr(F)_7]^{3-}$, $[MoF_7]^{-}$ $[M(F)_7]^{2-}$, M=Nb or Ta

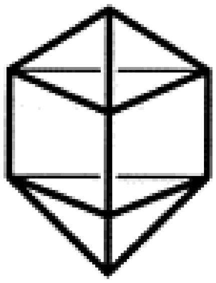


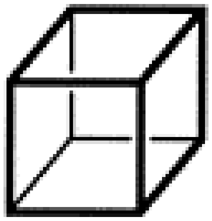


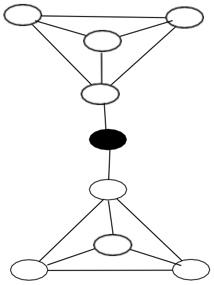


(viii) CN=8 cube, hexagonal bipyarmidal, bicapped trigonal prism, bicapped trigonal antiprism, example- $[Mo(CN)_8]^{3-}$, $[Ta(F)_8]^{3-}$, $[Zr(C_2O_4)_4]^{4-}$, $[Zr(acac)_4]$

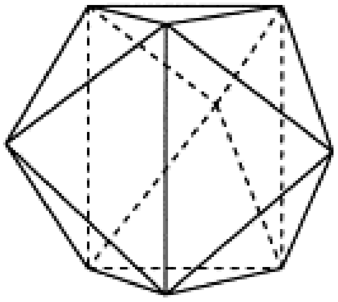


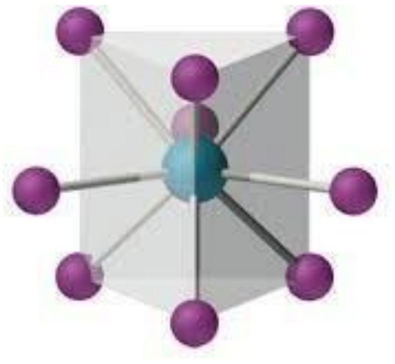






(ix) CN=9 tricapped trigonal prism, example- R$_9$eH $^{2-}$





UNIT-IV

ETHERS THIOETHERS AND EPOXIDES

Ethers (R–O–R')

Nomenclature

Common System: Name the alkyl groups alphabetically followed by "ether" (e.g., ethyl methyl ether).

IUPAC System: The smaller alkyl group is treated as an "alkoxy" substituent on the longer chain (e.g., methoxyethane for $CH_3OCH_2CH_3$).

Isomerism

Metamerism: Different alkyl groups attached to oxygen (e.g., C_3H_8O can be methoxyethane or ethoxyethane).

Functional Isomerism: Ethers are isomeric with alcohols (e.g., C_2H_6O can be ethanol or dimethyl ether).

Methods of Preparation

Williamson Ether Synthesis:

$$R–O-+R'–X \rightarrow R–O–R'+X$$

(SN2 reaction of alkoxide with alkyl halide)

Dehydration of Alcohols:

$$2R–OH \rightarrow H_2SO_4R–O–R+H_2O$$

(Primary alcohols give ethers at 140°C)

Electrophilic Substitution on Aromatic Rings (for aryl ethers):

$$Ar–OH+R–X+Base \rightarrow Ar–O–R$$

Reactions (Cleavage of C–O Linkage)

Acidic Cleavage with HI/HBr

$$R–O–R'+HX \rightarrow R–X+R'–OH$$

(Excess HX leads to complete cleavage: R–X and R'–X)

Autoxidation (Peroxide Formation): Ethers react with oxygen to form peroxides (R–O–O–R), which are explosive.

Thioethers (R–S–R')

(Similar to ethers but with sulfur replacing oxygen)

Nomenclature

Common: Name alkyl groups alphabetically + "sulfide" (e.g., dimethyl sulfide).

IUPAC: Alkylthio group (–SR) as a substituent (e.g., methylthioethane for $CH_3{-}S{-}CH_2CH_3$).

Methods of Preparation

Williamson-type Synthesis:

$$R{-}S{-}+R'{-}X \rightarrow R{-}S{-}R'+X$$

(SN2 reaction of thiolate ion with alkyl halide)

Reduction of Sulfoxides or Sulfones:

$$R{-}SO{-}R' \rightarrow R{-}S{-}R$$

Reactions (Cleavage of C–S Linkage)

Oxidation to Sulfoxides/Sulfones:

$$R{-}S{-}R'+[O] \rightarrow R{-}SO{-}R' \rightarrow [O]R{-}SO_2{-}R$$

Reaction with Halogens:

$$R{-}S{-}R'+Br_2 \rightarrow R{-}SBr+R'{-}Br$$

Epoxides (Oxiranes, Cyclic Ethers)

Nomenclature

Named as oxirane derivatives (e.g., ethylene oxide for C_2H_4O).

Can also be named as epoxy-substituted alkanes (e.g., 1,2-epoxypropane).

Methods of Preparation

Oxidation of Alkenes (Peracid Method):

$$RCH{=}CH_2+RCO_3H \rightarrow RCH(O)CH_2+RCO_2H$$

(Peracids like mCPBA used)

Intramolecular Williamson Reaction:

$$HO–CH_2CH_2–X+Base \rightarrow Epoxide$$

Reactions (Cleavage of C–O Linkage)

Acid-Catalyzed Ring Opening:

$$Epoxide+H_3O^+ \rightarrow TransDiol$$

Base-Catalyzed Ring Opening:

$$Epoxide+OH− \rightarrow Alcohol$$

Reaction with Nucleophiles (e.g., NH_3, ROH, CN^-):

$$Epoxide+Nu− \rightarrow OpenedProduct$$

Alkyl Group and Ethereal Oxygen

Alkyl Group (R–): A hydrocarbon fragment derived by removing one hydrogen from an alkane (e.g., methyl ($-CH_3$), ethyl ($-C_2H_5$)).

Ethereal Oxygen (–O–): The oxygen atom present in ethers (R–O–R'), linking two alkyl or aryl groups.

In ethers, the oxygen is sp^3 hybridized, forming a bent structure (like water) with bond angles around 110°.

Zeisel's Method for Estimation of Methoxy Group ($-OCH_3$)

Zeisel's method is a classical method used to determine the methoxy ($-OCH_3$) group in organic compounds.

Principle:

When a compound containing a methoxy ($-OCH_3$) group is heated with hydriodic acid (HI), it undergoes cleavage, forming methyl iodide (CH_3I):

$$R–OCH_3+HI \rightarrow R–OH+CH_3I$$

The formed CH_3I is absorbed in an alcoholic solution of silver nitrate ($AgNO_3$), where it reacts to form a precipitate of silver iodide (AgI).

The amount of AgI formed is used to calculate the number of methoxy groups in the compound.

Procedure:

The sample is treated with excess HI in a sealed apparatus and heated.

The evolved CH_3I is passed into an alcoholic solution of $AgNO_3$, precipitating AgI.

AgI is filtered, dried, and weighed to determine the methoxy content.

Calculation:

1 mole of CH_3I correspond to 1 mole of AgI (Molecular weight = 234.77 g/mol).

The amount of methoxy group present in the compound is determined using the formula:

Methoxy content=Mass of AgI×31.03234.77

(where 31.03 g/mol is the molecular weight of the $-OCH_3$ group).

Applications:

Used in structural analysis of natural products (e.g., anisole, lignin, flavonoids).

Determines the methoxy content in drugs and plant extracts.

Reactions of Epoxides

Epoxides (oxiranes) are highly reactive due to ring strain. They readily undergo nucleophilic attack, leading to ring opening.

Reaction with Alcohols (ROH)

Acid-Catalyzed:

$$\text{Epoxide}+\text{ROH}+\text{H}+\rightarrow\beta\text{-Alkoxy Alcohol}$$

The more substituted carbon is attacked due to carbocation-like behavior.

Example: Ethylene oxide + methanol → 2-Methoxyethanol.

Base-Catalyzed:

The less substituted carbon is attacked (SN2 mechanism).

Reaction with Ammonia and Ammonia Derivatives

With NH_3 (Ammonia): Forms β-amino alcohols.

$$\text{Epoxide}+\text{NH3}\rightarrow\beta\text{-Amino Alcohol}$$

With Amines (RNH_2, R_2NH): Forms secondary or tertiary amino alcohols.

Reaction with Lithium Aluminium Hydride ($LiAlH_4$)

Reductive Ring Opening:

$$\text{Epoxide} + LiAlH4 \rightarrow \text{Alcohol}$$

Hydride (H^-) attacks the less hindered carbon, leading to primary alcohol formation.

Example: Ethylene oxide + $LiAlH_4$ → Ethanol.

Thioethers (R–S–R')

Nomenclature

Common Name: Alkyl sulfides (e.g., dimethyl sulfide ($CH_3\text{–}S\text{–}CH_3$)).

IUPAC Name: Alkylthio derivatives (e.g., methylthioethane ($CH_3\text{–}S\text{–}C_2H_5$)).

Structure

Similar to ethers (R–O–R') but with sulfur instead of oxygen.

Sulfur is larger and less electronegative than oxygen, making thioethers more nucleophilic.

Preparation Methods

Williamson-type Synthesis:

$$R\text{–}S\text{–}+R'\text{–}X \rightarrow R\text{–}S\text{–}R'+X$$

(Alkyl halide + thiolate ion).

Reduction of Sulfoxides/Sulfones:

$$R\text{–}SO\text{–}R' \rightarrow R\text{–}S\text{–}R' (\text{using Zn/HCl})$$

Properties

More nucleophilic than ethers due to weaker C–S bond.

Easily oxidized to sulfoxides (R–SO–R') and sulfones ($R\text{–}SO_2\text{–}R'$).

Uses

Dimethyl sulfide: Used as a solvent and food additive.

Methionine (a thioether amino acid): Essential for protein synthesis.

Lubricants and pharmaceuticals: Used in organic synthesis.

Aldehydes and Ketones

Structure, Reactivity, and Key Reactions

Aldehydes and ketones are important classes of organic compounds containing the carbonyl functional group (-C=O). Aldehydes have at least one hydrogen attached to the carbonyl carbon, while ketones have two alkyl or aryl groups attached to it. Their nomenclature follows the IUPAC system, where aldehydes are named by replacing the “-e” of the corresponding alkane with “-al” (e.g., ethanal), and ketones are named by replacing “-e” with “-one” (e.g., propanone). Aromatic aldehydes and ketones, such as benzaldehyde and acetophenone, follow similar conventions.

The reactivity of aldehydes and ketones is primarily influenced by the polarity of the carbonyl group, making them susceptible to nucleophilic attack. Aldehydes are generally more reactive than ketones due to the presence of only one electron-donating alkyl/aryl group and less steric hindrance.

Preparation and Physical Properties

Aldehydes and ketones can be synthesized through several general methods, including oxidation of primary and secondary alcohols, ozonolysis of alkenes, and Friedel-Crafts acylation (for aromatic ketones). Some aldehydes are also prepared via hydroformylation of alkenes. Their physical properties are influenced by the polar nature of the carbonyl group, leading to relatively high boiling points compared to alkanes but lower than alcohols due to the absence of hydrogen bonding. They are moderately soluble in water due to hydrogen bonding interactions with water molecules.

Nucleophilic Addition Reactions

A characteristic reaction of aldehydes and ketones is nucleophilic addition, where a nucleophile attacks the electrophilic carbonyl carbon. This is the basis for many important organic transformations, including the formation of alcohols, cyanohydrins, and imines.

Base catalyzed reaction swith mechanism

Aldehydes and ketones undergo several important base-catalyzed reactions, primarily due to the acidity of α-hydrogen atoms and the electrophilic nature of the carbonyl carbon. The base deprotonates the reactant or activates it for nucleophilic attack, leading to the formation of new carbon-carbon or carbon-heteroatom bonds.

1. Aldol Condensation

Aldol condensation is a key carbon-carbon bond-forming reaction involving aldehydes and ketones with α-hydrogens. It consists of two steps: **aldol addition** followed by **dehydration** to form an α,β-unsaturated carbonyl compound.

Mechanism:

Enolate Formation: The base (e.g., OH^-) abstracts an α-hydrogen, generating an enolate ion.

$$RCH_2COH \rightleftharpoons RCH{=}CO^- + H_2O$$

Nucleophilic Attack: The enolate attacks another molecule of the carbonyl compound, forming a β-hydroxy aldehyde or ketone.

Dehydration: Under heat or basic conditions, the β-hydroxy compound undergoes elimination to form an α,β-unsaturated carbonyl compound.

$$RCH{=}CHCOH \rightarrow RCH{=}CHCO$$

Example: Acetaldehyde (CH_3CHO) reacts with itself to form crotonaldehyde.

2. Cannizzaro Reaction

This is a **disproportionation reaction** in which non-enolizable aldehydes (without α-hydrogen) react under strongly basic conditions, yielding an **alcohol** and a **carboxylate salt**.

Mechanism:

1. **Nucleophilic Attack:** The hydroxide ion attacks the carbonyl carbon, forming a tetrahedral intermediate.
2. **Hydride Transfer:** One molecule donates a hydride (H^-) to another aldehyde molecule.
3. **Product Formation:** The first aldehyde is reduced to an alcohol, while the second is oxidized to a carboxylate anion.

Example: Formaldehyde undergoes Cannizzaro reaction to give **methanol** and **formate ion**.

3. Perkin Reaction

This reaction is used for synthesizing **α,β-unsaturated carboxylic acids** by condensing **aromatic aldehydes** with acid anhydrides in the presence of a base.

Mechanism:

1. **Enolate Formation:** The base abstracts a proton from the acid anhydride, forming an enolate.

2. **Nucleophilic Attack:** The enolate attacks the carbonyl carbon of the aldehyde.
3. **Elimination:** The intermediate undergoes dehydration to form the α,β-unsaturated acid.

Example: Cinnamic acid synthesis from benzaldehyde and acetic anhydride.

4. Benzoin Condensation

This is a **nucleophilic addition reaction** where two aldehyde molecules (typically aromatic) react in the presence of cyanide ions (CN^-) to form an **α-hydroxy ketone (benzoin)**.

Mechanism:

1. **Cyanide Activation:** CN^- attacks the aldehyde, forming a cyanohydrin.
2. **Enolate Formation:** The cyanohydrin deprotonates to form an enolate.
3. **Nucleophilic Addition:** The enolate attacks another aldehyde molecule.
4. **Product Formation:** The cyanide ion is regenerated, and benzoin is formed.

Example: Benzaldehyde undergoes benzoin condensation to form **benzoin (α-hydroxy ketone).**

5. Haloform Reaction

Methyl ketones react with halogens (I_2, Br_2, Cl_2) in the presence of a base, producing a **haloform (e.g., CHI_3, chloroform, bromoform)** and a **carboxylate ion**.

Mechanism:

1. **Enolate Formation:** The base abstracts an α-hydrogen, forming an enolate.
2. **Halogenation:** The enolate reacts with halogen (X_2), replacing all three α-hydrogens.
3. **Cleavage:** The intermediate undergoes cleavage, forming a carboxylate and haloform.

Example: Acetone reacts with iodine and NaOH to form **iodoform (CHI_3)** and acetate ion.

6. Knoevenagel Reaction

This reaction forms α, β-unsaturated carbonyl compounds via the condensation of aldehydes or ketones with active methylene compounds (like malonates or cyanoacetates).

Mechanism:

1. **Enolate Formation:** The base abstracts a proton from the active methylene compound.
2. **Nucleophilic Attack:** The enolate attacks the carbonyl carbon of the aldehyde/ketone.

3. **Elimination:** The intermediate loses water to form the α, β-unsaturated product.

Example: Benzaldehyde reacts with ethyl cyanoacetate to give α, β-unsaturated nitriles.

Oxidation of Aldehydes

Aldehydes are highly susceptible to oxidation due to the presence of a hydrogen atom attached to the carbonyl carbon. This oxidation results in the formation of carboxylic acids or other oxidation products, depending on the oxidizing agent used.

1. Mild Oxidation (Formation of Carboxylic Acids)

Aldehydes can be oxidized to carboxylic acids using Tollens' reagent (ammoniacal silver nitrate, $Ag\,(NH_3)_2Ag\,(NH_3)\,_2\,Ag\,(NH_3)^{2+}$). In this reaction, silver ions (Ag^+) are reduced to metallic silver, forming a silver mirror on the reaction vessel.

$$RCHO^{+2}[Ag\,(NH_3)_2]\,^{+}+3OH^{-}\rightarrow RCOO^{-}+2Ag\downarrow+4NH_3+H_2O$$

Similarly, Fehling's solution, which contains Cu^{2+} ions in an alkaline medium, oxidizes aldehydes to carboxylates, reducing Cu^{2+} to Cu_2O, which precipitates as a red solid.

$$RCHO+2Cu_2{}^{+}+5OH^{-}\rightarrow RCOO^{-}+Cu_2O\downarrow+3H_2O$$

Strong Oxidation (Using Potassium Permanganate - $KMnO_4$ and Chromium-based Oxidants)

Aldehydes can also be oxidized by strong oxidizing agents like acidic potassium permanganate ($KMnO_4$) or chromic acid (H_2CrO_4) to yield carboxylic acids.

$$RCHO+[O]\rightarrow RCOOH$$

Oxidation of Ketones

Unlike aldehydes, ketones are more resistant to oxidation because they lack a hydrogen atom attached to the carbonyl carbon. However, under strong oxidative conditions, ketones can be cleaved into smaller carboxylic acids or carboxylates.

Baeyer-Villiger Oxidation (Ketones to Esters/Lactones)

The Baeyer-Villiger oxidation is a unique reaction where ketones are oxidized to esters or lactones using peracids (e.g., meta-chloroperbenzoic acid, mCPBA).

This reaction involves the insertion of an oxygen atom between the carbonyl carbon and the adjacent alkyl/aryl group.

$$RCOR'+RCO_3H\rightarrow RCOOR'+RCOOH$$

Example: Acetophenone oxidation gives phenyl acetate.

Oxidative Cleavage of Ketones

Under harsh oxidative conditions (e.g., $KMnO_4$, hot concentrated HNO_3, or ozone (O_3)), ketones undergo cleavage, producing smaller carboxylic acids.

$$CH_3COCH_3+3[O]\rightarrow CH_3COOH+HCOOH$$

Here, acetone is cleaved into acetic acid and formic acid.

Reduction Reactions of Aldehydes and Ketones

Aldehydes and ketones can be reduced to **alcohols or hydrocarbons** using different reducing agents. These reductions vary based on the reagent used and the reaction conditions. Below are the key reductions:

1. Clemmensen Reduction

Purpose: Converts aldehydes and ketones into the corresponding alkanes by completely removing the carbonyl oxygen.

Reagents: Zinc amalgam (Zn/Hg) + Concentrated HCl

Best for: Acid-sensitive compounds

Mechanism:

The carbonyl compound is protonated by HCl.

Zinc acts as a reducing agent, donating electrons to the carbonyl carbon.

The oxygen is gradually removed as water, yielding the alkane.

Example:

$$CH_3COCH_3\rightarrow Zn\ (Hg)HClCH_3CH_2CH_3$$

(Acetone → Propane)

2. Wolff-Kishner Reduction

Purpose: Converts aldehydes and ketones into alkanes under strongly basic conditions.

Reagents: Hydrazine (NH_2NH_2) + KOH/Ethanol, heat

Best for: Base-stable compounds

Mechanism:

1. Formation of hydrazone intermediate by reaction with hydrazine.
2. Under basic heat conditions, the hydrazone undergoes decomposition, releasing N_2 gas and forming an alkane.

Example:

$$C_6H_5COCH_3 \rightarrow NH_2NH_2\ KOH/\Delta\ C_6H_6CH_3$$

(Acetophenone → Ethylbenzene)

3. Meerwein–Ponndorf–Verley (MPV) Reduction

Purpose: Selective reduction of aldehydes and ketones to alcohols without affecting other functional groups.

- Reagents: Aluminum isopropoxide [(Al $(OiPr)_3$]) + Isopropanol
- Best for: Mild reduction of sensitive compounds

Mechanism:

1. The carbonyl compound forms a complex with Al $(OiPr)_3$.
2. A hydride transfer from isopropanol reduces the carbonyl to an alcohol.
3. The used isopropanol converts into acetone.

Example:

$$C_6H_5CHO \rightarrow Al\ (OiPr)_3]\ \{iPrOH\}\ C_6H_5CH_2OH$$

(Benzaldehyde → Benzyl alcohol)

4. Reduction with Lithium Aluminium Hydride ($LiAlH_4$)

Purpose: Strong reduction of aldehydes, ketones, carboxylic acids, esters, and amides into primary or secondary alcohols.

- Reagents: $LiAlH_4$ + Dry Ether
- Best for: Powerful reduction, especially for esters and carboxylic acids

Mechanism:

1. Nucleophilic attack by hydride ion (H^-) from $LiAlH_4$ on the carbonyl carbon.
2. Formation of an alkoxide intermediate.
3. Protonation with acid workup gives the alcohol.

Examples:

$$RCHO \rightarrow LiAlH_4H_2ORCH_2OH$$

(Aldehyde → Primary alcohol)

$$RCOR' \rightarrow LiAlH_4H_2ORCHOH-R$$

(Ketone → Secondary alcohol)

5. Reduction with Sodium Borohydride ($NaBH_4$)

Purpose: Mild reduction of aldehydes and ketones to alcohols but does not reduce esters or carboxylic acids.

- Reagents: $NaBH_4$ + Alcohol/Water
- Best for: Selective reduction under mild conditions

Mechanism:

- Hydride ion transfer from $NaBH_4$ to the carbonyl carbon.
- Formation of an alkoxide intermediate.
- Protonation in aqueous workup to form the alcohol.

Examples:

$$CH_3CHO \rightarrow [NaBH_4]\ \{H_2O\}\ CH_3CH_2OH$$

(Acetaldehyde → Ethanol)

$$CH_3COCH_3 \rightarrow [NaBH_4]\ \{H_2O\}\ CH_3CHOHCH_3$$

(Acetone → Isopropanol)

Michael Addition: Nucleophilic Addition to α, β-Unsaturated Carbonyl Compounds

Michael addition is a conjugate addition reaction where a nucleophile (Michael donor) adds to the β-carbon of an α, β-unsaturated carbonyl compound (Michael acceptor). This reaction is crucial in organic synthesis for forming C-C bonds and is widely used in the synthesis of complex molecules, including pharmaceuticals and natural products.

General Reaction

$$R_2C=CH-CO-R'+Nu- \rightarrow R_2C(Nu)-CH_2-CO-R'$$

Where:

- Michael acceptor: α, β-unsaturated carbonyl compound (e.g., enones, acrylates, nitroalkenes).
- Michael donor: Enolate, amines, thiols, cyanides, β-diketones, malonates, etc.
- Base catalyst: NaOH, KOH, Et_3N, etc.

Mechanism of Michael Addition

1. Formation of nucleophile: The Michael donor (e.g., enolate) is generated using a base.
2. Nucleophilic attack: The nucleophile attacks the β-carbon of the α, β-unsaturated carbonyl system via conjugate addition.
3. Protonation: The intermediate enolate gets protonated to form the final product.

Stepwise Mechanism

Step 1: Formation of Enolate (Nucleophile)

$$CH_2(COOEt)_2 + Base \rightarrow CH{-}(COOEt)_2$$

Step 2: Nucleophilic Attack at the β-Carbon

$$CH{-}(COOEt)_2 + CH_2{=}CH{-}CO{-}R \rightarrow \text{Michael Adduct (enolate form)}$$

Step 3: Protonation to Form Final Product

$$\text{Michael Adduct} + H+ \rightarrow \text{Final 1,5-Dicarbonyl Compound}$$

Examples of Michael Addition

1. Malonate Addition to α, β-Unsaturated Ketones
2. $(COOEt)_2CH_2 + CH_3CH{=}CHCOCH_3 \rightarrow (COOEt)_2CHCH_2CH_2COCH_3$
3. Michael Addition in Natural Product Synthesis

Used in steroid synthesis and alkaloids.

4. Michael Addition with Thiols and Amines

Example: Thiols (-SH) or Amines ($-NH_2$) can add to α, β-unsaturated esters.

Applications of Michael Addition

- Organic synthesis: Formation of 1,5-dicarbonyl compounds.
- Pharmaceuticals: Key step in making drug intermediates.
- Polymer chemistry: Used in synthesis of functional polymers.

UNIT-V

CARBOXYLIC ACIDS

Carboxylic Acids: Nomenclature, Structure, Preparation, and Reactions

Carboxylic acids are organic compounds containing a –COOH (carboxyl) functional group. They are widely found in nature and play a crucial role in biochemistry, industry, and pharmaceuticals. These acids are categorized into aliphatic carboxylic acids (such as acetic acid) and aromatic carboxylic acids (such as benzoic acid).

Nomenclature and Structure

Carboxylic acids are named according to the IUPAC system by replacing the "-e" of the parent alkane with "-oic acid." If multiple carboxyl groups are present, the suffix "-dioic acid" is used. Common names are still widely used, such as formic acid (methanoic acid) and acetic acid (ethanoic acid).

The carboxyl group (-COOH) consists of a carbonyl (C=O) and hydroxyl (-OH) group attached to the same carbon. The carbonyl group contributes to electron delocalization, making carboxylic acids more acidic than alcohols.

Preparation of Carboxylic Acids

Carboxylic acids can be synthesized through several methods, including:

Oxidation of Primary Alcohols and Aldehydes

Reaction:

$RCH_2OH+[O]\rightarrow RCOOH$

Example: Oxidation of ethanol produces acetic acid

Hydrolysis of Nitriles

Reaction:

$R-CN+H_2O+H+\rightarrow RCOOH+NH_3$

Example: Hydrolysis of benzonitrile gives benzoic acid.

Carbonation of Grignard Reagents

Reaction:

$RMgX+CO_2 \rightarrow RCOOMgX(acidworkup) \rightarrow RCOOH$

Example: Reaction of methylmagnesium bromide with CO_2 gives acetic acid.

From Acid Anhydrides and Esters

Hydrolysis of esters in acidic or basic medium leads to carboxylic acids.

Physical Properties of Carboxylic Acids

Carboxylic acids exhibit unique physical properties due to hydrogen bonding and polarity:

Boiling Points: Higher than corresponding alcohols and aldehydes due to strong intermolecular hydrogen bonding.

Solubility: Lower carboxylic acids (up to four carbons) are highly soluble in water, but solubility decreases as the hydrocarbon chain length increases.

Odor and Taste: Many carboxylic acids have pungent odors (e.g., acetic acid smells like vinegar).

Reactions of Carboxylic Acids

Carboxylic acids undergo various important chemical reactions, including:

Acidic Nature (Reaction with Bases)

Carboxylic acids are weak acids that react with bases to form carboxylate salts.

Reaction:

$RCOOH+NaOH \rightarrow RCOO−Na++H_2O$

Example: Acetic acid reacts with NaOH to form sodium acetate.

Reduction to Alcohols

Carboxylic acids can be reduced to primary alcohols using strong reducing agents like $LiAlH_4$.

Reaction:

$RCOOH+4[H] \rightarrow RCH_2OH+H_2O$

Esterification (Formation of Esters)

Carboxylic acids react with alcohols in the presence of acid catalysts (e.g., H_2SO_4) to form esters.

Reaction:

$RCOOH+R'OH \rightarrow H_2SO_4RCOOR'+H_2O$

Example: Acetic acid reacts with ethanol to form ethyl acetate.

Decarboxylation (Loss of CO_2)

When heated with soda lime (NaOH + CaO), carboxylic acids undergo decarboxylation, forming hydrocarbons.

Reaction:

$RCOOH \rightarrow NaOH/CaORH+CO_2$

Example: Sodium acetate upon decarboxylation gives methane.

Conversion to Acid Derivatives

Carboxylic acids can be converted into acid chlorides, anhydrides, amides, and esters.

Example:

$RCOOH+SOCl_2 \rightarrow RCOCl+SO_2+HCl$

(Formation of acid chlorides using thionyl chloride).

Acidic Nature and Effect of Substituents on Acidic Strength

Carboxylic acids are weak acids, but they are stronger than alcohols and phenols due to the presence of the electron-withdrawing carbonyl group (-CO) adjacent to the hydroxyl (-OH) group. The acidity arises from the ability of the carboxylate ion ($RCOO^-$) to delocalize the negative charge over two oxygen atoms through resonance, making the conjugate base more stable. The presence of electron-withdrawing groups ($-NO_2$, -Cl, -Br, -CN) increases acidity by stabilizing the carboxylate anion through inductive and resonance effects, while electron-donating groups ($-CH_3$, $-OCH_3$) decrease acidity by destabilizing the negative charge. The closer the substituent is to the carboxyl group, the greater its effect on acidity.

Hell-Volhard-Zelinsky (HVZ) Reaction

The HVZ reaction is a halogenation reaction specific to carboxylic acids with an α-hydrogen. It involves the substitution of an α-hydrogen by a halogen (usually bromine or chlorine) using a catalytic amount of phosphorus or phosphorus tribromide (PBr_3). This reaction is useful for synthesizing α-halo carboxylic acids, which serve as intermediates in the production of amino acids and other biologically active molecules.

Claisen Ester Condensation

This reaction occurs between two esters or one ester and a ketone in the presence of a strong base (such as sodium ethoxide) to form a β-keto ester or β-diketone. The reaction follows an enolate mechanism, where the ester enolate attacks another ester molecule, leading to carbon-carbon bond formation. This reaction is widely used in organic synthesis for the preparation of β-keto compounds, which serve as intermediates in pharmaceuticals and agrochemicals.

Bouveault-Blanc Reduction

The Bouveault-Blanc reduction is a method of reducing esters to alcohols using sodium metal in the presence of ethanol or another alcohol as a solvent. Unlike the use of $LiAlH_4$, which is more commonly applied in laboratory settings, this reduction is particularly useful in large-scale industrial processes for converting esters into primary alcohols efficiently. The reaction proceeds via the formation of an intermediate radical anion, followed by protonation and further reduction to yield the final alcohol.

Decarboxylation

Decarboxylation refers to the removal of a carboxyl (-COOH) group as carbon dioxide (CO_2), typically occurring under heat or in the presence of a base such as soda lime (NaOH + CaO). This reaction is essential in biochemical pathways, such as the Krebs cycle, and is widely used in organic synthesis to convert carboxylic acids into hydrocarbons. Aromatic carboxylic acids undergo decarboxylation more readily when an electron-withdrawing group is present, facilitating the loss of CO_2.

Hunsdiecker Reaction

The Hunsdiecker reaction involves the conversion of silver carboxylates into alkyl halides upon reaction with bromine or iodine. This reaction proceeds via a radical mechanism, where the decarboxylation step generates a free radical, which then reacts with the halogen to form the final halide product. It is particularly useful for converting carboxylic acids into halogenated hydrocarbons, which serve as key intermediates in organic synthesis.

Reducing Property of Formic Acid

Formic acid (HCOOH) is unique among carboxylic acids due to its ability to act as a reducing agent. Unlike other carboxylic acids, it contains an aldehyde-like hydrogen attached to the carbonyl carbon, allowing it to reduce metal ions such as Ag^+ to metallic silver in Tollens' test. Formic acid also decomposes into carbon monoxide (CO) and water upon heating or in the presence of acid catalysts, making it useful in carbon monoxide generation in laboratory and industrial applications. Additionally, it can reduce strong oxidizing agents such as potassium permanganate ($KMnO_4$) and dichromate ($K_2Cr_2O_7$), further demonstrating its reducing nature.

Reactions of Dicarboxylic Acids, Hydroxy Acids, and Unsaturated Acids

Reactions of Dicarboxylic Acids

Dicarboxylic acids contain two –COOH groups and exhibit unique reactivity due to their ability to form intramolecular and intermolecular hydrogen bonding. Some important reactions include:

Decarboxylation: When heated, dicarboxylic acids lose CO_2, forming monocarboxylic acids or hydrocarbons.

Formation of Anhydrides: Certain dicarboxylic acids, such as succinic acid, dehydrate upon heating to form cyclic anhydrides.

Esterification: Reaction with alcohols in the presence of acid catalysts produces diesters, which are useful in polymer synthesis.

Salt Formation: Reacting with bases forms dicarboxylate salts, often used in medicine and industrial applications.

Reactions of Hydroxy Acids

Hydroxy acids contain both –OH and –COOH functional groups, allowing them to undergo reactions characteristic of alcohols and carboxylic acids. Important reactions include:

Esterification: Hydroxy acids can form lactones (cyclic esters) upon intramolecular esterification, especially γ- and δ-hydroxy acids.

Oxidation: The hydroxyl group can be oxidized to a carbonyl group (forming keto acids).

Dehydration: Hydroxy acids can undergo dehydration to form unsaturated acids.

Complex Formation: Some hydroxy acids, such as citric acid, form metal complexes, making them useful in chelation therapy and industry.

Reactions of Unsaturated Acids

Unsaturated acids contain C=C bonds and show reactivity both at the carboxyl and alkene functional groups. Key reactions include:

Hydrogenation: The C=C bond can be hydrogenated to form saturated acids in the presence of catalysts like Ni, Pt, or Pd.

Addition Reactions:

Halogenation: Reaction with Br_2 or Cl_2 leads to dihalo acids.

Hydrohalogenation: Addition of HCl or HBr follows Markovnikov or anti-Markovnikov selectivity.

Polymerization: Unsaturated acids, such as acrylic acid, undergo polymerization to form important plastics and resins.

Oxidation: Strong oxidizing agents (e.g., $KMnO_4$) cleave the C=C bond, leading to dicarboxylic acids or ketones.

Carboxylic Acid Derivatives

Carboxylic acid derivatives include acid chlorides, esters, amides, and anhydrides, which are formed by replacing the hydroxyl group (-OH) in carboxylic acids with another functional group. These compounds exhibit nucleophilic acyl substitution due to the presence of the electrophilic acyl carbon.

Preparation of Carboxylic Acid Derivatives

Acid Chlorides (RCOCl)

Prepared by reacting carboxylic acids with thionyl chloride ($SOCl_2$), phosphorus trichloride (PCl_3), or phosphorus pentachloride (PCl_5).

Highly reactive due to the presence of the electronegative chlorine atom.

Esters (RCOOR')

Formed by Fischer esterification, where carboxylic acids react with alcohols in the presence of an acid catalyst (H_2SO_4 or HCl).

Also obtained from acid chlorides or anhydrides by reacting with alcohols.

Amides ($RCONH_2$)

Prepared by treating acid chlorides or esters with ammonia (NH_3) or amines (RNH_2, R_2NH).

Can also be synthesized by heating ammonium carboxylates.

Anhydrides (RCOO-COR')

Produced by dehydrating carboxylic acids at high temperatures.

Commonly prepared by treating acid chlorides with carboxylates.

Nucleophilic Acyl Substitution Reactions

Carboxylic acid derivatives undergo nucleophilic substitution at the acyl carbon, where the leaving group is replaced by a nucleophile.

Acyl Halides (RCOCl):

Highly reactive due to strong electron withdrawal by the halide.

React with water (forming acids), alcohols (forming esters), and amines (forming amides).

Anhydrides (RCOO-COR’):

React with alcohols to form esters and with amines to yield amides.

Esters (RCOOR’):

Undergo hydrolysis (acidic or basic) to form acids or carboxylate ions.

React with amines to form amides.

Amides ($RCONH_2$):

Less reactive but can hydrolyze under acidic or basic conditions to form acids or amines.

Important Named Reactions

Schotten-Baumann Reaction

Involves the synthesis of amides or esters from acid chlorides under alkaline conditions.

Commonly used in peptide synthesis.

Claisen Condensation

A carbon-carbon bond-forming reaction between two esters in the presence of a strong base to form a β-keto ester.

Useful in the synthesis of complex organic molecules.

Dieckmann Condensation

An intramolecular Claisen condensation, leading to the formation of cyclic β-keto esters from diesters.

Used in ring synthesis.

Reformatsky Reaction

Involves the reaction of α-halo esters with aldehydes or ketones in the presence of zinc to form β-hydroxy esters.

Related to the aldol condensation.

Hofmann Bromamide Degradation

Converts primary amides ($RCONH_2$) into primary amines (RNH_2) using bromine (Br_2) and a strong base (NaOH).

Results in the loss of the carbonyl carbon.

Curtius Rearrangement

Involves the thermal decomposition of acyl azides ($RCON_3$) to form isocyanates (RNCO), which further react with water to give primary amines.

Used for synthesizing amines and ureas.

Active Methylene Compounds and Their Synthetic Applications

Active methylene compounds contain a highly reactive methylene ($-CH_2-$) group situated between two electron-withdrawing groups (such as carbonyls). This enhances acidity, allowing these compounds to undergo various nucleophilic and condensation reactions.

Keto-Enol Tautomerism

Keto-enol tautomerism is an equilibrium between the keto form (C=O) and the enol form (C=C-OH) of carbonyl compounds. This interconversion occurs through proton transfer and is catalyzed by acids or bases. The keto form is generally more stable, but in some cases, the enol form is favored due to intramolecular hydrogen bonding or aromatic stability.

Example: Ethyl acetoacetate exists in equilibrium between its keto and enol forms.

This tautomerism is essential in reactions like the aldol condensation and Michael addition.

Diethyl Malonate: Preparation and Synthetic Applications

Preparation of Diethyl Malonate

Diethyl malonate ($CH_2(COOC_2H_5)_2$) is synthesized by esterification of malonic acid with ethanol in the presence of a strong acid catalyst (H_2SO_4).

Synthetic Applications of Diethyl Malonate

Alkylation:

The methylene hydrogen is acidic and can be deprotonated by a strong base (NaOEt).

The resulting enolate undergoes alkylation with alkyl halides, forming substituted malonates.

Hydrolysis and Decarboxylation:

Upon hydrolysis (NaOH) and acid treatment, malonic acid is obtained.

When heated, one CO_2 molecule is lost, forming carboxylic acids (malonic ester synthesis).

Synthesis of Barbiturates:

Diethyl malonate is used in the synthesis of barbiturates, which are important sedatives and anesthetics.

Preparation of α-Substituted Acids:

By choosing different alkyl halides, α-substituted carboxylic acids can be synthesized efficiently.

Ethyl Acetoacetate: Preparation and Synthetic Applications

Preparation of Ethyl Acetoacetate

Ethyl acetoacetate (CH_3COCH_2COOEt) is prepared via Claisen condensation of two molecules of ethyl acetate (EtOAc) in the presence of sodium ethoxide (NaOEt).

Synthetic Applications of Ethyl Acetoacetate

Alkylation Reactions:

The methylene group between the carbonyls is deprotonated by a base.

The enolate undergoes alkylation to form α-substituted ketones.

Hydrolysis and Decarboxylation:

Acidic hydrolysis of ethyl acetoacetate yields β-keto acids.

Upon heating, decarboxylation occurs, forming ketones (acetoacetic ester synthesis).

Synthesis of Amino Acids and Heterocycles:

Ethyl acetoacetate is a precursor in the synthesis of amino acids and heterocyclic compounds like pyrazoles and pyrimidines.

Michael Addition and Condensation Reactions:

The enolate form readily participates in Michael additions and aldol condensations, making it a versatile reagent in organic synthesis.

Halogen-Substituted Acids

Halogen-substituted carboxylic acids are organic compounds in which one or more hydrogen atoms in a carboxylic acid are replaced by halogen atoms (fluorine, chlorine, bromine, or iodine). These compounds exhibit increased acidity due to the electron-withdrawing inductive effect (-I effect) of halogens.

Nomenclature of Halogen-Substituted Acids

Halogen-substituted acids are named by indicating the position and type of halogen attached to the carboxylic acid.

Common Names: Based on the parent acid name.

Monohalo acids: Chloroacetic acid ($CH_2ClCOOH$), Bromoacetic acid ($CH_2BrCOOH$)

Dihalo acids: Dichloroacetic acid ($CHCl_2COOH$)

Trihalo acids: Trichloroacetic acid (CCl_3COOH)

IUPAC Naming:

Named as halogen derivatives of alkanoic acids.

Example: 2-Chloropropanoic acid ($CH_3CHClCOOH$).

Preparation of Halogen-Substituted Acids

Direct Halogenation (α-Halogenation of Carboxylic Acids)

The Hell-Volhard-Zelinsky (HVZ) reaction is the most common method for α-halogenation of carboxylic acids.

Reaction: Carboxylic acids react with Br_2 (or Cl_2) in the presence of phosphorus (P or PCl_3) to yield α-halo carboxylic acids.

Example:
$CH_3CH_2COOH + Br_2 \rightarrow CH_3CHBrCOOH$ (α-Bromopropionic acid)

Iodination from Unsaturated Acids

Iodination of unsaturated carboxylic acids occurs via electrophilic addition of iodine across the double bond.

Example:

$CH_2{=}CHCOOH + I_2 \rightarrow CH_2I\text{-}CHICOOH$ (α, β-Diiodopropionic acid)

From Alkyl Malonic Acids

Alkyl malonic acids ($RCH(COOH)_2$) can be halogenated at the α-position using halogens in acidic conditions.

This provides α-halo carboxylic acids, which can undergo further decarboxylation to yield monocarboxylic acids.

Example:

$CH_2(COOH)_2 + Br_2 \rightarrow CHBr(COOH)_2 \rightarrow CH_2BrCOOH$ (Bromoacetic acid)

Hydroxy Acids

Hydroxy acids are organic acids that contain one or more hydroxyl (-OH) groups in addition to the carboxyl (-COOH) group. They are classified based on the position of the hydroxyl group relative to the carboxyl group into α-hydroxy acids, β-hydroxy acids, and γ-hydroxy acids.

Nomenclature of Hydroxy Acids

Hydroxy acids are named using either common names or IUPAC names, depending on their structure.

Common Names:

Glycolic acid (α-Hydroxyethanoic acid) – $CH_2OHCOOH$

Lactic acid (α-Hydroxypropanoic acid) – $CH_3CHOHCOOH$

Malic acid (α-Hydroxybutanedioic acid) – $HOOCCH_2CHOHCOOH$

Citric acid (2-Hydroxy-1,2,3-propane-tricarboxylic acid)

IUPAC Naming:

Hydroxy acids are named as hydroxy derivatives of carboxylic acids.

The hydroxy group's position is indicated using numbers (e.g., 2-hydroxypropanoic acid for lactic acid).

Preparation of Hydroxy Acids

From Halo Acids

Hydrolysis of α-Halo Carboxylic Acids produces α-hydroxy acids.

Example:
$CH_2ClCOOH + H_2O \rightarrow CH_2OHCOOH$ (Glycolic acid)

From Amino Acids

Oxidative deamination of amino acids using HNO_2 leads to hydroxy acids.

Example:
$CH_3CH(NH_2)\ COOH + HNO_2 \rightarrow CH_3CHOHCOOH + N_2$ (Lactic acid)

From Aldehydic and Ketonic Acids

Aldol condensation of aldehydes or ketones followed by oxidation produces hydroxy acids.

Example:
Aldol condensation of Acetaldehyde

$2CH_3CHO \rightarrow CH_3CH(OH)CH_2CHO$

Oxidation yields lactic acid.

From Ethylene Glycol

Selective oxidation of ethylene glycol produces hydroxy acids.

Example:
$HOCH_2CH_2OH + O_2 \rightarrow HOCH_2COOH$ (Glycolic acid)

From Aldol Acetaldehyde

Aldol reaction produces β-hydroxy acids, which can be further oxidized to α-hydroxy acids.

Reactions of Hydroxy Acids

Action of Heat on α-, β-, and γ-Hydroxy Acids

α-Hydroxy Acids: Upon heating, they undergo dehydration to form α-lactones or polymerize.

Example: Lactic acid → Lactide (Cyclic dimer)

β-Hydroxy Acids: Heat-induced dehydration results in α, β-unsaturated acids.

Example:
$CH_3CH(OH)CH_2COOH \rightarrow CH_3CH{=}CHCOOH + H_2O$ (Crotonic acid)

γ-Hydroxy Acids: Heat treatment leads to intramolecular esterification, forming γ-lactones.

Example:
$HOCH_2CH_2CH_2COOH \rightarrow$ γ-Butyrolactone + H_2O