

LECTURE NOTES

On

METALLURGICAL THERMODYNAMICS AND KINETICS



ORISSA SCHOOL OF MINING ENGINEERING

Government of Odisha

ଓଡିଶା ଖଣି ଯାନ୍ତ୍ରୀକ ବିଦ୍ୟାଳୟ, କେଉଁଝର

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Metallurgical Engineering Department

Orissa School of Mining Engineering Keonjhar

Course code: Th-4

Semester: 3rd

Vision and Mission of the Department

VISION: To offer quality technical education In the field of Metallurgical Engineering with orientation towards industry, entrepreneurship, higher education and to strive for developing professionally competent technicians meeting the needs of the global economy.

MISSION:

M1 :To develop students in the field of Metallurgical Engineering as highly motivated, skillful and qualified manpower for employment and higher learning

M2 :To promote a conducive environment for all round development of students.

M3 :To promote linkages with external agencies to meet changing needs of industry and society.

M4 : To Improve Laboratories

Program Education Objectives (PEOs)

PEO 1:Diploma professionals will be able to make a successful career in metallurgical industries or higher studies to meet the needs of future requirements.

PEO 2:Diploma metallurgists will have technical and behavioral competencies through adequate exposure to industry.

PEO 3:To impart technological knowledge and skills for solving real-time engineering problems.

PEO4:To develop human resources with capabilities of effective communication, moral values and social responsibilities.

CONTENT

UNIT-I Basic Concepts of Thermodynamics Introduction: Definition of thermodynamics, system, surroundings, types of systems (open, closed, isolated), thermodynamic properties (intensive, extensive), state functions. Zeroth Law of Thermodynamics: Concept of thermal equilibrium, temperature measurement. First Law of Thermodynamics: Conservation of energy, internal energy, enthalpy, heat and work, heat capacity, specific heat. Applications: Brief idea about various processes isothermal, adiabatic, isobaric, isochoric.

UNIT-II Second and Third Law of Thermodynamics Entropy: Concept of entropy, entropy change in reversible and irreversible processes, entropy and disorder. Second Law Statements: Different statements of the second law Gibbs free energy: Definition of Gibbs free energy, its significance in determining spontaneity of reactions, relationship between Gibbs free energy and equilibrium constant. Third Law of Thermodynamics, Gibbs free energy (ΔG) & Helmholtz free energy (ΔA), Maxwell relations (No Derivation)

UNIT-III Phase Equilibria & Metallurgical Applications Solutions & Phase Rule : Ideal & non-ideal solutions, Raoult's Law, Henry's Law, Phase rule (Gibbs' phase rule), unary & binary phase diagrams, Ellingham Diagrams & Applications, Concept of Ellingham diagrams, Oxide stability & reduction reactions, Predominance Area Diagram.

UNIT-IV Chemical Kinetics & Reaction Rate Theory Fundamentals of Reaction Kinetics: Rate of reaction, order & molecularity, Activation energy & Arrhenius equation, Homogeneous vs. Heterogeneous reactions, Electrochemical Thermodynamics : Electrochemical cells, Nernst equation (Basic Level)

UNIT-V Thermodynamics in Metallurgical Processes (Basic level) Application of Thermodynamics in Extraction & Refining: Basics of Ironmaking & Steelmaking thermodynamics, Roasting, Smelting, Refining processes, Basic Concept of activity, & equilibrium constant

Unit-1

1. Introduction to Thermodynamics

1.1 What is Thermodynamics?

The word **thermodynamics** comes from two words:

- **Thermo** → Heat
- **Dynamics** → Motion or transformation

Definition

Thermodynamics is the branch of science that deals with heat, work, energy and their transformations.

In simple words:

Thermodynamics tells us how energy is transferred and converted from one form to another.

Examples

- A steam turbine converts **thermal energy into mechanical work.**
- An engine converts **chemical energy of fuel into mechanical work.**
- A refrigerator uses **work to transfer heat from a cold region to a hot region.**
- A boiler converts water into steam by supplying heat.

2. Thermodynamic System, Surroundings and Boundary

Whenever we study a thermodynamic process, we divide the universe into three parts:

System

A **system** is the particular quantity of matter or region of space selected for study.

Examples:

- Gas inside a cylinder
- Water inside a boiler
- Steam inside a turbine

Surroundings

Everything outside the system that can interact with the system is called the **surroundings**.

Boundary

The real or imaginary surface separating the system from its surroundings is called the **boundary**.

The boundary may be:

- **Fixed** – does not move
- **Movable** – can move, e.g., piston
- **Real** – physically exists
- **Imaginary** – assumed for analysis

3. Types of Thermodynamic Systems

Thermodynamic systems are mainly classified as:

1. Open system
2. Closed system
3. Isolated system

3.1 Open System

An **open system** allows both **mass and energy** to cross its boundary.

Example

A **steam turbine**.

Steam enters and leaves the turbine, while heat and work interactions may also occur.

Examples

- Turbine
- Compressor
- Pump
- Boiler

- Automobile engine

3.2 Closed System

A **closed system** allows **energy transfer but not mass transfer** across its boundary.

Example

The gas remains inside the cylinder, but heat and work can cross the boundary.

Example

A sealed pressure cooker or piston-cylinder arrangement.

3.3 Isolated System

An **isolated system** allows **neither mass nor energy** to cross its boundary.

Example

An ideal thermos flask.

Comparison

System Mass Transfer Energy Transfer

Open Yes Yes

Closed No Yes

Isolated No No

4. Thermodynamic Properties

A **property** is a measurable characteristic of a thermodynamic system.

Examples:

- Pressure P
- Temperature T
- Volume V
- Density ρ
- Internal energy U

- Enthalpy H

Properties are classified into:

1. Intensive properties
2. Extensive properties

5. Intensive Properties

An **intensive property** does not depend on the amount of matter present in the system.

Examples

- Temperature
- Pressure
- Density
- Specific volume
- Specific heat

For example, if a tank of water is divided into two equal parts, the temperature of each part can remain the same as the original water.

Therefore, temperature is an intensive property.

Intensive property = Independent of mass

6. Extensive Properties

An **extensive property** depends on the amount of matter present in the system.

Examples

- Mass
- Volume
- Internal energy
- Enthalpy
- Entropy

If the amount of water is doubled, its total volume and total mass are also doubled.

Extensive property = Depends on mass

Difference

Intensive

Independent of amount of matter

Temperature

Pressure

Density

Specific volume

Extensive

Depends on amount of matter

Mass

Volume

Internal energy

Enthalpy

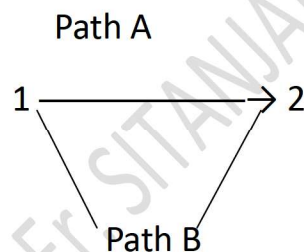
7. State Function

A **state function** is a thermodynamic property whose value depends only on the **initial and final states**, not on the path followed.

Examples

- Temperature
- Pressure
- Volume
- Internal energy
- Enthalpy
- Entropy

Suppose a gas changes from state 1 to state 2.



The change in a state function is the same for both paths.

For example:

$$\Delta U = U_2 - U_1$$

It does not depend on how the gas reached state 2.

Important

Heat and work are NOT state functions.

They depend on the path followed.

8. Zeroth Law of Thermodynamics

The **Zeroth Law of Thermodynamics** establishes the concept of **thermal equilibrium** and provides the basis for temperature measurement.

Statement

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

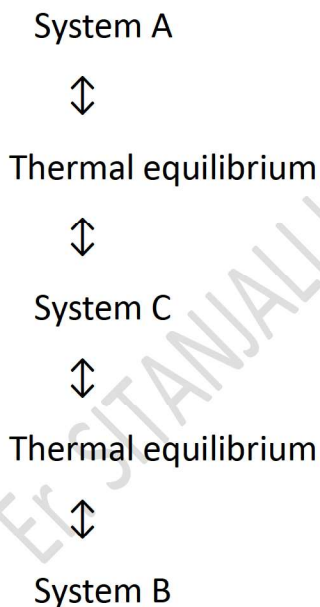
Suppose:

- A is in thermal equilibrium with C.
- B is in thermal equilibrium with C.

Then:

A is in thermal equilibrium with B

Diagram



Therefore:

A ↔ B are in thermal equilibrium

9. Thermal Equilibrium

Two bodies are said to be in **thermal equilibrium** when there is **no net flow of heat between them**.

This occurs when they have the same temperature.

$$T_A = T_B$$

Example

If a hot cup of tea is kept in a room, heat flows from the tea to the surroundings until both reach the same temperature.

At equilibrium:

$$T_{\text{tea}} = T_{\text{room}}$$

10. Temperature Measurement

Temperature is a measure of the thermal state or degree of hotness or coldness of a body.

Temperature can be measured using instruments such as:

- Mercury thermometer
- Alcohol thermometer
- Thermocouple
- Resistance thermometer
- Gas thermometer

Common temperature scales

Celsius scale

°C

Kelvin scale

K

Relationship:

$$T(K) = T(^{\circ}C) + 273.15$$

For engineering calculations, Kelvin temperature is generally used.

Example:

$$27^{\circ}\text{C}=27+273=300\text{K}$$

11. First Law of Thermodynamics

The **First Law of Thermodynamics** is based on the **law of conservation of energy**.

Statement

Energy can neither be created nor destroyed; it can only be converted from one form into another.

For a thermodynamic system:

$$Q=\Delta U+W$$

where:

- Q = Heat supplied to system
- ΔU = Change in internal energy
- W = Work done by system

Therefore:

$$\Delta U=Q-W$$

Simple explanation

When heat is supplied to a system, the energy supplied is used for:

1. Increasing internal energy
2. Doing work

Therefore:

Heat supplied=Increase in internal energy+Work done

12. Internal Energy

Internal energy is the total microscopic energy stored inside a substance due to the motion and interactions of its molecules.

It is represented by:

$$U$$

It includes:

- Molecular kinetic energy
- Molecular potential energy
- Vibrational energy
- Rotational energy
- Other microscopic forms of energy

Internal energy is a **state function**.

Therefore:

$$\Delta U = U_2 - U_1$$

Unit

SI unit:

J

Engineering unit:

kJ

13. Enthalpy

Enthalpy is a thermodynamic property that combines **internal energy and flow energy**.

It is represented by H.

$$H = U + PV$$

For a change:

$$\Delta H = \Delta U + \Delta(PV)$$

For constant pressure, when only pressure-volume work is involved:

$$Q_p = \Delta H$$

Specific enthalpy

$$h = u + Pv$$

Applications

Enthalpy is very useful in:

- Boilers
- Steam turbines
- Compressors
- Heat exchangers
- Refrigeration systems
- Combustion processes

14. Heat

Heat is energy transferred between two bodies because of a temperature difference.

Heat always flows naturally from:

Higher temperature → Lower temperature

Important point

Heat is **not stored in a body as heat**. It is energy transferred because of temperature difference.

Heat is represented by:

Q

SI unit:

Joule(J)

15. Work

Work is energy transfer that occurs when a force acts through a distance.

In thermodynamics, one important type is **pressure-volume work**.

For a piston-cylinder:

$$W = \int_{V_1}^{V_2} P dV$$

For constant pressure:

$$W = P(V_2 - V_1)$$

Expansion

If gas expands:

$$V_2 > V_1$$

Work is done **by the gas**.

Compression

If gas is compressed:

$$V_2 < V_1$$

Work is done **on the gas**.

16. Heat Capacity

Heat capacity is the amount of heat required to raise the temperature of a body by 1°C or 1 K .

$$C = Q / \Delta T$$

Therefore:

$$Q = C \Delta T$$

Unit

J/K

Heat capacity depends on the amount of material.

17. Specific Heat

Specific heat is the amount of heat required to raise the temperature of **unit mass** of a substance by 1°C or 1 K .

$$c = Q / m \Delta T$$

Therefore:

$$Q = mc \Delta T$$

where:

- Q = Heat supplied
- m = Mass
- c = Specific heat
- ΔT = Change in temperature

Unit

$$\text{J}/(\text{kg}\cdot\text{K})$$

or

$$\text{kJ}/(\text{kg}\cdot\text{K})$$

18. Specific Heat at Constant Volume — C_v

The amount of heat required to raise the temperature of unit mass of a substance by 1 K **at constant volume** is called specific heat at constant volume.

$$C_v$$

For an ideal gas:

$$Q_v = mC_v\Delta T$$

At constant volume:

$$W=0$$

Therefore, from the First Law:

$$Q_v = \Delta U$$

19. Specific Heat at Constant Pressure — C_p

The amount of heat required to raise the temperature of unit mass of a substance by 1 K **at constant pressure** is called specific heat at constant pressure.

$$C_p$$

For an ideal gas:

$$Q_p = mC_p\Delta T$$

Since expansion can occur at constant pressure, some heat is used to perform work.

Therefore, for gases:

$$C_p > C_v$$

For an ideal gas:

$$C_p - C_v = R$$

where R is the gas constant.

20. Different Thermodynamic Processes

A **thermodynamic process** is the change of a system from one state to another.

Important processes are:

1. Isothermal
2. Adiabatic
3. Isobaric
4. Isochoric

21. Isothermal Process

An **isothermal process** occurs at **constant temperature**.

$$T = \text{constant}$$

For an ideal gas:

$$PV = \text{constant}$$

Therefore:

$$P_1V_1 = P_2V_2$$

For an ideal gas, since temperature remains constant:

$$\Delta U = 0$$

From First Law:

$$Q = W$$

Example

Slow expansion of gas while it remains in contact with a constant-temperature heat reservoir.

22. Adiabatic Process

An **adiabatic process** is one in which **no heat is transferred** between the system and surroundings.

$$Q = 0$$

From First Law:

$$Q = \Delta U + W$$

Therefore:

$$\Delta U = -W$$

For a reversible adiabatic process involving an ideal gas:

$$PV^\gamma = \text{constant}$$

where:

$$\gamma = C_p / C_v$$

Examples

- Rapid compression of gas
- Rapid expansion of gas
- Gas compression in an insulated cylinder

23. Isobaric Process

An **isobaric process** occurs at **constant pressure**.

$$P = \text{constant}$$

Work done:

$$W = P(V_2 - V_1)$$

For an ideal gas:

$$V/T = \text{constant}$$

Therefore:

$$V_1/T_1 = V_2/T_2$$

Example

Heating a gas in a cylinder with a freely movable piston while maintaining constant pressure.

24. Isochoric Process

An **isochoric process** occurs at **constant volume**.

$$V = \text{constant}$$

Since volume does not change:

$$W = 0$$

Therefore, from the First Law:

$$Q = \Delta U$$

For an ideal gas:

$$P/T = \text{constant}$$

Therefore:

$$P_1/T_1 = P_2/T_2$$

Example

Heating a gas inside a rigid, sealed container.

25. Comparison of Important Thermodynamic Processes

Process	Constant Property	Main Equation	Important Point
Isothermal	Temperature	$PV = C$	T constant
Adiabatic	Heat transfer	$Q = 0$	No heat transfer
Isobaric	Pressure	$V/T = C$	P constant
Isochoric	Volume	$P/T = C$	V constant, $W = 0$

26. Quick Revision Chart

Laws

Zeroth Law



Thermal Equilibrium



Temperature Measurement

First Law



Conservation of Energy



$$Q = \Delta U + W$$

Important properties

U = Internal Energy

$$H = U + PV$$

$$Q = mc\Delta T$$

$$C_p - C_v = R \text{ (ideal gas)}$$

Important processes

Isothermal: $T = C$

Adiabatic: $Q=0$

Isobaric: $P=C$

Isochoric: $V=C$

Important Points for Examination

Students should particularly remember these points:

1. **Thermodynamics** deals with heat, work and energy transformations.
2. **System** is the part selected for study.
3. **Open system**: mass + energy can cross the boundary.
4. **Closed system**: only energy can cross the boundary.
5. **Isolated system**: neither mass nor energy crosses the boundary.
6. **Intensive properties** do not depend on mass.
7. **Extensive properties** depend on mass.
8. **State functions** depend only on initial and final states.
9. **Heat and work are not state functions.**
10. **Zeroth Law** establishes thermal equilibrium.
11. **First Law** is the law of conservation of energy.
12. $Q = \Delta U + W$
13. $H = U + PV$
14. **Heat flows naturally from high temperature to low temperature.**
15. $Q = mc\Delta T$
16. $C_p > C_v$ for an ideal gas.
17. **Isothermal**: temperature constant.
18. **Adiabatic**: no heat transfer.
19. **Isobaric**: pressure constant.
20. **Isochoric**: volume constant and hence $W=0$.

Unit-2

1. Introduction to the Second Law of Thermodynamics

The **First Law of Thermodynamics** tells us that energy is conserved. However, it does not tell us:

- In which direction a process will occur.
- Whether a process is possible or spontaneous.
- Why heat naturally flows from hot to cold.
- Why all heat cannot be converted completely into work.

The **Second Law of Thermodynamics** answers these questions.

Simple meaning

The Second Law tells us about the **direction of a thermodynamic process** and the **possibility of conversion of heat into work**.

Examples

- Heat flows naturally from a **hot body to a cold body**.
- A gas naturally expands into an empty space.
- A hot cup of tea cools down naturally, but it does not become hotter by taking heat from the surroundings spontaneously.

2. Entropy

Definition

Entropy is a thermodynamic property that indicates the degree of energy dispersal or disorder of a system.

It is represented by:

$$S$$

The change in entropy is:

$$\Delta S = S_2 - S_1$$

For a reversible process:

$$dS = \frac{\delta Q_{rev}}{T}$$

Therefore:

$$\Delta S = \int_1^2 \frac{\delta Q_{rev}}{T}$$

where:

- S = Entropy
- Q_{rev} = Reversible heat transfer
- T = Absolute temperature

SI unit

J/K

For specific entropy:

J/(kg·K)

3. Physical Meaning of Entropy

Entropy can be understood as a measure of the **degree of randomness or disorder** of a system.

Example: Ice → Water → Steam

Ice Water Steam

Highly ordered → More random → Highly random

Low entropy → → High entropy

When ice melts:

$$\Delta S > 0$$

When water changes into steam:

$$\Delta S > 0$$

because molecular freedom increases.

Important note

"Entropy = disorder" is a useful basic explanation, but entropy is more accurately related to **energy dispersal and the number of possible microscopic arrangements**.

4. Entropy and Disorder

Generally:

Greater molecular disorder $\Rightarrow$ Greater entropy

For example:

Solid $\rightarrow$ Liquid $\rightarrow$ Gas

Generally:

$$S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$$

Why?

In a solid, atoms or molecules are closely arranged and have limited freedom of movement.

In a liquid, they have greater freedom.

In a gas, molecules move freely in a much larger space.

5. Entropy Change in a Reversible Process

For a reversible process:

$$dS = \delta Q_{\text{rev}} / T$$

Therefore:

$$\Delta S = \int \delta Q_{\text{rev}} / T$$

If temperature is constant:

$$\Delta S = Q_{\text{rev}} / T$$

Example

If 1000 J of heat is reversibly supplied to a system at 500 K:

$$\Delta S = 1000 / 500 = 2 \text{ J/K}$$

$$\Delta S = 2 \text{ J/K}$$

6. Entropy Change in an Irreversible Process

An irreversible process is a process that occurs naturally and cannot be exactly reversed without producing changes in the surroundings.

Examples:

- Free expansion of a gas
- Heat transfer through a finite temperature difference
- Friction
- Mixing of gases
- Rapid expansion

For calculating entropy change between two equilibrium states, we can use a **reversible path** connecting those states because entropy is a state function.

Thus:

$$\Delta S = \int \delta Q_{\text{rev}} / T$$

even when the actual process is irreversible.

Important point

For an irreversible process:

$$\Delta S_{\text{universe}} > 0$$

7. Entropy Generation

Irreversible processes produce entropy.

The entropy balance can be expressed as:

$$\Delta S_{\text{system}} = \int \delta Q / T + S_{\text{gen}}$$

where S_{gen} is entropy generated due to irreversibility.

For a reversible process:

$$S_{\text{gen}} = 0$$

For an irreversible process:

$$S_{\text{gen}} \geq 0$$

Therefore:

$$S_{\text{gen}} \geq 0$$

This is one of the important consequences of the Second Law.

8. Second Law of Thermodynamics

The Second Law has several equivalent statements.

The two most important statements are:

1. **Kelvin–Planck statement**
2. **Clausius statement**

9. Kelvin–Planck Statement

Statement

It is impossible to construct a heat engine operating in a cycle that converts all the heat supplied to it completely into work.

Here:

- Q_H = Heat absorbed from hot reservoir
- Q_L = Heat rejected
- W = Work obtained

Energy balance:

$$Q_H = W + Q_L$$

Therefore:

$$W < Q_H$$

10. Clausius Statement

Statement

Heat cannot, by itself, flow from a colder body to a hotter body.

In simple words:

Heat cannot naturally flow from cold to hot

To transfer heat from cold to hot, external work is required.

Example: Refrigerator

A refrigerator uses work to transfer heat from a low-temperature region to a high-temperature region.

11. Equivalence of Kelvin–Planck and Clausius Statements

The Kelvin–Planck and Clausius statements are **equivalent forms of the Second Law**. Violation of one statement would result in violation of the other.

Easy way to remember

Kelvin–Planck:

Heat cannot be completely converted into work.

Clausius:

Heat cannot spontaneously flow from cold to hot.

12. Entropy Statement of Second Law

The Second Law can also be expressed using entropy.

For an isolated system:

$$\Delta S_{\text{isolated}} \geq 0$$

Therefore:

Reversible process

$$\Delta S_{\text{universe}} = 0$$

Irreversible process

$$\Delta S_{\text{universe}} > 0$$

Thus:

$$\Delta S_{\text{universe}} \geq 0$$

This is called the **entropy principle**.

13. Entropy Change of the Universe

The universe can be considered as:

System + Surroundings

Therefore:

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

For a reversible process:

$$\Delta S_{\text{universe}} = 0$$

For an irreversible process:

$$\Delta S_{\text{universe}} > 0$$

A process is impossible if:

$$\Delta S_{\text{universe}} < 0$$

14. Spontaneous and Non-Spontaneous Processes

A **spontaneous process** is a process that can occur naturally under given conditions without continuous external intervention.

Examples:

- Heat flowing from hot to cold.
- Gas expanding into an evacuated space.
- Iron rusting under suitable conditions.

A spontaneous process does **not necessarily mean a fast process**.

Important

Spontaneity is determined by thermodynamic conditions, while the rate of a process is determined by kinetics.

15. Gibbs Free Energy

Definition

Gibbs free energy is a thermodynamic quantity used to determine the **spontaneity and equilibrium of a process or chemical reaction at constant temperature and pressure**.

It is represented by:

$$G$$

Definition:

$$G=H-TS$$

Therefore:

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

for constant temperature.

where:

- G = Gibbs free energy
- H = Enthalpy
- T = Absolute temperature
- S = Entropy

16. Significance of Gibbs Free Energy

The most important use of Gibbs free energy is to determine whether a process is **spontaneous, non-spontaneous or at equilibrium** at constant temperature and pressure.

Case 1: $\Delta G < 0$

$$\Delta G < 0$$

The process is **spontaneous** in the forward direction.

Case 2: $\Delta G > 0$

$$\Delta G > 0$$

The forward process is **non-spontaneous** under the given conditions.

Case 3: $\Delta G = 0$

$$\Delta G = 0$$

The system is at **equilibrium**.

Summary

ΔG Meaning

ΔG Meaning

$\Delta G < 0$ Spontaneous

$\Delta G > 0$ Non-spontaneous

$\Delta G = 0$ Equilibrium

17. Gibbs Free Energy and Equilibrium Constant

The relationship between Gibbs free energy and equilibrium constant is:

$$\Delta G^\circ = -RT \ln K$$

where:

- ΔG° = Standard Gibbs free energy change
- R = Gas constant
- T = Absolute temperature
- K = Equilibrium constant

Interpretation

If:

$$K > 1$$

then:

$$\ln K > 0$$

and therefore:

$$\Delta G^\circ < 0$$

The reaction tends to favour products.

If:

$$K < 1$$

then:

$$\Delta G^\circ > 0$$

The reaction tends to favour reactants.

If:

$$K=1$$

then:

$$\Delta G^\circ = 0$$

18. Gibbs Free Energy and Reaction Spontaneity

For a reaction:

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

The spontaneity depends on both **enthalpy change** and **entropy change**.

Example 1

If:

$$\Delta H < 0, \quad \Delta S > 0$$

then:

$$\Delta G < 0$$

The process is spontaneous at all temperatures, assuming these quantities remain approximately constant.

Example 2

If:

$$\Delta H > 0, \quad \Delta S < 0$$

then:

$$\Delta G > 0$$

The process is non-spontaneous at all temperatures, under the same assumption.

19. Gibbs–Helmholtz Equation

The Gibbs–Helmholtz equation relates Gibbs free energy to temperature.

A commonly used form is:

$$\left(\frac{\partial(\Delta G/T)}{\partial T} \right)_P = -\Delta H / T^2$$

This relationship is useful for studying how Gibbs free energy changes with temperature.

20. Third Law of Thermodynamics

Statement

The entropy of a perfect crystalline substance approaches zero as the temperature approaches absolute zero.

Mathematically:

$$S \rightarrow 0 \text{ as } T \rightarrow 0\text{K}$$

for a perfect crystal.

Meaning

At absolute zero:

$$T = 0\text{K}$$

a perfect crystal has only one possible arrangement of its particles, so its entropy is taken as zero.

Importance

The Third Law provides a reference point for determining **absolute entropy**.

It is useful in:

- Calculation of absolute entropy
- Chemical thermodynamics
- Phase equilibrium
- Low-temperature studies
- Determination of thermodynamic properties

21. Gibbs Free Energy vs Helmholtz Free Energy

There are two important thermodynamic free energies:

1. **Gibbs free energy**
2. **Helmholtz free energy**

Gibbs Free Energy

It is represented by:

$$G$$

Definition:

$$G=H-TS$$

Since:

$$H=U+PV$$

we get:

$$G=U+PV-TS$$

Useful at:

Constant temperature and pressure

Spontaneity condition:

$$\Delta G < 0$$

22. Helmholtz Free Energy

Helmholtz free energy is represented by:

$$A$$

It is also sometimes represented by F.

Definition:

$$A=U-TS$$

where:

- A = Helmholtz free energy
- U = Internal energy
- T = Temperature
- S = Entropy

Useful at:

Constant temperature and volume

For a spontaneous process at constant T,V:

$$\Delta A < 0$$

At equilibrium:

$$\Delta A = 0$$

23. Difference Between Gibbs and Helmholtz Free Energy

Gibbs Free Energy

$$G = H - TS$$

$$G = U + PV - TS$$

Useful at constant T,P

$\Delta G < 0$: spontaneous

Important in chemical reactions and phase equilibrium

Easy memory trick

Gibbs $\rightarrow G \rightarrow$ Constant P

Helmholtz $\rightarrow A \rightarrow$ Constant V

Helmholtz Free Energy

$$A = U - TS$$

$$A = U - TS$$

Useful at constant T,V

$\Delta A < 0$: spontaneous

Important in constant-volume systems

24. Maxwell Relations

Maxwell relations are important thermodynamic equations derived from the mathematical properties of thermodynamic state functions.

You **do not need to derive them** according to the syllabus, but you should know their forms and applications.

There are **four Maxwell relations**.

Maxwell Relation 1

From:

$$dU = TdS - PdV$$

we obtain:

$$(\partial V/\partial T)_S = -(\partial S/\partial P)_V$$

Maxwell Relation 2

From:

$$dH = TdS + VdP$$

we obtain:

$$(\partial P/\partial T)_S = (\partial S/\partial V)_P$$

Maxwell Relation 3

From:

$$dA = -SdT - PdV$$

we obtain:

$$(\partial V/\partial S)_T = (\partial T/\partial P)_V$$

Maxwell Relation 4

From:

$$dG = -SdT + VdP$$

we obtain:

$$(\partial P/\partial S)_T = -(\partial T/\partial V)_P$$

Easy way to remember

Thermodynamic function Differential equation Maxwell relation

U	$dU = TdS - PdV$	$(\partial V/\partial T)_S = -(\partial S/\partial P)_V$
H	$dH = TdS + VdP$	$(\partial P/\partial T)_S = (\partial S/\partial V)_P$
A	$dA = -SdT - PdV$	$(\partial V/\partial S)_T = (\partial T/\partial P)_V$
G	$dG = -SdT + VdP$	$(\partial P/\partial S)_T = -(\partial T/\partial V)_P$

25. Important Thermodynamic Relationships

Students should remember the following equations:

Entropy

$$dS = \delta Q_{\text{rev}} / T$$

Enthalpy

$$H = U + PV$$

Gibbs Free Energy

$$G = H - TS$$

Helmholtz Free Energy

$$A = U - TS$$

Gibbs free-energy change

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

Equilibrium constant

$$\Delta G^\circ = -RT \ln K$$

Third Law

$$S = 0 \text{ at } 0\text{K for a perfect crystal}$$

Entropy principle

$$\Delta S_{\text{universe}} \geq 0$$

26. Very Important Concept: First Law vs Second Law

First Law

Conservation of energy

Energy cannot be created or destroyed

Deals mainly with quantity of energy

$$Q = \Delta U + W$$

Does not predict spontaneity

Second Law

Direction of energy transfer

Determines whether a process is possible

Deals with quality/direction of energy

$$\Delta S_{\text{universe}} \geq 0$$

Predicts spontaneity

Example

The First Law allows heat to be converted into work according to energy conservation.

But the Second Law tells us that **100% conversion of heat into work in a cyclic heat engine is impossible.**

27. Important Concept: Reversible vs Irreversible Process

Reversible Process

Idealized process

Can be reversed without net change

No entropy generation

$$S_{\text{gen}} = 0$$

Occurs infinitely slowly in idealization

No friction ideally

Maximum possible work can be obtained from an expansion

Irreversible Process

Real process

Cannot be completely reversed

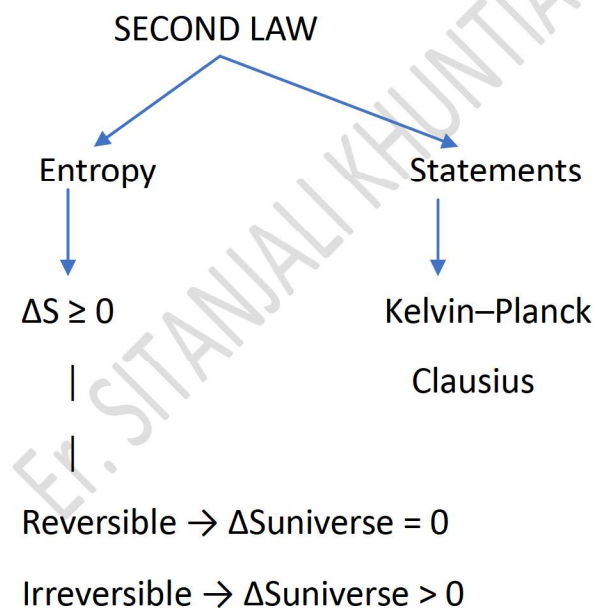
Entropy is generated

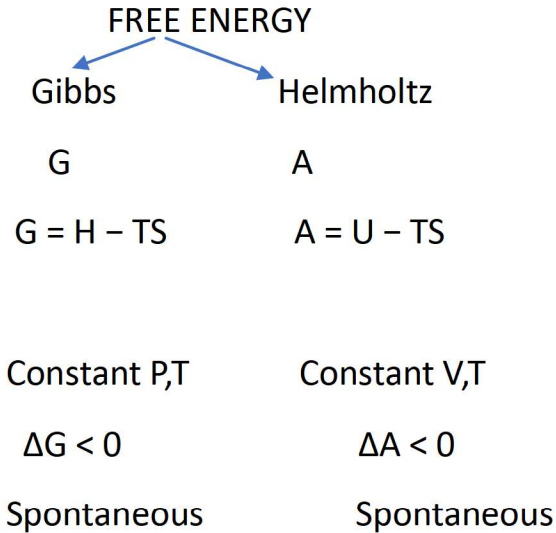
$$S_{\text{gen}} > 0$$

Usually occurs at finite rates

Friction may be present

Less work is obtained





29. Examination-Oriented Important Questions

Short-answer questions

1. Define entropy.
2. What is entropy generation?
3. State the Second Law of Thermodynamics.
4. State Kelvin–Planck statement.
5. State Clausius statement.
6. What is Gibbs free energy?
7. Write the equation for Gibbs free energy.
8. What is Helmholtz free energy?
9. State the Third Law of Thermodynamics.
10. What is the significance of the Third Law?
11. What is a spontaneous process?
12. What is the relation between ΔG° and K?
13. What is the condition for equilibrium in terms of Gibbs free energy?
14. What are Maxwell relations?
15. Write the four Maxwell relations.

Important numerical formulas

$$\Delta S = \delta Q_{\text{rev}} / T$$

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

$$\Delta G^\circ = -RT \ln K$$

$$\Delta S_{\text{universe}} \geq 0$$

$$G = H - TS$$

$$A = U - TS$$

30. One-Page Final Revision

Topic	Key Point / Formula
Entropy	Measure of energy dispersal/disorder
Entropy change	$\Delta S = \int \delta Q_{\text{rev}} / T$
Reversible process	$\Delta S_{\text{universe}} = 0$
Irreversible process	$\Delta S_{\text{universe}} > 0$
Second Law	$\Delta S_{\text{universe}} \geq 0$
Kelvin–Planck	Complete conversion of heat into work is impossible
Clausius	Heat cannot naturally flow from cold to hot
Gibbs energy	$G = H - TS$
Gibbs change	$\Delta G = \Delta H - T\Delta S$
Spontaneous	$\Delta G < 0$ at constant T,P
Equilibrium	$\Delta G = 0$
Non-spontaneous	$\Delta G > 0$
Equilibrium constant	$\Delta G^\circ = -RT \ln K$
Third Law	$S \rightarrow 0$ as $T \rightarrow 0\text{K}$ for a perfect crystal
Helmholtz energy	$A = U - TS$

Topic

Key Point / Formula

Helmholtz condition $\Delta A < 0$ for spontaneity at constant T,V

Maxwell relations Four relations connecting thermodynamic properties

★ **Most important formulas to memorize**

$$\Delta S = \delta Q_{\text{rev}} / T$$

$$\Delta S_{\text{universe}} \geq 0$$

$$G = H - TS$$

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

$$\Delta G^\circ = -RT \ln K$$

$$A = U - TS$$

$$S(0K) = 0 \text{ for a perfect crystal}$$

These equations, along with the **Kelvin–Planck and Clausius statements**, are the most important points for this unit.

UNIT–III

PHASE EQUILIBRIA & METALLURGICAL APPLICATIONS

1. Solutions

A **solution** is a homogeneous mixture of two or more components.

Components of a solution

- **Solvent:** Component present in larger amount.
- **Solute:** Component present in smaller amount.

Example

In a Cu–Ni alloy:

- Cu and Ni are components.
- If Cu is present in larger quantity, Cu is the solvent.
- Ni is the solute.

Solutions can be:

1. **Solid solutions**
2. **Liquid solutions**
3. **Gaseous solutions**

In metallurgy, **solid solutions** are particularly important.

2. Solid Solutions

A **solid solution** is a solid phase in which atoms of one or more elements are dissolved in the crystal structure of another element.

There are two main types:

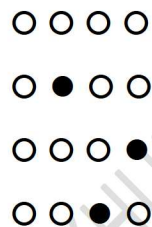
(a) Substitutional Solid Solution

Solute atoms replace some solvent atoms in the crystal lattice.

Example:

Cu-Ni alloy

Ni atoms substitute for Cu atoms.



○ = solvent atoms

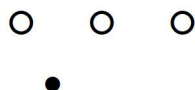
● = solute atoms

(b) Interstitial Solid Solution

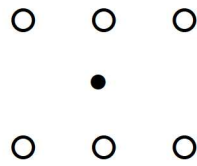
Small solute atoms occupy the spaces between solvent atoms.

Example:

Carbon in Iron



Carbon atoms occupy interstitial spaces in the iron lattice.



○ = Fe atom

● = C atom

3. Ideal and Non-Ideal Solutions

Ideal Solution

An **ideal solution** is a solution in which the interactions between different types of molecules are approximately equal to the interactions between similar molecules.

For an ideal solution:

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

and

$$\Delta V_{\text{mix}}=0$$

The solution obeys **Raoult's Law** over the entire composition range.

Examples

Some systems approximately behaving ideally include:

- Benzene–toluene
- Cu–Ni, approximately over suitable ranges

4. Non-Ideal Solutions

A **non-ideal solution** does not obey Raoult's Law over the entire composition range.

This occurs because the interactions between unlike atoms/molecules differ from those between like atoms/molecules.

There are two types:

Positive deviation

The vapour pressure is **higher** than predicted by Raoult's Law.

This generally occurs when unlike interactions are weaker.

Negative deviation

The vapour pressure is **lower** than predicted by Raoult's Law.

This generally occurs when unlike interactions are stronger.

Comparison

Ideal solution

Obeys Raoult's Law

$\Delta H_{mix}=0$

No significant deviation

A–B interactions approximately equal to A–A and B–B

Non-ideal solution

Deviates from Raoult's Law

$\Delta H_{mix} \neq 0$, generally

Positive or negative deviation

A–B interactions differ significantly

5. Raoult's Law

Raoult's Law describes the vapour pressure of a component in an **ideal solution**.

For component A:

$$P_A = X_A P_A^0$$

where:

- P_A = Partial vapour pressure of A in solution
- X_A = Mole fraction of A
- P_A^0 = Vapour pressure of pure A

For a two-component solution:

$$P_A = X_A P_A^0$$

$$P_B = X_B P_B^0$$

Total vapour pressure:

$$P = P_A + P_B$$

Therefore:

$$P = X_A P_A^0 + X_B P_B^0$$

Since:

$$X_A + X_B = 1$$

6. Simple Example of Raoult's Law

Suppose:

$$X_A = 0.4$$

and

$$P_A^0 = 100 \text{ kPa}$$

Then:

$$P_A = X_A P_A^0$$

$$P_A = 0.4 \times 100$$

$$P_A = 40 \text{ kPa}$$

So, the partial vapour pressure of A is **40 kPa**.

7. Henry's Law

Henry's Law is generally used to describe the behaviour of a **dilute solute** in a solution.

Statement

At constant temperature, the concentration or partial pressure of a dilute solute is proportional to its concentration in the solution, with the proportionality expressed through Henry's constant.

A common form is:

$$P_i = K_H X_i$$

where:

- P_i = Partial pressure of component i
- X_i = Mole fraction of component i
- K_H = Henry's law constant

Difference between Raoult's Law and Henry's Law

Raoult's Law

Mainly describes solvent/ideal-solution

Henry's Law

Mainly describes dilute solute

Raoult's Law

behaviour

$$P_i = X_i P_i^0$$

Uses vapour pressure of pure component

Ideal-solution concept

Henry's Law

behaviour

$$P_i = K_H X_i$$

Uses Henry's constant

Dilute-solution concept

8. Phase

A **phase** is a physically and chemically homogeneous portion of a system having uniform properties and separated from other portions by a definite boundary.

Examples

- Ice → one phase
- Water → one phase
- Ice + water → two phases
- Water + steam → two phases

In metallurgy:

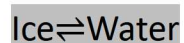
- Ferrite is a phase.
- Austenite is a phase.
- Cementite is a phase.

9. Phase Equilibrium

When two or more phases coexist in a system and their properties remain unchanged with time, they are said to be in **phase equilibrium**.

Example

At the melting temperature:



Both phases can coexist in equilibrium.

In an alloy:

may coexist at equilibrium.

10. Gibbs Phase Rule

The **Gibbs Phase Rule** gives the relationship between the number of components, phases and degrees of freedom of a system at equilibrium.

The general equation is:

$$F=C-P+2$$

where:

- F = Degrees of freedom
- C = Number of components
- P = Number of phases

Meaning of Degrees of Freedom

Degrees of freedom are the number of independent variables such as temperature, pressure and composition that can be changed without changing the number of phases present.

11. Reduced Phase Rule for Condensed Systems

For metallurgical systems where pressure is constant:

$$F=C-P+1$$

This is commonly called the **condensed phase rule**.

For a one-component system

$$C=1$$

Therefore:

$$F=1-P+1$$

$$F=2-P$$

For a two-component system

$$C=2$$

Therefore:

$$F=3-P$$

12. Application of Phase Rule

For a binary alloy:

$$C=2$$

Using:

$$F=C-P+1$$

One phase region

$$P=1$$

$$F=2-1+1=2$$

Therefore:

$$F=2$$

Two variables can be changed independently.

Two phase region

$$P=2$$

$$F=2-2+1=1$$

Therefore:

$$F=1$$

Only one independent variable can be changed.

Three phases

$$P=3$$

$$F=2-3+1=0$$

Therefore:

$$F=0$$

The system is **invariant**.

13. Unary Phase Diagram

A **unary phase diagram** represents a system containing **only one component**.

Example:

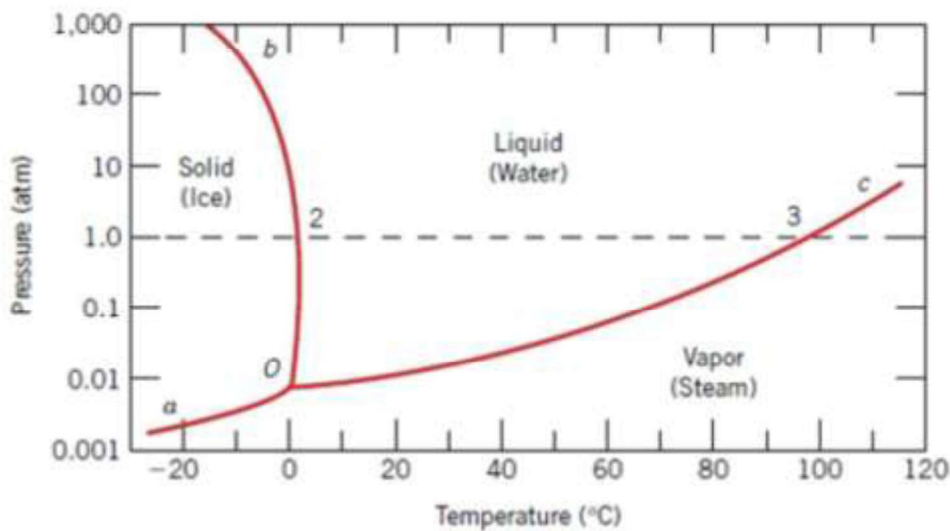
Water system

It shows the relationship between:

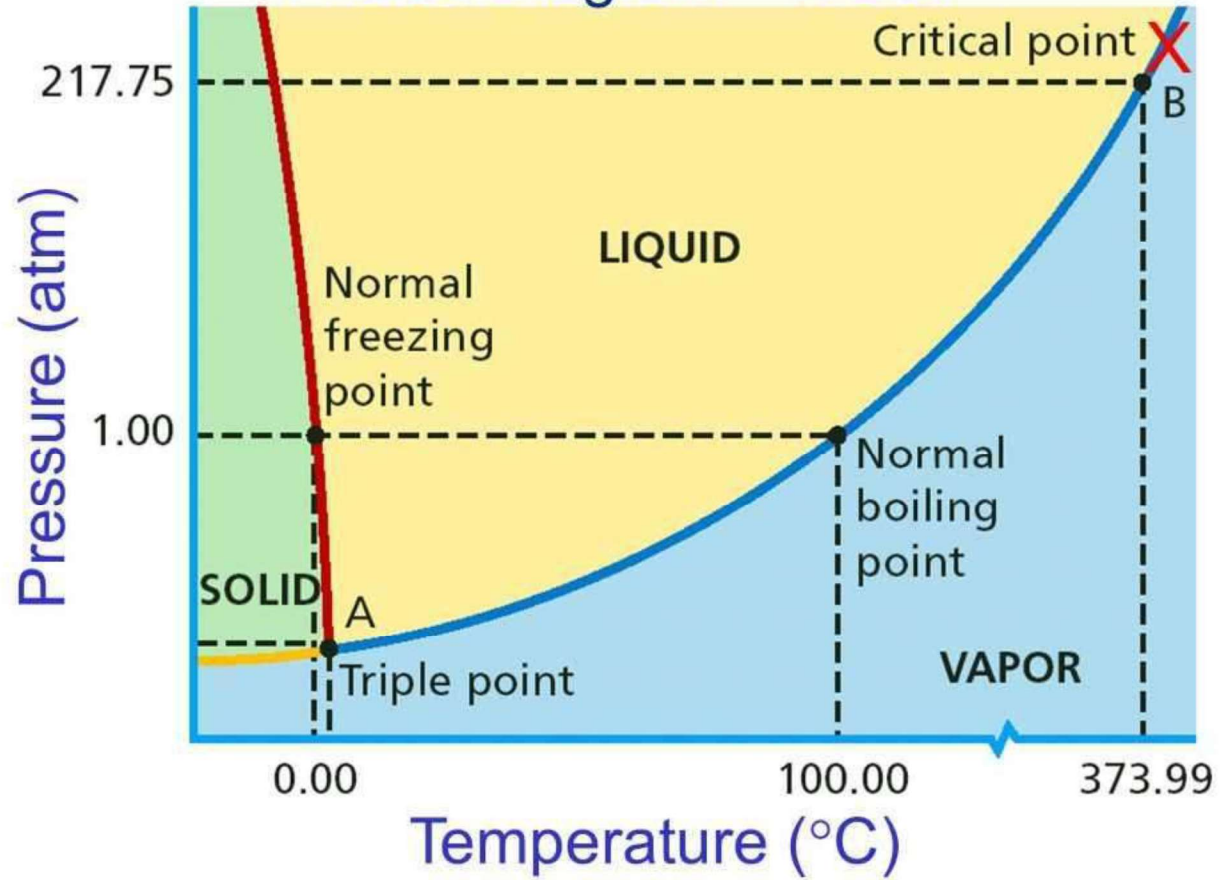
- Temperature
- Pressure
- Phases

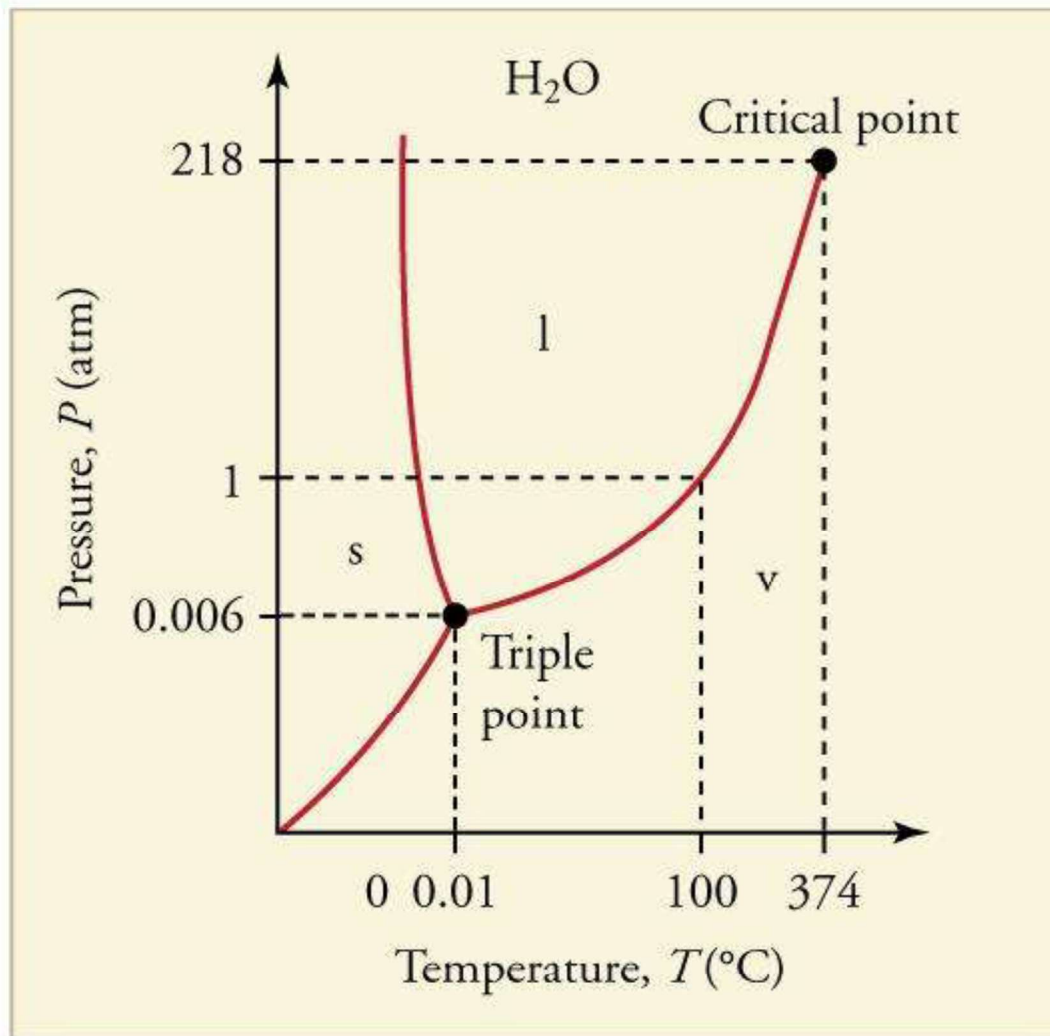
The important phases of water are:

- Solid
- Liquid
- Vapour



Phase Diagram - Water





Important point: Triple Point

At the **triple point**, three phases coexist in equilibrium:

Solid + Liquid + Vapour

For a one-component system:

$$C=1, \quad P=3$$

Using the general phase rule:

$$F=1-3+2=0$$

Therefore, the triple point is **invariant**.

14. Binary Phase Diagram

A **binary phase diagram** represents a system containing **two components**.

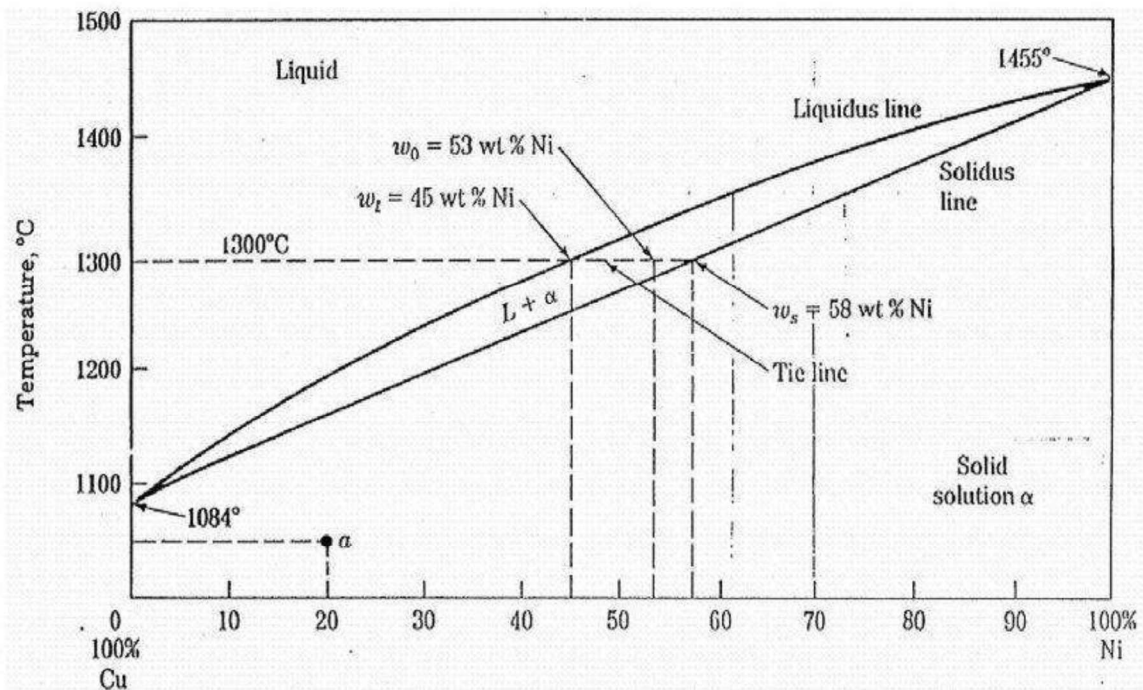
Examples:

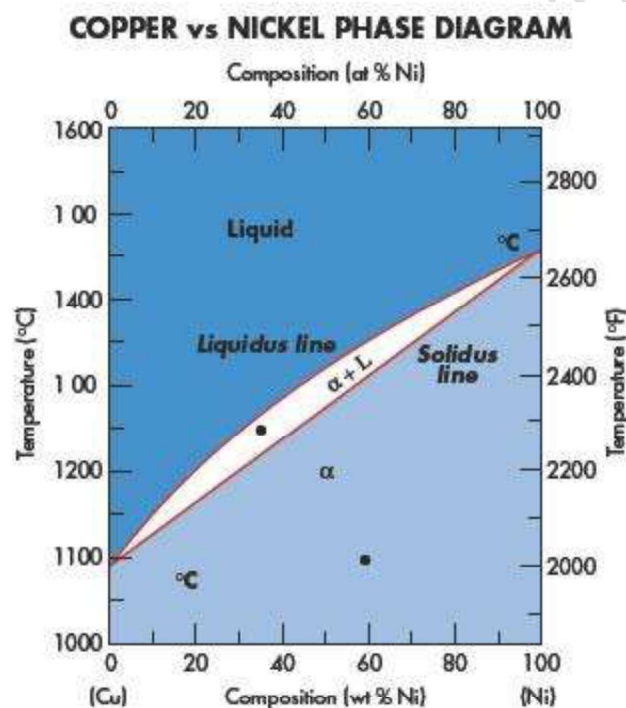
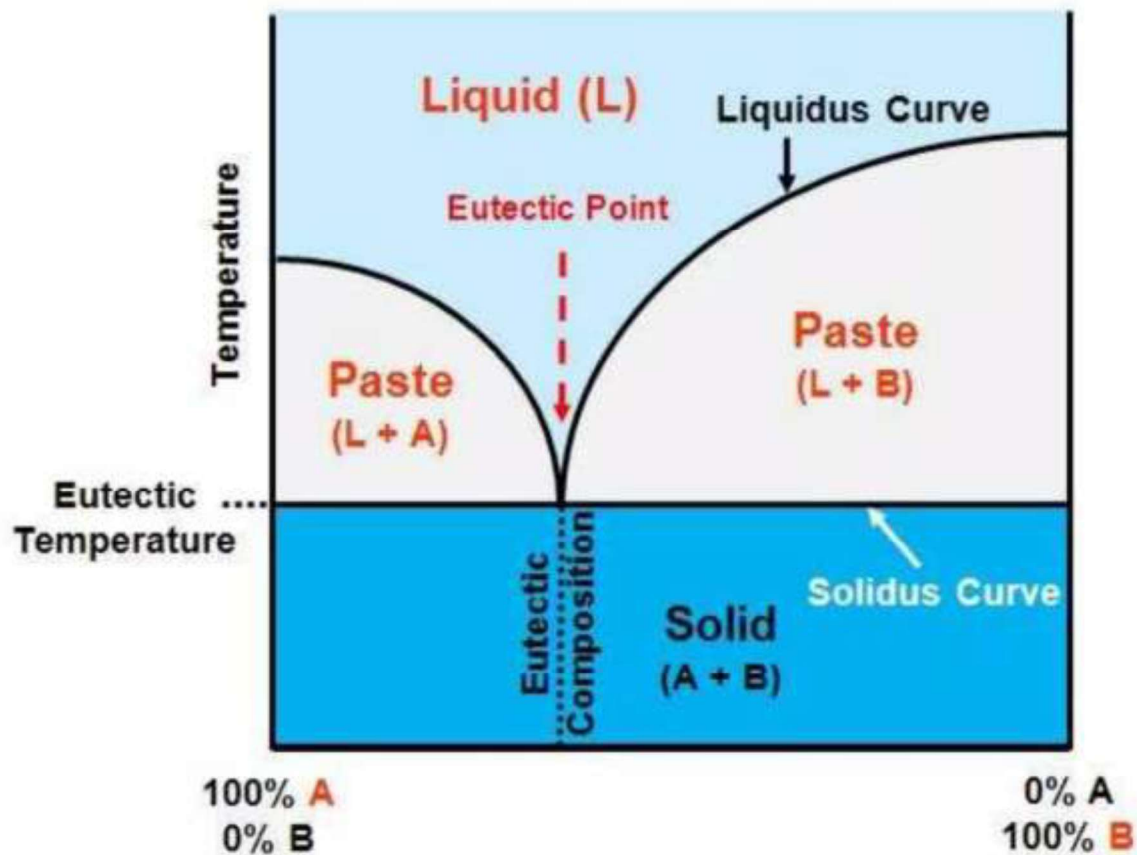
- Cu–Ni
- Pb–Sn
- Fe–C

The axes generally represent:

- **Temperature** on vertical axis
- **Composition** on horizontal axis

Copper Nickel Phase Diagram





5

Information obtained from binary phase diagrams

1. Phases present

2. Composition of phases
3. Temperature of phase transformation
4. Melting and solidification temperatures
5. Solubility limits
6. Amount of each phase
7. Microstructure after cooling

15. Important Terms in Binary Phase Diagrams

Liquidus Line

The **liquidus line** separates the completely liquid region from the liquid + solid region.

Above the liquidus:

Liquid

Solidus Line

The **solidus line** separates the completely solid region from the liquid + solid region.

Below the solidus:

Solid

Eutectic Point

At the eutectic point:

$L \rightarrow \alpha + \beta$

A liquid transforms into two solid phases at a fixed temperature and composition.

16. Lever Rule

The **lever rule** is used to determine the relative amounts of two phases present in a two-phase region of a binary phase diagram.

For phases $\alpha + \beta$:

$$W_{\alpha} = (C_{\beta} - C_0) / (C_{\beta} - C_{\alpha})$$

and

$$W_{\beta} = (C_{\beta} - C_{\alpha}) / (C_0 - C_{\alpha})$$

where:

- C_0 = Overall alloy composition
- C_{α} = Composition of α phase
- C_{β} = Composition of β phase

Important

$$W_{\alpha} + W_{\beta} = 1$$

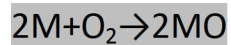
17. Ellingham Diagram

The **Ellingham diagram** is one of the most important tools in extractive metallurgy.

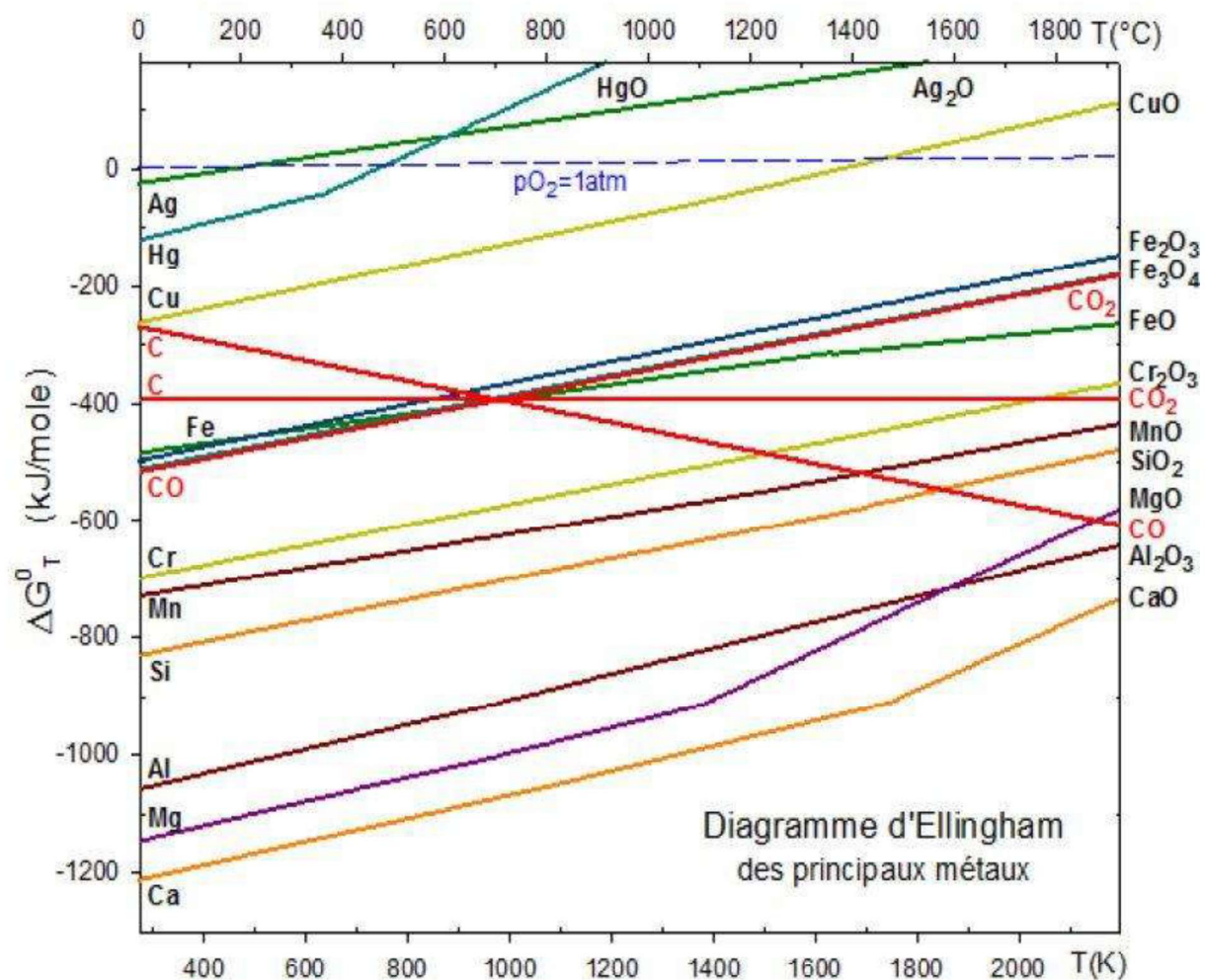
Definition

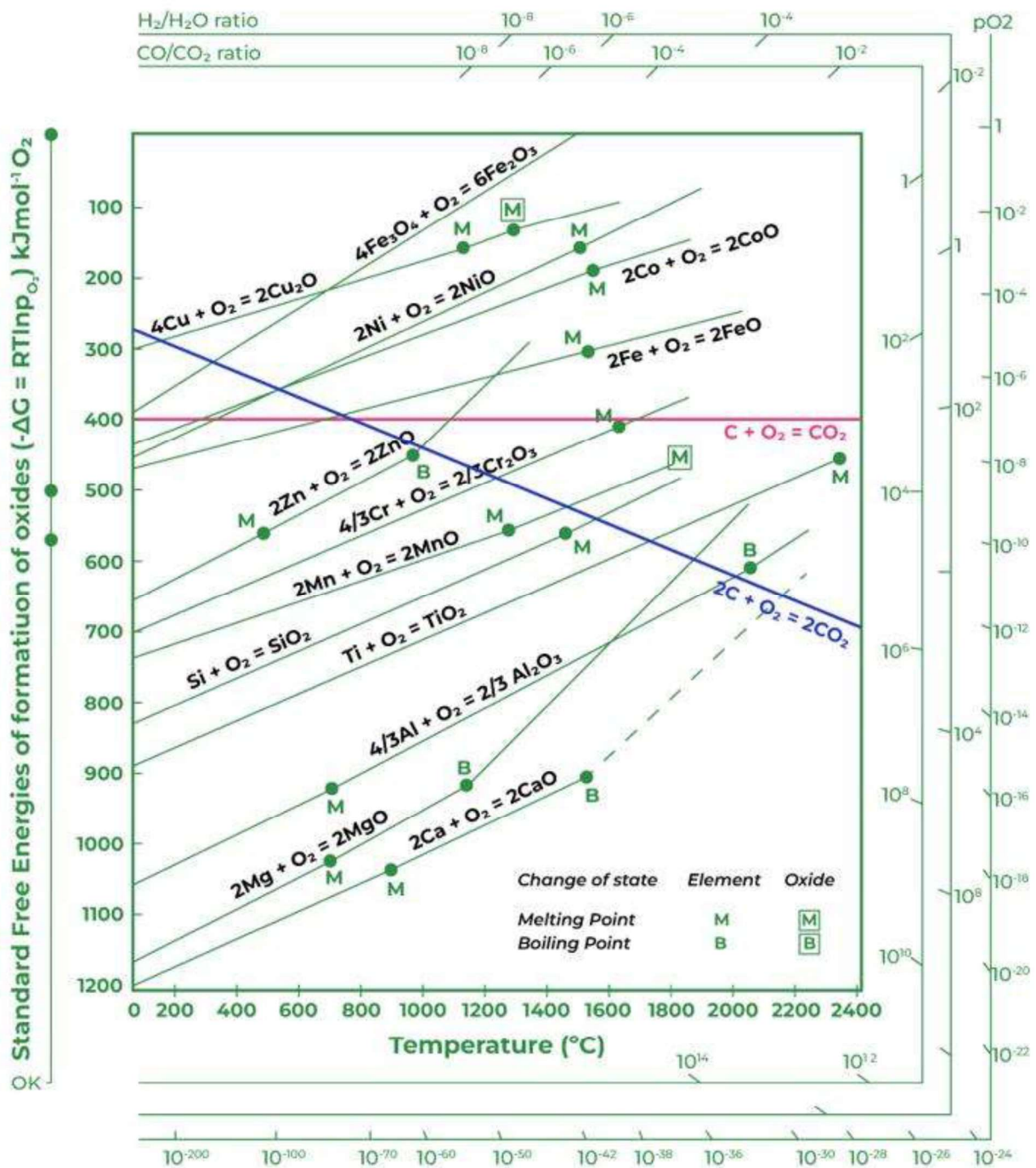
An Ellingham diagram is a graphical representation of the standard Gibbs free energy change (ΔG°) for oxidation reactions as a function of temperature.

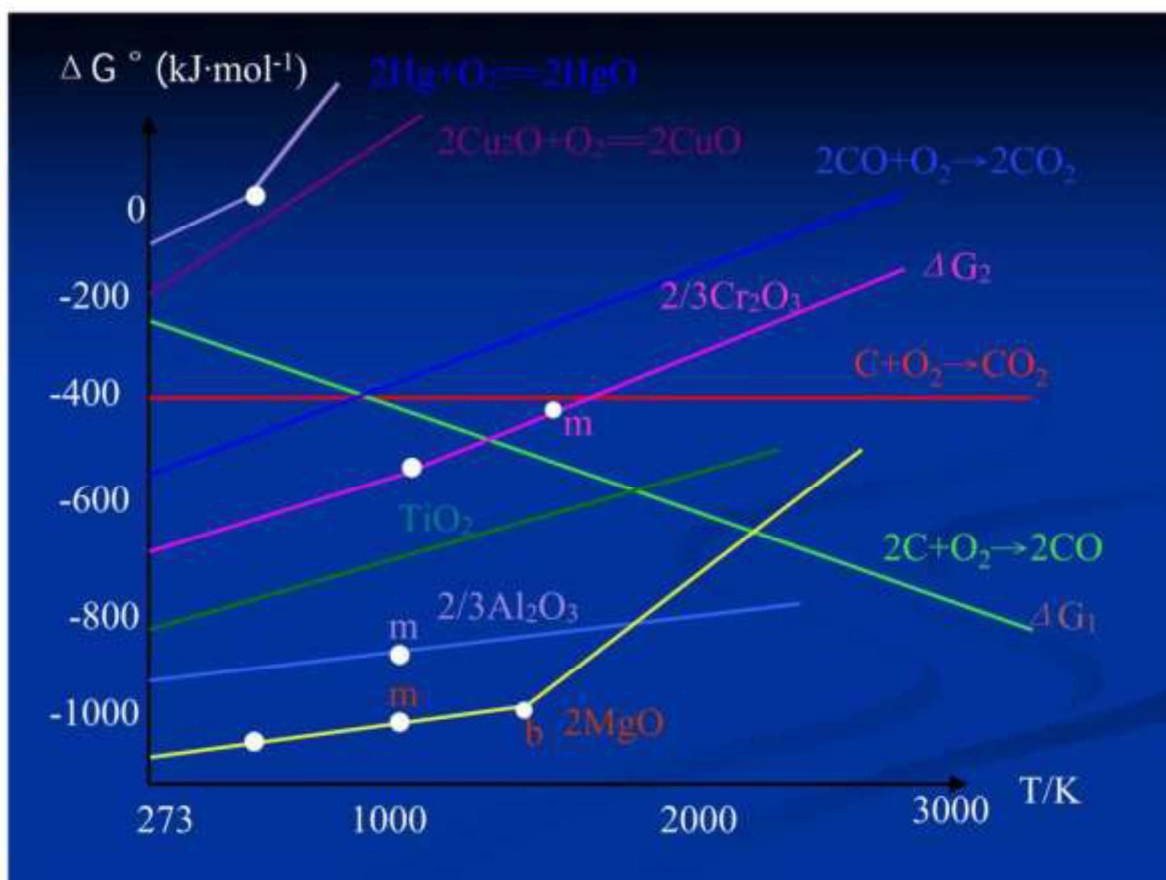
For a metal oxidation reaction:



the Gibbs free energy change is plotted against temperature.

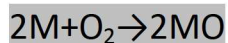






18. Basic Concept of Ellingham Diagram

For an oxidation reaction:



we can write:

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

Since:

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

the graph of ΔG° against temperature is approximately a straight line.

Slope

$$\text{Slope} = -\Delta S^\circ$$

Intercept

$$\text{Intercept} = \Delta H^\circ$$

19. Interpretation of Ellingham Diagram

The most important rule is:

Lower line $\Rightarrow$ More stable oxide

If the oxidation reaction has a more negative ΔG° , it is more thermodynamically favourable.

Therefore:

- Lower line $\rightarrow$ greater oxide stability
- Higher line $\rightarrow$ lower oxide stability

20. Applications of Ellingham Diagram

Ellingham diagrams are widely used in metallurgy.

1. Selection of reducing agent

They help determine whether a reducing agent such as:

- Carbon
- Carbon monoxide
- Hydrogen
- Aluminium
- Silicon

can reduce a particular metal oxide.

2. Determine reduction temperature

They help estimate the temperature at which reduction becomes thermodynamically possible.

3. Compare oxide stability

The relative stability of different metal oxides can be compared.

4. Extraction of metals

They are used in designing and understanding metallurgical extraction processes.

5. Selection of reducing conditions

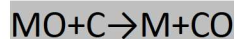
They help select suitable temperature and atmosphere for reduction.

21. Reduction of Metal Oxides Using Carbon

Suppose we want to reduce:



using carbon:



The reaction is thermodynamically possible when the overall Gibbs free energy change becomes negative:

$$\Delta G^\circ < 0$$

The Ellingham diagram helps determine the temperature range where this condition can be achieved.

Important idea

A reducing agent can reduce a metal oxide if the oxidation of the reducing agent is **more thermodynamically favourable** than the oxidation of the metal.

22. Oxide Stability

Oxide stability refers to the tendency of a metal oxide to remain in its oxide form rather than being reduced to the metal.

If:

$$\Delta G^\circ$$

for oxide formation is highly negative, the oxide is highly stable.

Example

Aluminium oxide:



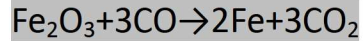
is very stable because its formation has a highly negative Gibbs free energy.

Therefore, aluminium cannot generally be extracted from its oxide by simple carbon reduction. **Electrolysis** is used industrially.

23. Reduction Reactions

Reduction is the removal of oxygen from a metal oxide or, more generally, a decrease in oxidation state.

Example

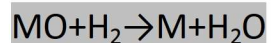


Here, iron oxide is reduced to iron.

Common reducing agents

- Carbon
- Carbon monoxide
- Hydrogen
- Aluminium
- Silicon

Example using hydrogen



24. Oxidation and Reduction

Oxidation

Oxidation generally involves:

Addition of oxygen

or

Loss of electrons

Reduction

Reduction generally involves:

Removal of oxygen

or

Gain of electrons

Easy memory trick

OIL RIG

OIL = Oxidation Is Loss of electrons

RIG = Reduction Is Gain of electrons

25. Predominance Area Diagram

A **predominance area diagram** shows which phase or compound is thermodynamically stable under different conditions of **temperature, gas composition or partial pressure**.

In metallurgical applications, these diagrams are useful for understanding which oxide, sulfide or metal is stable under a particular atmosphere.

For example, depending on oxygen partial pressure, a metal system may have regions where:

M

is stable, followed by:

MO

and possibly:

M₃O₄

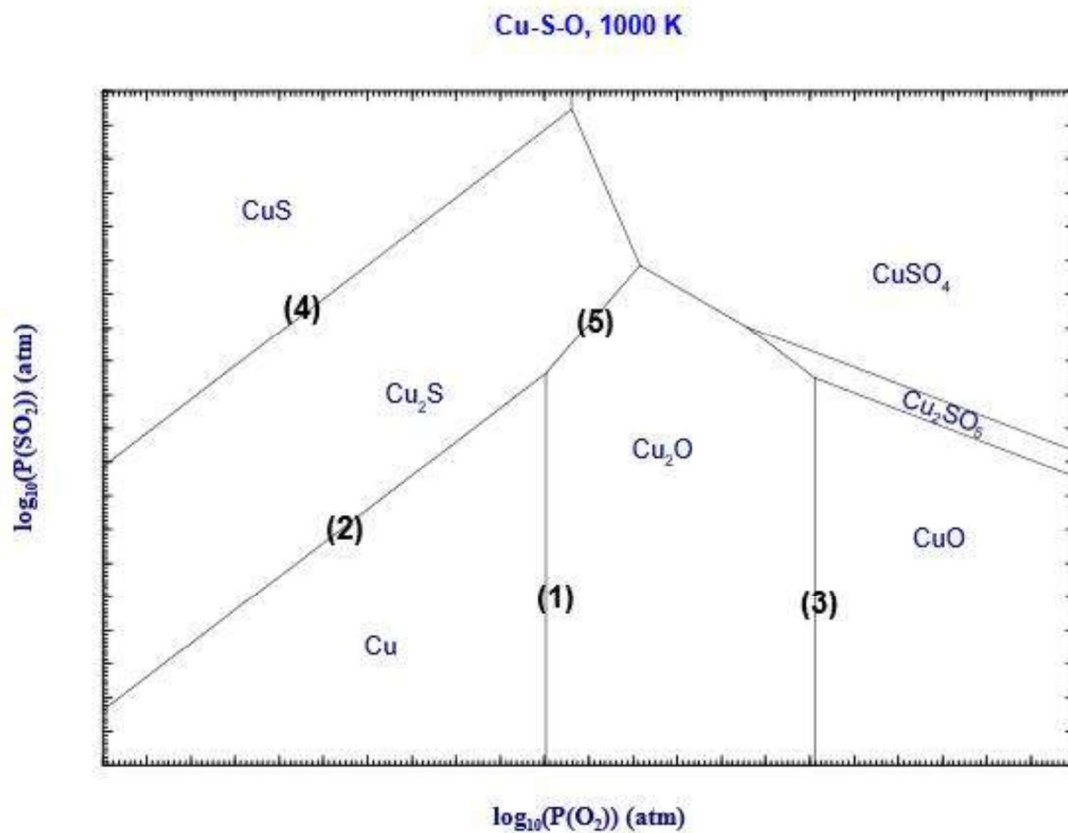
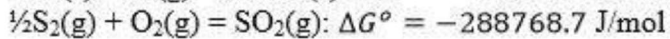
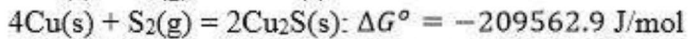
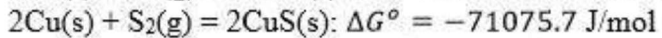
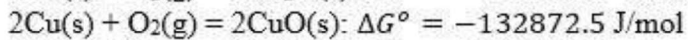
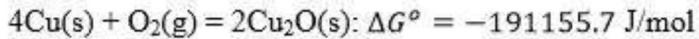
or

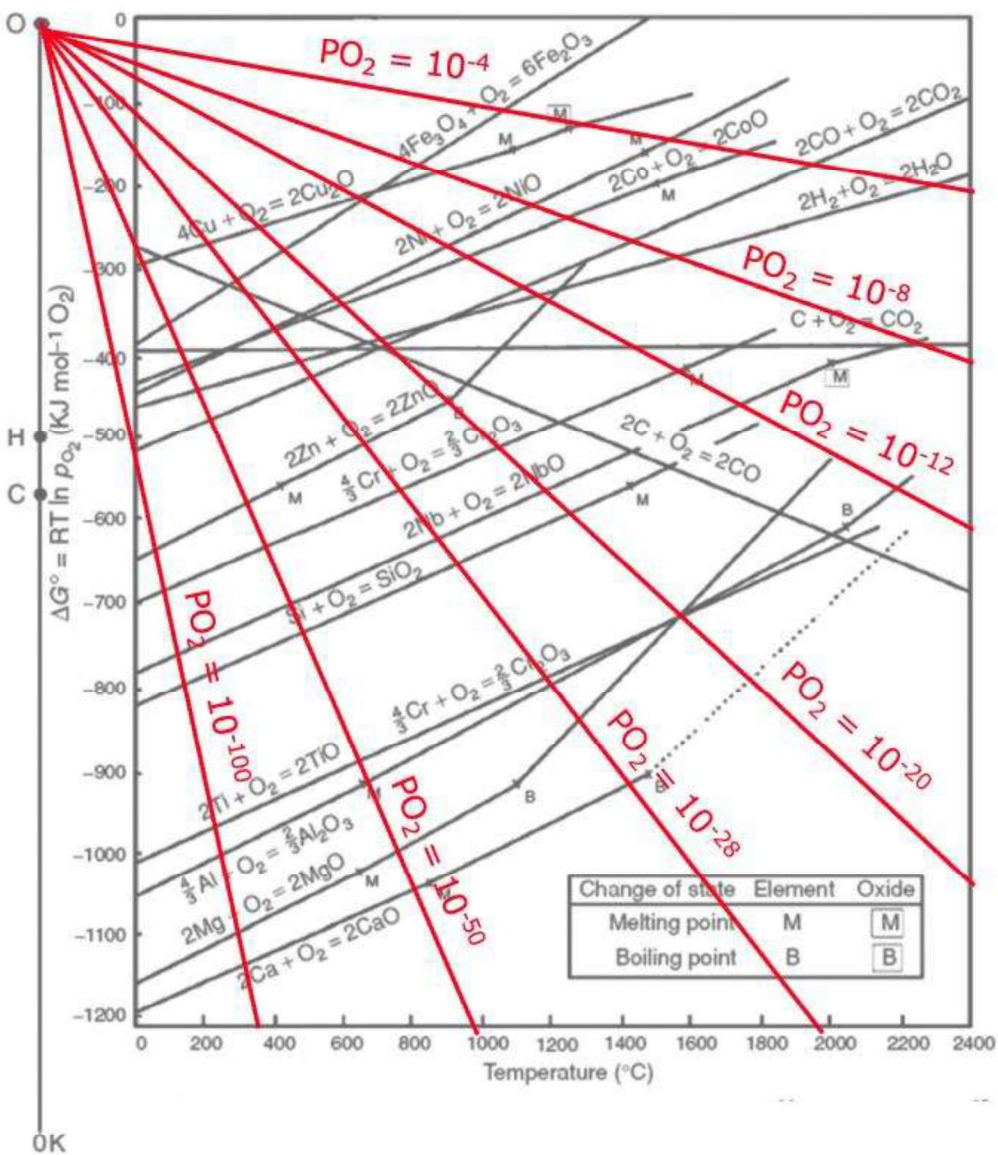
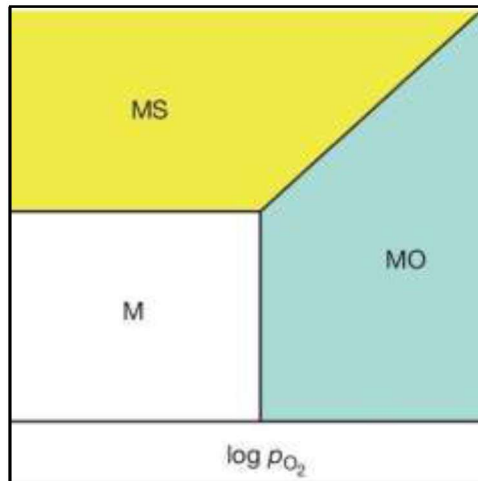
M₂O₃

as the oxygen potential increases.

2. (30) The following diagram is so-called “predominance diagram” of Cu at 1000 K depending on O_2 and SO_2 partial pressure. This diagram tells what is the most stable Cu species (metal, oxide or sulfide) at given gas partial pressure condition.

Based on the following Gibbs energy of reaction values at 1000 K, please find the mathematical functions (variables are $\log P(O_2)$ and/or $\log P(SO_2)$) for the phase boundaries of (1) to (5). Each boundary has its own function.





26. Oxygen Potential

Oxygen potential indicates the tendency of an environment to oxidize a material.

A high oxygen potential means:

Strongly oxidizing atmosphere

A low oxygen potential means:

Reducing atmosphere

Effect of oxygen potential

Low oxygen potential



Metal



Lower oxide



Higher oxide



High oxygen potential

Thus, predominance diagrams help determine which phase is stable at a given oxygen potential.

27. Metallurgical Importance of Predominance Area Diagrams

They are useful for:

1. **Roasting processes**
2. **Reduction of metal oxides**
3. Controlling furnace atmosphere
4. Studying oxidation of metals
5. Predicting stable oxide phases
6. Designing extraction processes
7. Controlling oxidation and reduction during heat treatment
8. Studying corrosion behaviour

28. Relationship Between Ellingham and Predominance Diagrams

Both are important thermodynamic tools, but they provide different information.

Ellingham Diagram

Plots ΔG° vs temperature

Mainly used for oxide stability

Useful for selecting reducing agents

Very important in extraction metallurgy

Temperature is the main variable

Predominance Area Diagram

Shows stable phases under different conditions

Shows phase stability regions

Useful for controlling atmosphere

Useful in oxidation/reduction and corrosion studies

Temperature and gas composition/oxygen potential may be variables

29. Metallurgical Applications of Phase Equilibria

Phase equilibrium concepts are widely used in metallurgy.

1. Alloy design

Phase diagrams help select compositions to obtain desired properties.

2. Casting

They help determine:

- Solidification temperature
- Solidification range
- Phases formed
- Microstructure

3. Heat treatment

Phase diagrams help select appropriate temperatures for:

- Annealing
- Normalizing
- Hardening

4. Steel production

Fe–C phase diagram is essential for understanding:

- Ferrite
- Austenite
- Cementite
- Pearlite
- Eutectoid transformation

5. Metal extraction

Ellingham diagrams help determine:

- Suitable reducing agents
- Reduction temperature
- Oxide stability

6. Corrosion

Predominance diagrams help determine stable oxide regions and oxidation behaviour.

UNIT–V

THERMODYNAMICS IN METALLURGICAL PROCESSES

1. Application of Thermodynamics in Metallurgy

Metallurgical processes involve many chemical reactions, such as:

- Reduction of metal oxides
- Oxidation of impurities
- Formation of slags
- Roasting of ores
- Smelting
- Refining of molten metals

Thermodynamics helps us answer:

1. **Is the reaction possible?**
2. **In which direction will the reaction proceed?**
3. **What temperature is required?**
4. **Which reducing agent should be used?**
5. **How stable is a metal oxide?**
6. **What is the equilibrium composition?**

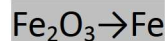
2. Thermodynamics of Extraction of Metals

Most metals are found in nature in the form of **compounds**, such as:

- Oxides
- Sulphides
- Carbonates
- Silicates

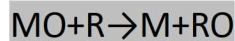
The purpose of extraction metallurgy is to convert these compounds into **metals**.

For example:



This requires a suitable **reduction reaction**.

General reduction reaction



where:

- MO = Metal oxide
- M = Metal
- R = Reducing agent

A thermodynamic analysis determines whether this reaction is feasible.

3. Gibbs Free Energy in Metal Extraction

The most important thermodynamic equation used is:

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

For a reaction:

If

$$\Delta G < 0$$

the reaction is **thermodynamically spontaneous** in the forward direction.

If

$$\Delta G > 0$$

the forward reaction is **not spontaneous** under the specified conditions.

If

$$\Delta G = 0$$

the system is at **equilibrium**.

Important

A negative ΔG indicates **thermodynamic feasibility**, but it does not necessarily mean that the reaction will be fast. The reaction rate depends on **kinetics**.

4. Ellingham Diagram and Metal Extraction

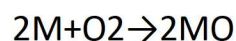
The Ellingham diagram introduced in Unit III is particularly important in extraction metallurgy.

It plots:

$$\Delta G^\circ \text{ versus Temperature}$$

for oxidation reactions.

For example:



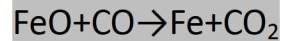
Main rule

$$\text{Lower line} = \text{more stable oxide}$$

A reducing agent can reduce a metal oxide when the oxidation of the reducing agent is more favourable thermodynamically.

Example

Reduction of iron oxide by carbon monoxide:



The feasibility depends on temperature and the thermodynamic conditions.

5. Ironmaking

What is Ironmaking?

Ironmaking is the production of molten iron (hot metal) from iron ore.

The main raw materials are:

- Iron ore
- Coke
- Limestone
- Hot blast/air

A major industrial route is the **blast furnace process**.

6. Thermodynamics of Blast Furnace Ironmaking

Iron ores commonly contain iron in oxidized forms such as:

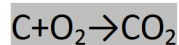


The overall objective is:

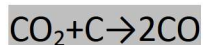


Important reduction reactions

First, carbon burns:

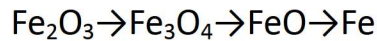


Then:

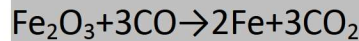


Carbon monoxide acts as an important reducing agent.

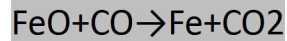
Reduction can occur in stages:



For example:



and:

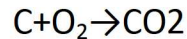


7. Role of Coke in Ironmaking

Coke performs several important functions:

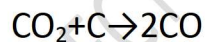
1. Fuel

It provides heat through combustion:



2. Reducing-agent generation

It helps generate CO:

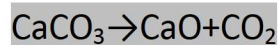


3. Structural support

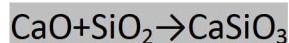
Coke provides permeability and supports the burden inside the blast furnace.

8. Role of Limestone

Limestone is mainly used as a **flux**.



The CaO then reacts with acidic gangue such as silica:



This produces **slag**.

Purpose of slag

Slag:

- Collects impurities
- Separates from molten iron

- Protects molten metal from oxidation
- Helps control furnace chemistry

9. Steelmaking Thermodynamics

What is Steelmaking?

Steelmaking is the process of converting **hot metal or other iron-bearing materials into steel** by controlling carbon and removing unwanted impurities.

Important impurities include:

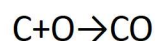
- Carbon
- Silicon
- Manganese
- Phosphorus
- Sulphur

10. Oxidation Reactions in Steelmaking

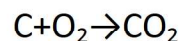
In steelmaking, oxygen is supplied to oxidize impurities.

For example:

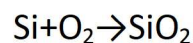
Carbon oxidation



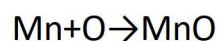
or



Silicon oxidation



Manganese oxidation



The oxides formed enter the **slag**.

11. Role of Slag in Steelmaking

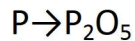
Slag is a molten mixture of oxides.

It plays an important role in:

- Removing impurities
- Protecting molten steel
- Controlling oxidation potential
- Removing phosphorus
- Assisting sulphur removal
- Controlling furnace chemistry

Example of phosphorus removal

A simplified representation is:



followed by its incorporation into the basic slag.

A **basic slag rich in CaO** is generally favourable for phosphorus removal under suitable oxidizing conditions.

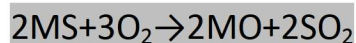
12. Roasting

Definition

Roasting is the heating of an ore in the presence of excess or controlled air/oxygen, generally below its melting point.

It is mainly used for **sulphide ores**.

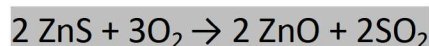
General reaction



where MS is a metal sulphide.

Example

Zinc sulphide:

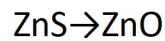


13. Purpose of Roasting

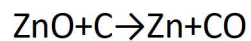
Roasting is carried out to:

1. Convert sulphide into oxide.
2. Remove sulphur as SO_2 .
3. Prepare the ore for further reduction.
4. Produce a suitable feed for subsequent extraction steps.

Example



Then the oxide can be reduced:

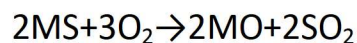


14. Thermodynamics of Roasting

Thermodynamics helps determine:

- Whether oxidation is feasible.
- Suitable temperature.
- Oxygen potential required.
- Stability of the oxide.
- Equilibrium composition of gases.

For:



we consider:

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

If:

$$\Delta G^\circ < 0$$

the reaction is thermodynamically favourable under standard conditions.

15. Smelting

Definition

Smelting is a high-temperature process in which a metal-bearing material is heated with a suitable reducing agent and flux to produce molten metal and slag.

Main products

Molten metal + Slag

Example

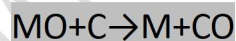
Ironmaking in a blast furnace is a major example of a smelting process.

16. Purpose of Smelting

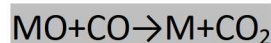
Smelting helps to:

- Reduce metal compounds.
- Separate metal from gangue.
- Form a molten metal phase.
- Transfer impurities into slag.

General reaction



or:



17. Thermodynamics of Smelting

Important factors include:

Temperature

Temperature affects:

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

and therefore affects reaction feasibility.

Oxygen potential

Controls whether the atmosphere is:

- Oxidizing
- Neutral
- Reducing

Composition

The activities of components affect equilibrium.

Slag composition

Controls the distribution of impurities between metal and slag.

18. Refining

Definition

Refining is the process of removing unwanted impurities from a crude or impure metal to obtain metal of higher purity.

Examples:

- Refining of pig iron to steel
- Copper refining
- Zinc refining
- Aluminium refining

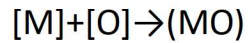
19. Thermodynamics of Refining

Refining is based on differences in the thermodynamic behaviour of:

- Metal
- Impurities
- Oxides
- Slag
- Gas phase

For example, an impurity may preferentially oxidize and enter the slag.

General reaction



where:

- $[M]$ represents a species dissolved in metal
- (MO) represents a species in slag

Thermodynamics determines the equilibrium distribution of the impurity.

20. Activity

Activity is an important concept in metallurgical thermodynamics.

Definition

Activity is the effective concentration of a component in a solution, taking into account the interactions between its particles.

It is represented by:

$$a$$

For a component i:

$$a_i = \gamma_i X_i$$

where:

- a_i = Activity
- γ_i = Activity coefficient
- X_i = Mole fraction

21. Activity in an Ideal Solution

For an ideal solution:

$$\gamma_i = 1$$

Therefore:

$$a_i = X_i$$

So, in an ideal solution, activity is equal to mole fraction.

22. Activity in a Non-Ideal Solution

For a non-ideal solution:

$$\gamma_i \neq 1$$

Therefore:

$$a_i \neq X_i$$

The activity coefficient represents the deviation from ideal behaviour.

If:

$$\gamma_i > 1$$

the component shows positive deviation from ideal behaviour.

If:

$$\gamma_i < 1$$

the component shows negative deviation from ideal behaviour.

23. Importance of Activity in Metallurgy

Activity is important because real metallurgical systems are generally **not ideal**.

It is used to understand:

- Metal–slag reactions
- Steelmaking
- Alloy behaviour
- Reduction reactions
- Oxidation reactions
- Equilibrium calculations
- Distribution of impurities

For example, the thermodynamic equation for a reaction is written using activities:

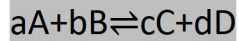
$$\Delta G = \Delta G^\circ + RT \ln Q$$

where Q is the reaction quotient expressed in terms of activities.

24. Equilibrium Constant

The **equilibrium constant K** indicates the relative amounts of products and reactants when a reaction reaches equilibrium.

For a general reaction:



the equilibrium constant is:

$$K = \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

where a represents activity.

25. Relation Between Gibbs Free Energy and Equilibrium Constant

The most important equation is:

$$\Delta G^\circ = -RT \ln K$$

At equilibrium:

$$\Delta G = 0$$

and:

$$Q = K$$

Meaning of K

If:

$$K \gg 1$$

Products are strongly favoured.

If:

$$K \ll 1$$

Reactants are strongly favoured.

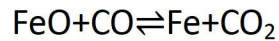
If:

$$K \approx 1$$

Neither side is overwhelmingly favoured.

26. Example of Equilibrium Constant

Consider:



The equilibrium constant is:

$$K = a_{\text{Fe}} P_{\text{CO}_2} / a_{\text{FeO}} P_{\text{CO}}$$

For pure solid Fe and pure solid FeO, their activities are approximately:

$$a_{\text{Fe}} = 1$$

$$a_{\text{FeO}} = 1$$

Therefore:

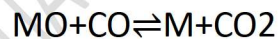
$$K = P_{\text{CO}_2} / P_{\text{CO}}$$

under the appropriate standard-state assumptions.

This type of relationship is very useful in **ironmaking**.

27. Equilibrium and Reduction

Consider:



The reaction quotient is:

$$Q = a_{\text{M}} P_{\text{CO}_2} / a_{\text{MO}} P_{\text{CO}}$$

At equilibrium:

$$Q = K$$

If:

$$Q < K$$

the reaction proceeds in the **forward direction**.

If:

$$Q > K$$

$$Q = K$$

the system is at **equilibrium**.

28. Le Chatelier's Principle

Le Chatelier's principle is useful for understanding how equilibrium responds to changes in conditions.

When a system at equilibrium is disturbed, it tends to shift in a direction that opposes the disturbance.

Examples

Changing:

- Temperature
- Pressure
- Gas composition
- Concentration/activity

can shift the equilibrium.

This is particularly important in:

- Blast furnace reactions
- Gas reduction of oxides
- Roasting
- Refining