UNIT 5: PHASE EQUILIBRIUM AND CORROSION

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1. Phase Equilibrium

Phase equilibrium refers to a **state where multiple phases (solid, liquid, gas) coexist in thermodynamic balance** without any net phase transformation over time.

1.1 Phase Diagram of a Single Component System (Water System)

- A **phase diagram** represents different phases of a substance as a function of **temperature and pressure**.
- The **water system** is a **one-component (unary) system** consisting of **ice (solid), water (liquid), and steam (gas)**.

Key Features of the Water Phase Diagram

1. **Triple Point (T_3P)**: The unique condition where solid, liquid, and gas phases coexist in equilibrium. For water: T3P=0.01°C,P=4.58 mmHg(611Pa)T_3P = 0.01°C, P = 4.58 \text{ mmHg} (611 Pa)T3P=0.01°C,P=4.58 mmHg(611Pa)
2. **Critical Point**: The temperature and pressure beyond which liquid and gas are indistinguishable (supercritical fluid). Tc=374°C,Pc=218 atmT_c = 374°C, P_c = 218 \text{ atm}Tc=374°C,Pc=218 atm
3. **Sublimation Curve**: Separates solid and vapor phases.
4. **Vaporization Curve**: Separates liquid and vapor phases (boiling point changes with pressure).
5. **Fusion Curve**: Separates solid and liquid phases (melting/freezing point).

Diagram Representation:
The **fusion curve** for water slopes **negatively** due to the anomalous expansion of water (ice is less dense than liquid water).

1.2 Phase Diagram of a Binary Eutectic System (Copper-Silver System, CuAg)

A **binary phase diagram** shows phase equilibrium in a system with **two components** (Cu and Ag).

Key Features of Cu-Ag Phase Diagram

- **Eutectic Point**: The lowest temperature at which a **liquid phase** directly converts into **two solid phases**.
- **Eutectic Composition**: 28.1% Cu and 71.9% AgTE=779°C28.1\% \text{ Cu and 71.9\% Ag} \quad T_E = 779°C28.1% Cu and 71.9% AgTE=779°C •
  Regions in the Cu-Ag Diagram:
  1. **Liquid Region**: At high temperatures, Cu and Ag exist as a completely miscible liquid.
  2. **Solid Solution Regions**: Below the eutectic temperature, **α-phase (Ag-rich solid)** and **β-phase (Cu-rich solid)** exist.
  3. **Eutectic Mixture**: At the eutectic composition, liquid transforms into a fine mixture of α and β phases simultaneously.

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2. Corrosion

Corrosion is the **gradual deterioration of metals** due to chemical or electrochemical reactions with their environment.

2.1 Types of Corrosion

(i) Dry (Chemical) Corrosion • Occurs due to **direct chemical reactions** with **oxygen, halogens, and acidic gases**.

- Example: Oxidation of metals at high temperatures. 4Fe+3O2→2Fe2O34Fe + 3O_2 \rightarrow 2Fe_2O_34Fe+3O2→2Fe2O3

(ii) Wet (Electrochemical) Corrosion

- Involves **electrochemical reactions** in the presence of **moisture (electrolyte)**.
- **Types of Wet Corrosion:**
  1. **Galvanic Corrosion**: Occurs when two dissimilar metals are in contact with an electrolyte (e.g., Fe and Cu in seawater).
  2. **Pitting Corrosion**: Localized attack leading to deep pits in metals (e.g., stainless steel in chloride solutions).
  3. **Stress Corrosion Cracking (SCC)**: Caused by combined stress and corrosive environment (e.g., brass under ammonia exposure).
  4. **Intergranular Corrosion**: Occurs along grain boundaries, reducing mechanical strength.

2.2 Mechanism of Corrosion

(i) Direct Oxidation Mechanism

- Metal reacts **directly** with oxygen or other reactive gases. 2Mg+O2→2MgO2Mg + O_2 \rightarrow 2MgO2Mg+O2→2MgO

(ii) Electrochemical (Wet) Corrosion Mechanism

- Metal acts as an **anode** (oxidation occurs) and another surface acts as a **cathode** (reduction occurs).

Example: Rusting of Iron

- **Anodic Reaction (Oxidation):** Fe→Fe2++2e−Fe \rightarrow Fe^{2+} + 2e^Fe→Fe2++2e−
- **Cathodic Reaction (Reduction of Oxygen in Water):** O2+4H++4e−→2H2OO_2 + 4H^+ + 4e^- \rightarrow 2H_2OO2+4H++4e−→2H2O
- **Overall Reaction:** 4Fe+3O2+6H2O→4Fe(OH)34Fe + 3O_2 + 6H_2O \rightarrow 4Fe(OH)_34Fe+3O2+6H2O→4Fe(OH)3
- **Further oxidation leads to hydrated ferric oxide (rust):** 4Fe(OH)3→2Fe2O3.xH2O(Rust)4Fe(OH)_3 \rightarrow 2Fe_2O_3 \cdot xH_2O \quad (\text{Rust})4Fe(OH)3→2Fe2O3.xH2O(Rust)

2.3 Prevention of Corrosion

(i) Barrier Protection

- **Painting, coating, and galvanization** (zinc coating on iron).

(ii) Cathodic Protection

- **Sacrificial Anode**: A more reactive metal (e.g., Zn or Mg) is attached to iron structures to corrode instead of iron.

(iii) Corrosion Inhibitors

- Chemicals like **chromates and phosphates** slow down corrosion reactions.

(iv) Alloying

- **Stainless steel (Fe-Cr-Ni alloy)** resists corrosion better than pure iron.

Outcomes

Understanding phase diagrams and equilibrium in single and binary component systems.

Learning about different types of corrosion and their electrochemical mechanisms.
Studying effective corrosion prevention techniques used in industries.