UNIT -2

1. Limitations of First Law of Thermodynamics

Definition

The First Law states that **energy can neither be created nor destroyed**.

Limitations

- Does not indicate the direction of heat flow.
- Cannot determine whether a process is possible.
- Does not explain irreversibility.
- Cannot determine maximum efficiency.
- Does not consider energy quality.

Example
A hot cup of tea cools naturally in a room, but a cold cup never becomes hot by itself.

2. Thermal Reservoir

Definition

A thermal reservoir is a body having very large heat capacity, so its temperature remains constant while exchanging heat.

Types

Heat Source
Supplies heat.

Examples

- Sun
- Boiler
- Furnace

Heat Sink
Absorbs heat.

Examples

- Atmosphere
- River
- Ocean

3. Heat Engine

Definition

A heat engine converts heat energy into mechanical work.

Components

- Heat Source (High Temperature)
- Working Fluid
- Heat Sink (Low Temperature)

Working

Heat Input = Q_1

↓

Heat Engine

↓

Work Output = W

↓

Heat Rejected = Q_2

Efficiency

$$\eta=\frac{W}{Q_1}=\frac{Q_1-Q_2}{Q_1}$$

4. Refrigerator

Definition

A refrigerator removes heat from a low-temperature region and rejects it to a high-temperature region.

COP

COPR=QLWCOP_R=\frac{Q_L}{W}COPR=WQL

Higher COP means better refrigerator.

Examples

- Domestic refrigerator
- Air conditioner

5. Heat Pump

Definition

A heat pump transfers heat from a low-temperature source to a high-temperature space.

Used for heating rooms.

COP

COPHP=QHWCOP_{HP}=\frac{Q_H}{W}COPHP=WQH

Relation

COPHP=COPR+1COP_{HP}=COP_R+1COPHP=COPR+1

6. Performance Parameters

Heat Engine

Efficiency

$$\eta=\frac{W}{Q_H}$$

Refrigerator

Coefficient of Performance

$$COP_R=\frac{Q_L}{W}$$

Heat Pump

$$COP_{HP}=\frac{Q_H}{W}$$

7. Second Law of Thermodynamics

Definition

The Second Law states that **heat cannot be completely converted into work without any losses.**

It explains

- Direction of heat transfer
- Efficiency limits
- Entropy generation

8. Kelvin–Planck Statement

"It is impossible to construct a cyclic heat engine that converts all the supplied heat into work."

Impossible:

100% Heat → 100% Work

Some heat must always be rejected.

9. Clausius Statement

"Heat cannot flow from a colder body to a hotter body without external work."

Example

Refrigerator requires electricity.

10. Equivalence of Kelvin–Planck and Clausius Statements

Violation of one automatically violates the other.

Therefore,

Kelvin–Planck ⇔ Clausius

11. Corollaries

- No heat engine has 100% efficiency.
- Heat always flows naturally from hot to cold.
- Refrigerator requires work.

12. PMM-II

Perpetual Motion Machine of Second Kind

A machine producing continuous work without energy input.

Impossible.

Reason

Violates Second Law.

13. Carnot Principle

No engine operating between two temperatures can be more efficient than a Carnot engine.

14. Carnot Cycle

Four reversible processes

1. Isothermal Expansion
2. Adiabatic Expansion
3. Isothermal Compression
4. Adiabatic Compression

Efficiency

$$\eta=1-\frac{T_L}{T_H}$$

Where

TH = High temperature

TL = Low temperature

15. Thermodynamic Temperature Scale

Also called

Absolute Temperature Scale

Unit

Kelvin (K)

Relationship

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

16. Clausius Inequality

For any cyclic process

$$\oint \frac{\delta Q}{T} \le 0$$

Equal (=0)

Reversible process

Less than (<0)

Irreversible process

17. Entropy

Definition

Entropy is the measure of randomness or disorder.

Symbol

S

Unit

kJ/kg·K

Equation

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

18. Principle of Entropy Increase

For isolated system

$$\Delta S \ge 0$$

- Reversible: $\Delta S = 0$
- Irreversible: $\Delta S > 0$

19. Entropy Equation

For reversible process

$$\Delta S=\int \frac{\delta Q}{T}$$

Ideal Gas

$$\Delta S=C_p\ln\frac{T_2}{T_1}-R\ln\frac{P_2}{P_1}$$

20. Availability (Energy)

Definition

Availability is the **maximum useful work** obtainable as a system reaches equilibrium with its surroundings.

Unavailable Energy

Cannot be converted into useful work.

21. Irreversibility

Definition

Loss of useful work due to friction, heat transfer through finite temperature difference, mixing, etc.

Equation

$$I=T_0S_{gen}$$

where:

- I = Irreversibility
- T_0 = Surrounding temperature
- S_{gen} = Entropy generated

22. Thermodynamic Potentials

Internal Energy

UUU

Enthalpy

H=U+PVH=U+PVH=U+PV

Helmholtz Function

F=U−TSF=U-TSF=U−TS

Gibbs Function

G=H−TSG=H-TSG=H−TS

23. Maxwell Relations

Important equations

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

Used for deriving thermodynamic properties.

24. Third Law of Thermoynamics

Statement

The entropy of a perfect crystal at **0 K** is **zero**.

Mathematically

S=0at T=0 KS=0 \quad \text{at } T=0\text{ K}S=0at T=0 K

Applications

- Calculation of absolute entropy
- Low-temperature engineering
- Cryogenics