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Subject: Physics
Weightage: High
Title: Thermodynamics

THERMODYNAMICS

Thermodynamics

Thermodynamics is concerned with the work done by a system and the heat it exchanges with its surroundings.

When the system is taken quasistatically from an initial equilibrium state i to another final equilibrium state f , the total work done by the system is:

$$W = \int_{V_i}^{V_f} P dV$$

The work is represented by the area under the P-V curve. If $V_f > V_i$, the work done by the gas is positive. If the volume decreases, the work done by the gas is negative.

First Law of Thermodynamics

Both the total work done W and the total heat transfer Q to or from the system depend on the thermodynamic path. However, the difference $Q - W$ is the same for all paths between the given initial and final equilibrium states, and it is equal to the change in internal energy ΔU of the system.

$$\Delta U = Q - W$$

Applications of the First Law of Thermodynamics

a) Isobaric Process

A process that occurs at constant pressure.

- **Work done:** $W = P(V_f - V_i)$
- **Heat absorbed:** $Q = nC_P\Delta T$
- **Change in internal energy:** $\Delta U = nC_V\Delta T$

b) Isochoric Process

A process that occurs at constant volume.

- **Work done:** $W = 0$ (since $\Delta V = 0$)
- **Heat absorbed:** $Q = nC_V\Delta T$
- **Change in internal energy:** $\Delta U = Q = nC_V\Delta T$

c) Adiabatic Process

A process where no heat is exchanged between the system and its surroundings ($Q = 0$).

- **Work done:** $W = -\Delta U = \frac{nR(T_i - T_f)}{\gamma - 1}$

- **Relation between P, V, T:**

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

$$TV^{\gamma-1} = \text{constant}$$

$$P^{1-\gamma}T^\gamma = \text{constant}$$

Where $\gamma = C_P/C_V$ is the adiabatic index.

d) Isothermal Process

A process that occurs at constant temperature. For an ideal gas, the equation of the process is given by:

$$PV = nRT = \text{constant}$$

- **Work done:**

$$W = \int_{V_i}^{V_f} P dV = nRT \int_{V_i}^{V_f} \frac{dV}{V}$$

$$W = nRT \ln \left| \frac{V_f}{V_i} \right| = nRT \ln \left| \frac{P_i}{P_f} \right|$$

- **Change in internal energy:** For an ideal gas, $\Delta U = 0$ (since temperature is constant).
- **Heat absorbed:** $Q = W$ (from First Law).

Specific Heat Capacities of Gases

- **Molar specific heat at constant volume (C_V):** Heat required to raise the temperature of 1 mole of gas by 1 K at constant volume.
- **Molar specific heat at constant pressure (C_P):** Heat required to raise the temperature of 1 mole of gas by 1 K at constant pressure.

Important Relations:

- **Mayer's Relation:**

$$C_P - C_V = R$$

- **Ratio of specific heats (Adiabatic Index):**

$$\gamma = \frac{C_P}{C_V}$$

Carnot Cycle

An ideal reversible thermodynamic cycle consisting of four processes:

1. **Isothermal Expansion (1 → 2):** Heat Q_1 absorbed from source at T_1 .

$$W_1 = Q_1 = nRT_1 \ln \left(\frac{V_2}{V_1} \right) \quad (\text{positive})$$

2. **Adiabatic Expansion (2 → 3):** No heat exchange ($Q = 0$).

$$W_2 = -\Delta U = \frac{nR(T_1 - T_2)}{1 - \gamma} \quad (\text{positive})$$

3. **Isothermal Compression (3 → 4):** Heat Q_2 rejected to sink at T_2 .

$$W_3 = Q_2 = nRT_2 \ln \left(\frac{V_4}{V_3} \right) \quad (\text{negative})$$

4. **Adiabatic Compression (4 → 1):** No heat exchange ($Q = 0$).

$$W_4 = -\Delta U = \frac{nR(T_2 - T_1)}{1 - \gamma} \quad (\text{negative})$$

Efficiency of Carnot Engine (η):

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{Q_2}{Q_1}$$

Where T_1 is source temperature and T_2 is sink temperature.

Second Law of Thermodynamics

- **Clausius Statement:** "It is impossible for a self-acting machine, unaided by any external agency, to transfer heat from a body at a lower temperature to a body at a higher temperature."
- **Kelvin-Planck Statement:** "It is impossible to construct a heat engine that operates in a cycle and produces no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of work."

Entropy (S)

A measure of the disorder or randomness of a system.

$$\Delta S = \frac{Q_{rev}}{T}$$

For a reversible process, $\Delta S_{universe} = 0$. For an irreversible process, $\Delta S_{universe} > 0$.

Third Law of Thermodynamics

"The entropy of a perfectly crystalline substance is zero at absolute zero temperature (0 K) "

