Chapter

4 Thermodynamics

Quick Review

Thermodynamics

Zeroth Law

- If two systems are each in thermal equilibrium with a third system, they are also in thermal equilibrium.
- When two objects are at the same temperature, they are in thermal equilibrium.

First Law

- When amount of heat Q added to system, its internal energy is increased by an amount ΔU and the remaining is lost in the form of work done W.
  $Q = \Delta U + W$

Second Law

- **Kelvin Plank statement:** It is impossible to extract an amount of heat Q_H from a hot reservoir and use it all to do work W.
- **Clausis statement:** It is not possible for heat to flow from a colder body to a warmer body without any work having been done.

Heat

- Q added to system $\Rightarrow Q > 0$
- Q taken out from system $\Rightarrow Q < 0$
- Thermal equilibrium $\Rightarrow Q = 0$

Work Done

- Expansion $\Rightarrow W > 0$
- Compression $\Rightarrow W < 0$
- $\Delta V = 0 \quad \Rightarrow W = 0$

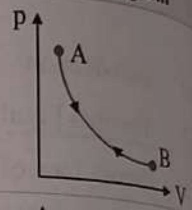
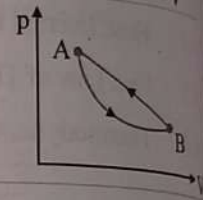
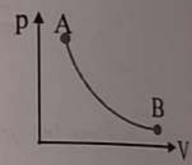
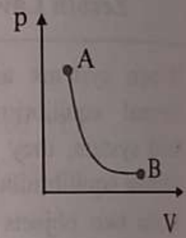
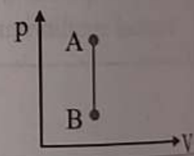
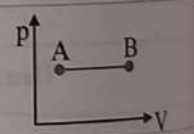
Internal Energy

- Temperature increases $\Rightarrow \Delta U > 0$
- Temperature decreases $\Rightarrow \Delta U < 0$
- Thermal equilibrium $\Rightarrow \Delta U = 0$

➢ **Thermodynamic equilibrium:** A system is in thermodynamic equilibrium if the following three conditions of equilibrium are satisfied simultaneously.

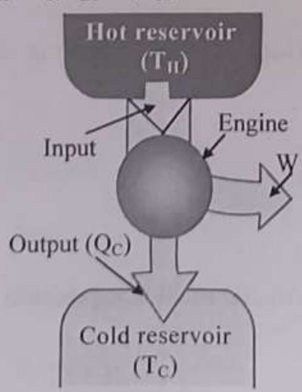
Type of Equilibrium	Condition
Mechanical Equilibrium	No unbalanced forces and equal pressure
Chemical Equilibrium	No chemical reactions or matter transfer, uniform chemical composition
Thermal Equilibrium	Uniform temperature

Thermodynamic process
- Procedure by which initial state of system changes to final state
- Most of the processes are quasi static (very slow)

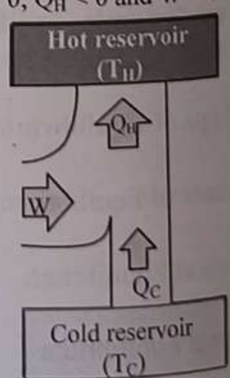
Process	Constants	Variables	Properties/Characteristics	P-V diagram
Reversible	None	Pressure (P), Volume (V), Temperature (T), Heat (Q)	• The changes can be retraced in reverse direction e.g., melting of ice, freezing of water, condensation of steam etc.	
Irreversible	None	P, V, T, Q	• The changes cannot be retraced in reverse direction e.g., Puncturing an inflated balloon, burning a candle, etc.	
Isothermal	T	P, V, Q	• Equation of state: PV = constant • No change in internal energy, energy is exchanged with the environment. • Energy exchanged is used to do work. • It is a very slow change.	
Adiabatic	Q	P, V, T	• Equation of state: PV^{γ} = constant • No exchange of heat with the surroundings. The system is perfectly insulated from its environment. • All the work is utilized to change the internal energy of the system. • The change is very rapid.	
Isochoric	V	P, T, Q	• No work is done. • Energy exchanged is used to change internal energy.	
Isobaric	P	V, T, Q	• Energy exchanged is used to do work and also to change internal energy, i.e., to increase its temperature.	

Second Law of Thermodynamics

Heat Engine
- Devices that transform heat partly into work or mechanical energy
- $T_H > T_C$, $Q_H > 0$, $Q_C < 0$



Refrigerator
- Extracts heat from a cold region and delivers it to the surrounding, further cooling the cold region.
- $Q_C > 0$, $Q_H < 0$ and $W < 0$



Formulae

1. Work done:

i. $dW = PdV = P(V_f - V_i)$ ii. $W = \int_{V_i}^{V_f} PdV$

iii. $W_{adi} = \frac{nR(T_f - T_i)}{(1-\gamma)} = \frac{(P_f V_f - P_i V_i)}{(1-\gamma)}$

2. First law of thermodynamics:

i. $\Delta U = |Q| - |W|$

ii. $Q = \Delta U + W$

3. Equation of state: $PV = nRT$

4. Isothermal process:

i. $PV = \text{constant}$

ii. $W_{iso} = nRT\, ln\left(\frac{V_f}{V_i}\right) = nRT ln\left(\frac{P_i}{P_f}\right)$

5. Heat exchanged during isobaric process:

$Q = nC_P (T_f - T_i)$

6. Heat exchanged during isochoric process:

$Q = \Delta U = nC_V (T_f - T_i)$

7. Adiabatic process:

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

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

8. Cyclic process: $Q = W$

9. Heat engine:

i. Work done:

$W = |Q_H| - |Q_C|$

ii. Efficiency of heat engine:

$$\eta = \frac{W}{Q_H} = 1 + \frac{Q_C}{Q_H} = 1 - \frac{|Q_C|}{|Q_H|}$$

iii. For Carnot engine: $\eta = 1 - \frac{T_C}{T_H}$

10. Refrigerator:

i. Work done: $|W| = |Q_H| - |Q_C|$

ii. Coefficient of performance:

$$K = \frac{|Q_C|}{|W|} = \frac{|Q_C|}{|Q_H| - |Q_C|}$$

iii. For air conditioners: $K = \frac{H}{P}$

Where, H = rate of heat removed

P = power required for removing heat

iv. Carnot refrigerator: $K = \frac{T_C}{T_H - T_C}$

Shortcuts

1. For monatomic gas, the work done is nRdT. The internal energy is 1.5 times work done $(C_v = \frac{3}{2}R)$. The heat supplied is 2.5 times work done $(C_P = \frac{5}{2}R)$

2. i. The fraction of heat energy used to increase the internal energy of gas is, $\frac{\Delta U}{\Delta Q} = \frac{1}{\gamma}$.

ii. Fraction of given heat energy utilised in doing external work is given by the formula, $\left(\frac{\Delta W}{\Delta Q}\right) = \left(1 - \frac{1}{\gamma}\right)$

3. For adiabatic process,

i. $P^{1-\gamma} T^{\gamma} = \text{constant}$ i.e., $P \propto T^{\left(\frac{\gamma}{\gamma-1}\right)}$

ii. $TV^{\gamma-1} = \text{constant}$ .i.e. $T \propto \frac{1}{V^{\gamma-1}}$