UNIT- IV :Thermodynamics:-I

The first law of thermodynamics-statement

The **First Law of Thermodynamics** states that:

"Energy can neither be created nor destroyed, but it can be transformed from one form to another. The total energy of an isolated system remains constant."

Mathematically, it is expressed as:

$\Delta U = q + w$

where:

ΔU = Change in internal energy of the system

q = Heat absorbed by the system

w = Work done on the system

Definition of internal energy and enthalpy.

Internal Energy (U)

Definition:

Internal energy is the total energy contained within a system due to the sum of all microscopic forms of energy, i.e., translational, rotational, vibrational, electronic, and nuclear energies of molecules or atoms.

Explanation:

It is a **state function** (depends only on the state of the system, not on the path).

Internal energy cannot be measured directly; only its **change (ΔU)** is measurable.

According to the **First Law of Thermodynamics**:

$\Delta U = q + w$

where q is heat absorbed and w is work done.

Example: When a gas is heated in a closed container, its molecules move faster, increasing their kinetic energy → this contributes to an increase in **internal energy**.

Enthalpy (H)

Definition:

Enthalpy is the total heat content of a system at constant pressure. It is defined as:

H=U+PV

where:

H = Enthalpy

U = Internal energy

P = Pressure of the system

V = Volume of the system

Explanation:

Enthalpy is also a **state function**.

Change in enthalpy (ΔH) represents the heat absorbed or released at constant pressure.

$\Delta H = \Delta U + P\Delta V$

If $\Delta H > 0$: the process is **endothermic** (heat absorbed).

If $\Delta H < 0$: the process is **exothermic** (heat released).

Example: In combustion of methane, heat is released, hence ΔH is negative (exothermic).

Heat capacities and their relationship.

Heat Capacity (C)

Definition:

The heat capacity of a system is the amount of heat required to raise its temperature by **1 °C**

$C = \frac{q}{\Delta T}$

where:

q = heat supplied

Δ_T= rise in temperature

It depends on the **nature of the substance** and the **conditions of heating** (constant volume or constant pressure).

Types of Heat Capacities

Heat Capacity at Constant Volume (Cv)

Heat required to raise the temperature of 1 mole of gas by 1 K at **constant volume**.

$Cv = (\frac{dT}{dU})_V$

(Since no work is done at constant volume, heat supplied increases internal energy).

Heat Capacity at Constant Pressure (Cp)

Heat required to raise the temperature of 1 mole of gas by 1 K at **constant pressure**.

$Cp = (\frac{dT}{dU})_P$

(Heat supplied increases both internal energy and work done by expansion).

Relationship between Cp and Cv : Mayer's Relation ($Cp - Cv = R$)

For an ideal gas: $Cp - Cv = R$

where R = Universal gas constant.

Derivation (short exam version):

H=U+PV

For 1 mole of ideal gas, PV=RT

H=U+PV =H=U+RT

dH =dU+RdT

$\frac{dH}{dT} = \frac{dU}{dT} + R$

$Cp = (\frac{dH}{dT})_P$ & $Cv = (\frac{dU}{dT})_V$

$$Cp - Cv = R$$

Joule-Thomson effect- Joule-Thomson coefficient.

Joule–Thomson Effect

Definition:

*The **Joule–Thomson effect** (or Joule–Kelvin effect) is the change in temperature of a real gas (or liquid) when it is allowed to expand adiabatically (no heat exchange) through a porous plug or a valve from a region of high pressure to a region of low pressure, without performing external work.*

- ***For ideal gases** → No change in temperature (because internal energy depends only on temperature). Joule–Thomson coefficient = 0.*
- ***For real gases** → Temperature may increase or decrease depending on the initial temperature and pressure.*
- *The temperature change occurs due to the change in potential energy of intermolecular forces.*

Mathematical Expression:

The Joule–Thomson coefficient is given by:

$\mu_{JT} = (\frac{\partial T}{\partial P})_H$ *Where:* μ_{JT} *= Joule–Thomson coefficient (K/Pa or K/bar)*

T = temperature P = pressure H = enthalpy (constant during the process)

Interpretation:

- *If* $\mu_{JT} > 0$ *: Gas cools on expansion (most gases below inversion temperature).*
- *If* $\mu_{JT} < 0$ *: Gas warms on expansion (most gases above inversion temperature).*

Example:

- *Oxygen, nitrogen, and* CO_2 *cool during expansion at room temperature.*
- *Hydrogen and helium warm during expansion at room temperature (because their inversion temperature is much lower than room temperature).*

Inversion Temperature

Definition:

*The **inversion temperature** (Ti) is the temperature at which the Joule–Thomson coefficient changes sign i.e., the temperature above which a gas warms on expansion, and below which it cools on expansion.*

Condition:

At inversion temperature: $\mu_{JT} = 0$

Physical Meaning:

Below T_i: Expansion → cooling (basis of gas liquefaction by Linde's process).

Above T_i: Expansion → heating.

Applications:

Liquefaction of gases (Linde and Claude processes).

Understanding natural gas pipeline cooling.

Cryogenics and refrigeration engineering.

Calculation of w, for the expansion of perfect gas under isothermal, reversible conditions.

Reversible Isothermal Expansion (T = constant)

For an ideal gas at constant T: PV=nRT

$\Rightarrow P = \frac{nRT}{V}$

Work (on the system) in a reversible process:

$$w = -\int_{V_1}^{V_2} PdV$$

$$w = -\int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$w = -nRT[lnV]_{V_1}^{V_2}$$

$$w = -nRTln(\frac{V_2}{V_1})$$

Result (work done on system):

$$w_{iso,rev} = -nRTln(\frac{V_2}{V_1})$$

Result (work done by the system)

$$W_{by} = +nRTln(\frac{V_2}{V_1})$$

In terms of pressures (since $P_1 V_1 = P_2 V_2$ = nRT):

$$W_{by} = +nRTln(\frac{P_1}{P_2})$$

$$w_{iso,rev} = -nRTln(\frac{P_1}{P_2})$$

Calculation of w, for the expansion of perfect gas under adiabatic reversible conditions.

For a reversible adiabatic process of an ideal gas:

q=0 ⇒ ΔU = w.

Also, $PV^{\gamma} = const$ (*with* $\gamma = \frac{C_P}{C_V}$.

$$W_{by} = \int_{V_1}^{V_2} PdV$$

$$= \int_{V_1}^{V_2} K V^{-\gamma} dV$$

$$= K \int_{V_1}^{V_2} V^{-\gamma} dV$$

$$= K \int_{V_1}^{V_2} \frac{1}{V^{\gamma}} dV$$

$$= \frac{K}{1-\gamma} [V^{1-\gamma}]_{V_1}^{V_2}$$

$$= \frac{K}{1-\gamma} [(V_2)^{1-\gamma} - (V_1)^{1-\gamma}]$$

$$= \frac{K}{1-\gamma} [\frac{V_2}{V_2^{\gamma}} - \frac{V_1}{V_1^{\gamma}}]$$

$$= \frac{K}{1-\gamma} [\frac{V_2}{V_2^{\gamma}}] - \frac{K}{1-\gamma} [\frac{V_1}{V_1^{\gamma}}]$$

Since K= $P_1 V_1^{\gamma} = P_2 V_2^{\gamma}$

$\Rightarrow \frac{K}{V_1^{\gamma}} = P_1$ & $\frac{K}{V_2^{\gamma}} = P_2$ this becomes

$$W_{by} = \frac{P_2 V_2 - P_1 V_1}{1-\gamma}$$

Result (work done by the system)

$$W_{by,adia,rev} = \frac{P_2 V_2 - P_1 V_1}{1-\gamma}$$

Result (work done on system):

$$w_{adia,,rev} = \frac{P_1 V_1 - P_2 V_2}{1-\gamma}$$

State function.

Definition:

A state function is a property of a system whose value depends only on the initial and final states of the system, and not on the path by which the system reaches that state.

Key Idea:

State functions are determined by the state of the system (such as pressure, temperature, volume, composition).

They are independent of the method or process used to change the system.

For example, elevation above sea level is a state function (depends only on starting and ending points), but distance travelled to reach that height is not.

Examples of State Functions:

Internal energy (U)

Enthalpy (H)

Entropy (S)

Helmholtz free energy (A)

Gibbs free energy (G)

Pressure (P)

Temperature (T)

Volume (V)

Non-State Functions (Path Functions):

Heat (q)

Work (w)

These depend on the path followed by the system during a process.

Importance in Thermodynamics:

Since state functions depend only on the state, they help in simplifying thermodynamic calculations.

For example, to calculate ΔU (change in internal energy), only the initial and final states are needed, not the intermediate steps.

Temperature dependence of enthalpy of formation

Enthalpy (H)

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Explanation:

Enthalpy is also a **state function**.

Change in enthalpy (ΔH) represents the heat absorbed or released at constant pressure.

$\Delta H = \Delta U + P\Delta V$

If ΔH >0: the process is **endothermic** (heat absorbed).

If ΔH< 0: the process is **exothermic** (heat released).

Example: In combustion of methane, heat is released, hence ΔH is negative (exothermic).

Temperature Dependence of Enthalpy of Formation

Definition:

The enthalpy of formation (ΔHf°) of a compound is the heat change when 1 mole of the compound is formed from its constituent elements in their standard states (The **standard state** of a substance is its **most stable physical form at 1 bar (or 1 atm)**

pressure and at a specified temperature, usually 298 K (25 °C).)at a given temperature and pressure. However, ΔHf° varies with temperature because heat capacity changes with temperature.

Kirchhoff's equation.

Kirchhoff's law states that the **temperature dependence of the enthalpy (heat) of a reaction** is related to the **difference in heat capacities** of products and reactants.In other words, The **enthalpy change of a reaction varies with temperature**, and the rate of this variation is equal to the **difference between the heat capacities of products and reactants**.

Mathematical Expression

For a reaction:

$aA + bB \rightarrow cC + dD$

The enthalpy change at temperature T is:

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^{T} \Delta Cp \, dT$$

where,

ΔH_T = enthalpy change at temperature T

ΔH_{T_0} = enthalpy change at reference temperature T_0 (usually 298 K)

ΔCp = ∑νCp (products) - ∑νCp (reactants) (difference in molar heat capacities at constant pressure)

Derivation

By definition, enthalpy is a function of **T and P**

$dH = CpdT$

For a reaction: $d(\Delta H) = \Delta CpdT$

Integrating between T_0 and T

$$\Delta H_T - \Delta H_{T_0} = + \int_{T_0}^{T} \Delta Cp \, dT$$

$$\Delta H_T = \Delta H_{T_0} + \int_{T_0}^{T} \Delta Cp \, dT$$