Thermodynamics-I

❖ Thermodynamic Terms:

Sytem: A definite enclose part of the universe under study in thermodynamics is called the system & it consist of a definite amount of matter.

Surroundings: The rest of the universe separated from the system by a boundary is called its surroundings that can interact with the system.

Boundary: Region separating the system & its surroundings is called the boundary across which transfer of matter or energy can occur.

When matter can be transferred through the boundary it is **permeable** & when no matter can be transferred it is **impermeable.**

The boundary of the system is called **diathermic** if it allows the migration of heat from system to surroundings & vice – versa & when it does not do so, it is called **adiabatic.**

Universe: The combination of system & surroundings is called the universe.

❖ Classification of System:

Open System: A system which can exchange both matter (mass) & energy with its surroundings is said to be open system.

For example, hot tea in a open cup where from tea, both vapor (mass) & heat (energy) can enter into surroundings.

Close System: A system which can exchange only energy not mass with its surroundings is called close system.

For example, hot water kept in a close container which can exchange only heat not vapor with surroundings.

Isolated system: A system which can't exchange either mass or energy with its surroundings is called an isolated system.

A system separated by fixed adiabatic wall from the surroundings behaves as an isolated system. A perfect isolated system is an abstract concept since no wall is perfectly adiabatic.

For example, liquid taken in a thermo - flask approximates to an isolated system.

➢ Classify the following systems as open, closed & isolated systems:

1. **Tea placed in a thermo flask**: Isolated system
2. **Tea placed in a cup**: Open system
3. **Tea placed in a tea-pot:** Closed system.
4. **Human body**: Open system
5. **Thermometer**: Closed system

- ➤ What is the difference between isolated system & adiabatic system?

  Adiabatic system: An adiabatic system is a system that has no exchange of energy or matter with the surroundings environment.

  Adiabatic system does not gain or lose energy but internal energy can be changed due to work done by the system or on the system. So, energy of adiabatic system is not conserved.

  Isolated system: An isolated system is a system that has no transfer of energy & matter through its boundaries & has no surroundings environment. So, the energy of an isolated system is conserved because the internal energy of an isolated system cannot be changed due to absence of surroundings environment.

- ➤ For which of the following system the energy is conserved (i) Closed system (ii) Open system (iii) Isolated system & (iv) a system enclosed in adiabatic walls.

  (i) Closed system —> Not conserved

  (ii) Open system —> Not conserved

  (iii) Isolated system —> Conserved

  (iv) Adiabatic system —> not conserved.

- ➤ A system must be isolated if neither heat nor matter can enter or leave the system—justify or criticize.

  Adiabatic system does not gain or lose energy but internal energy can be changed due to work done by the system or on the system. So, energy of adiabatic system is not conserved.

  An isolated system is a system that has no transfer of energy & matter through its boundaries & has no surroundings environment. So, the energy of an isolated system is conserved because the internal energy of an isolated system cannot be changed due to absence of surroundings environment.

- ➤ As no heat enters a system under adiabatic condition, its energy is conserved during expansion – justify or criticize.

  An adiabatic system is a system that has no exchange of energy or matter with the surroundings environment.

  Adiabatic system does not gain or lose energy but internal energy can be changed due to work done by the system or on the system. So, energy of adiabatic system is not conserved.

- ➤ A gas expands (i) Isothermally from volume V_1 to V_2 (ii) adiabatically from volume V_3 to V_4 in a leak proof container. Identify the type of system in each case (closed / open/ isolated), with proper reasons.

  (i) In first case, gas expands isothermally in a leak proof container, so mass will not be transferred with the surroundings, so it is closed system.

  ii) Since gas expands adiabatically in a leak proof container, so the system is isolated as mass & energy will not be transferred.

❖ Properties of System:

<u>Extensive Property</u>: Properties whose magnitudes depend on the amount of the matter that is mass dependent are called extensive property.

For example; mass, volume, length, heat capacity, internal energy, enthalpy, entropy, free energy, number of moles etc.

<u>Intensive Property</u>: Properties whose magnitudes do not depend on the amount of the matter that is mass independent are called extensive property.

For example; pressure, temperature, dipole moment, surface tension, viscosity, refractive index, E.M.F. of cell etc.

Ratio of two extensive properties is always intensive property. For example:

Density (m/V), specific heat (heat capacity / mass), chemical potential (G/n), specific volume (volume/mass), molar heat capacity (heat capacity/n), molar enthalpy (H/n) etc.

➢ Two thermodynamic function Y & Z are given as Y = f (T,P,n_i) & Z = f (T,P,X_i) where n_i & X_i represent mole number & mole fraction of ith species. Identify Y & Z as extensive or intensive.

Here P & T are both mass independent, so intensive property but n_i is mass dependent, ie, extensive property whereas X_i is the ratio of two extensive property (ratio of moles), so X_i is intensive property. Hence Y is extensive as it depends on n_i which is extensive whereas Z is intensive as X_i is intensive property.

➢ Identify the extensive properties from the list below:

Pressure, heat capacity, volume, concentration.

Heat capacity & volume.

➢ Why pressure is intensive property?

Pressure does not depend upon the amount of substance because it is defined as force per unit area (F/A) where both F (F = mg) & A is extensive property. So, P is intensive property.

➢ Identify intensive quantities from the following:

(i)   Mass

(ii)   Heat capacity

(iii)   Specific heat

(iv)   Density

Density & specific heat are intensive properties.

❖ State Function & Path Function:

State function: A state function is a property whose value does not depend on the path taken to reach that specific value, only depends on initial & final state of the system.

For example: Enthalpy (H), entropy (S), internal energy (U), free energy etc. are state functions.

Differential form of the state functions are called exact differential, i.e. dH is an exact differential.

Path function: A path function is a property whose value depends on the path taken to reach that specific value, does not depend on initial & final state of the system.

For example: Work (w) & heat (q) are path functions.

Differential form of the path functions are called inexact differential.

❖ Zeroth Law of Thermodynamics:

If two systems are in thermal equilibrium with a third system, then they are also in thermal equilibrium with each other. This is known as zeroth law of thermodynamics.

If a system A is in thermal equilibrium with other system B & a system C is in thermal equilibrium with B. Then according to zeroth law of thermodynamics, system A & C also are in thermal equilibrium with each other.

❖ Work Done During Expansion of an Ideal Gas:

a. Isothermal reversible expansion: The work done by the gas for a small volume change dV should be given by –

$$w_{exp} = - \int_{V_1}^{V_2} P \, dV$$

$$For \ an \ ideal \ gas, PV = nRT, or, \qquad P = \frac{nRT}{V}$$

$$Now, w_{exp} = - \int_{V_1}^{V_2} P \, dV$$

$$= - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln\left(\frac{V_2}{V_1}\right)$$

$$= -2.303 \, nRT \log\left(\frac{V_2}{V_1}\right)$$

Again for an ideal gas,

$$P_1V_1 = P_2V_2, so, \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$Hence, \quad w = -2.303nRT\log\left(\frac{P_1}{P_2}\right)$$

The units of $'w'$ depends on the units of R.

b. <u>Adiabatic reversible expansion</u>:

From first law of thermodynamics, $q = \Delta U - w$

For adiabatic process $q = 0, so -$

$$w = \Delta U = n\overline{C_V}(T_2 - T_1)$$

$$= n\overline{C_V}\left(\frac{P_2V_2}{nR} - \frac{P_1V_1}{nR}\right)$$

$$= \frac{\overline{C_V}}{R}(P_2V_2 - P_1V_1)$$

$$= \left[\frac{(P_2V_2 - P_1V_1)}{\left(R/\overline{C_V}\right)}\right]$$

$$= \frac{(P_2V_2 - P_1V_1)}{\gamma - 1}$$

$$= \frac{nR(T_2 - T_1)}{\gamma - 1}$$

1. If $T_2 > T_1, w$ is positive & we say that work is done on the system.
2. If $T_2 < T_1, w$ is positive & we say that work is done by the system.

c. <u>Isothermal irreversible process</u>:

Suppose an ideal gas expands against external pressure P & its volume changes by an amount dV then work done w can be given by $w = -PdV$

For a finite change from V_1 to V_2,

Total work done,

$$w_{irr} = -P(V_2 - V_1)$$

1. If $V_2 > V_1, then\ w_{irr}\ is\ -ve, i.e.$, work is done by the system.
2. If $V_2 < V_1, then\ w_{irr}\ is\ +ve, i.e.$, work is done on the system.

d. <u>Isothermal free expansion</u>:

We know,

$$w = -PdV$$

For free expansion, there is no opposing pressure, so, $P = 0, so,$

$$w = 0$$

> ➤ Deduce the expression for the work done in the reversible isothermal expansion of one mole of an ideal gas.

The work done by the gas for a small volume change dV should be given by –

$$w_{exp} = -\int_{V_1}^{V_2} PdV$$

$$For\ an\ ideal\ gas, PV = nRT, or, \qquad P = \frac{nRT}{V}$$

$$Now, w_{exp} = -\int_{V_1}^{V_2} PdV$$

$$= -\int_{V_1}^{V_2} \frac{nRT}{V}dV = -nRT\ln\left(\frac{V_2}{V_1}\right)$$

$$= -2.303\ nRT\log\left(\frac{V_2}{V_1}\right)$$

Again for an ideal gas,

$$P_1V_1 = P_2V_2, so, \frac{V_2}{V_1} = \frac{P_1}{P_2}$$

$$Hence, \qquad w = -2.303nRT\log\left(\frac{P_1}{P_2}\right)$$

> ➤ Under what conditions the isothermal expansion of a gas does becomes a free expansion?

The isothermal expansion of a gas will become a free expansion when opposing pressure is zero, i.e. when gas expands against a vacuum.

> ➤ Calculate the work done in isothermal reversible expansion from volume V_1 to V_2 for 1 mole of a gas obeying the equation $P(V - b) = RT$

$$P(V - b) = RT, Or, P = \frac{RT}{V - b}$$

$$Now, \qquad |W_{rev.exp}| = \int_{V_1}^{V_2} PdV$$

$$= RT\int_{V_1}^{V_2} \frac{dV}{V - b}$$

$$= RT\ln\left(\frac{V_2 - b}{V_1 - b}\right)$$

> ➤ Calculate the work involved in (i) Isothermal irreversible free expansion & (ii) Isochoric Process.

(i) For free expansion process, $P_{opp.}$ = 0. Hence $|W_{iso.rev.exp.}| = P_{opp.}dV = 0$.

(ii) For isochoric process, volume remains constant, so $dV = 0$. Hence, $|W_{isochoric}| = P_{opp.}dV = 0$.

❖Distinguish between reversible & irreversible process:

Reversible Process	Irreversible Process
1. The process is carried out infinitesimally slowly 2. At any stage, the equilibrium is not disturbed 3. It takes infinite time for completion. 4. Work obtained in this process is maximum.	1. It is carried out rapidly 2. Equilibrium may exist only after the completion of the process. 3. It takes a finite time for completion. 4. Work obtained in this process is not maximum