

UNIT - I PART B + C QUESTIONS

1. Reversible and Irreversible Processes:

Processes occur when there exists a driving force for a change of state between the parts of the system & between the system and the surroundings. If this driving force is finite, the process is irreversible and if it is infinitesimal in magnitude, the process is reversible.

* All Spontaneous processes occurring in nature are irreversible. They cannot be reversed without the use of external energy. If the system undergoing an irreversible process were to be brought back to its initial state, the surroundings would have to undergo some change through heat & work interactions.

- Ex: (i) The free expansion of a gas is a highly irreversible process.
- (ii) When a gas at a high pressure is expanded by passing through a valve, it undergoes an irreversible change, because it cannot be compressed back to the original pressure without resort to energy from an external source compressed.
- (iii) The natural processes like diffusion of a solute from a concentrated solution to a dilute one, the transfer of heat from a hot body to a cold body, rusting of iron in the presence of atmospheric oxygen, mixing of two pure gases, are all irreversible.

(2)

* In contrast, the direction of a reversible process can be changed by an infinitesimal change in the forces acting on the system. A system undergoing a reversible process can be brought back to its original state, leaving no change in the surroundings.

Ex:

(i) Consider water and water vapour in equilibrium contained in a cylinder provided with a frictionless piston. The external force on the piston is kept equal to the force due to the vapour pressure of water at the given temperature. By increasing the force acting on the piston by an infinitesimally small amount, the vapour will condense; and decreasing it slightly will make water to vaporise. The process is very close to a reversible process as the work required to condense a certain amount of water vapour would be equal to that required to vaporise the same quantity of water.

(ii) Consider the chemical reaction occurring in a galvanic cell in which the electrodes made of zinc and platinum are immersed in an aqueous solution of hydrochloric acid. $\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2$
The electrodes are connected through an external circuit to a potentiometer. The system is in equilibrium when the applied potential difference is balanced by the e.m.f. produced by the cell. By increasing or decreasing the potential difference slightly, the reaction can be carried out in the forward or reverse direction. Similarly, heat transfer between two bodies may be made nearly reversible by bringing down the temperature difference between them to a very small value.

d. Constant Volume Process

From the general mathematical statement of the first law of thermodynamics for nonflow process.

$$dU = dQ - dW \quad \text{--- (1)}$$

Consider one mole of an ideal gas undergoing a constant volume process. Since the volume remains constant, there is no work of expansion and $dW = 0$; the heat supplied is equal to the product of heat capacity and rise in temperature, i.e. $dQ = C_V dT$. C_V is the heat capacity at constant volume.

$$\text{(1)} \Rightarrow dU = dQ - \underset{0}{dW} = C_V dT$$

$$\boxed{dU = dQ = C_V dT}$$

Constant Pressure Process:

Consider the reversible expansion of an ideal gas in a cylinder. The pressure inside the cylinder is kept constant at P by maintaining a constant force over the piston. The heat supplied is the product of heat capacity and rise in temperature; $dQ = C_P dT$. Where C_P is the heat capacity at constant pressure. The work involved is the work of expansion done against the surrounding atmosphere, which, for a reversible process is given by $dW = PdV$.

$$\text{Wk}, \quad dU = dQ - dW \quad \text{--- (1)}$$

$$\text{Substitute } dQ = C_P dT \text{ and } dW = PdV \text{ in eqn (1)}$$

$$\text{(1)} \Rightarrow dU = C_P dT - PdV \quad \text{--- (2)}$$

$$\text{(2)} \quad dU + PdV = C_P dT \quad \text{--- (3)}$$

$$\text{Wk}, \quad H = U + PV \quad \text{--- (4)}$$

$$dH = dU + d(PV)$$

$$= dU + PdV + V \frac{dP}{\cancel{V_0}}$$

④
∵ Constant pressure process

$$dH = dU + PdV \quad \text{--- (5)}$$

Comparing eqn (3) and (5)

$$dH = C_p dT$$

Thus, for the process occurring at constant pressure, the following general result applicable for all gases whether ideal & not.

$$dH = dQ = C_p dT$$

3. (a) State Functions

(i) State functions can be expressed as difference between two states.

(ii) State functions are represented by a point on a graph.

(iii) \oint (State functions) = 0

(iv) State functions are independent of time

Path Functions

(i) Path functions are absolute quantities

(ii) Path functions are represented by area.

(iii) \oint (Path functions) $\neq 0$

(iv) Path functions are time dependent.

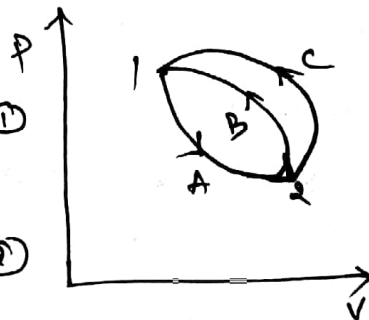
(b) P.T internal energy is a state function

Proof: Process 1A2

$$dQ_{1A2} = dU_{1A2} + dW_{1A2} \quad \text{--- (1)}$$

Process 2B1

$$dQ_{2B1} = dU_{2B1} + dW_{2B1} \quad \text{--- (2)}$$



(5)

Eqn (1) + (2) gives

$$(dQ_{1A2} + dQ_{2B1}) = (dU_{1A2} + dU_{2B1}) + (dW_{1A2} + dW_{2B1}) \quad \text{--- (3)}$$

From 1st law of thermodynamics, for cycle 1A2B1,

$$(dQ_{1A2} + dQ_{2B1}) = (dW_{1A2} + dW_{2B1}) \quad \text{--- (4)}$$

Equating eqn (3) and (4) we get

$$dU_{1A2} + dU_{2B1} = 0$$

$$dU_{1A2} = -dU_{2B1} \quad \text{--- (5)}$$

On similar grounds,

$$dU_{1A2} = -dU_{2C1} \quad \text{--- (6)}$$

On equating eqn (5) and (6)

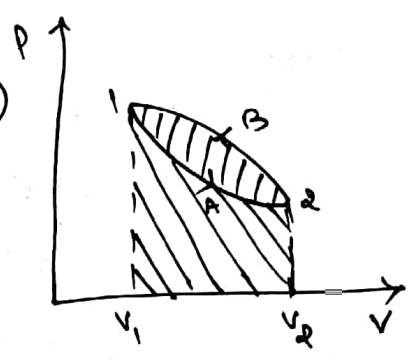
$$dU_{2B1} = dU_{2C1}$$

Hence it is proved.

P.T work is a path function

$$\therefore \text{Area}(1V_1V_22A1) \neq \text{Area}(1V_1V_22B1)$$

$$\therefore W_{1A2} \neq W_{1B2}$$



- * work is not a property of a system
- * work is a path function
- * work is an inexact differential.

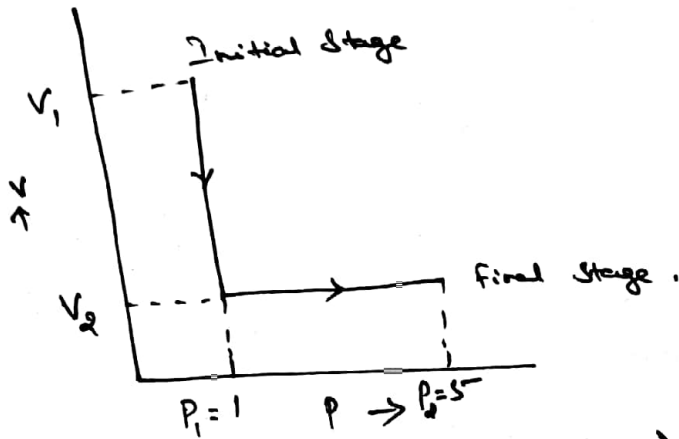
4. Cooling at constant pressure followed by heating at constant volume:

Given data: $P_1 = 1 \text{ bar}$; $P_2 = 5 \text{ bar}$

$$V_1 = 0.02479 \text{ m}^3 / \text{mol}$$

$$C_v = 20.785 \text{ J/mol K}; C_p = 29.099 \text{ J/mol K}$$

(6)



$$V_2 = V_1 \frac{P_1}{P_2} = 0.02479 \left(\frac{1}{5} \right) = 0.004958 \text{ m}^3$$

(a) During the first step the air is cooled at the constant pressure of 1 bar until the final volume of 0.004958 m^3 is reached. The temperature of the air at the end of this cooling step is:

$$T' = T_1 \frac{V_2}{V_1} = 298.15 \left(\frac{0.004958}{0.02479} \right) = 59.63 \text{ K}$$

$$Q = \Delta H = C_p \Delta T = 29.099 (59.63 - 298.15)$$

$$Q = \Delta H = -6941 \text{ J}$$

Also,

$$\Delta U = \Delta H - \Delta(PV) = \Delta H - P \Delta V$$

$$= -6941 - (1 \times 10^5) (0.004958 - 0.02479)$$

$$\Delta U = -4958 \text{ J}$$

During the second step the volume is held constant at V_2 while the air is heated to its final state.

$$\Delta U = Q = C_v \Delta T = 20.785 (298.15 - 59.63)$$

$$\Delta U = Q = 4958 \text{ J}$$

The complete process represents the sum of its steps. Hence,

$$Q = -6941 + 4958 = -1983 \text{ J}$$

(7)

$$\Delta U = -4958 + 4958 = 0$$

Since the first law applies to the entire process,
 $\Delta U = Q + W$ and therefore

$$0 = -1983 + W$$

$$W = 1983 \text{ J}$$

$\Delta H = \Delta U + \Delta(PV)$, also applies to the entire process. But $T_1 = T_2$, and therefore, $P_1 V_1 = P_2 V_2$.

Hence $\Delta(PV) = 0$, and

$$\Delta H = \Delta U = 0$$

5. Given:

Liquid state: $T_1 = 80^\circ\text{C}$, $P_1 = 200 \text{ kPa}$

Vapour state: $T_2 = 125^\circ\text{C}$, $P_2 = 100 \text{ kPa}$

Velocity: $u_1 = 3 \text{ m/s}$; $u_2 = 200 \text{ m/s}$

Enthalpy of inlet stream: $H_1 = 334.9 \text{ kJ/kg}$

Enthalpy of outlet stream: $H_2 = 2726.5 \text{ kJ/kg}$

Heat transferred through the coil per unit mass of water } $Q = ?$

By first law of thermodynamics for flow process

$$\Delta H + \frac{\Delta u^2}{2} + g \Delta z = Q - W$$

Since it is horizontal coil, there is no elevation.

No work is done.

$$\therefore \Delta H + \frac{\Delta u^2}{2} = Q$$

$$(H_2 - H_1) + \frac{u_2^2 - u_1^2}{2} = Q$$

$$(2726.5 - 334.9) + \frac{200^2 - 3^2}{2} \frac{\text{m}^2}{\text{s}^2} \times 10^{-3} \frac{\text{kJ} \cdot \text{s}^2}{\text{kg} \cdot \text{m}^2} = Q$$

$$Q = \underline{\underline{2411.595 \text{ kJ/kg}}}$$

b. Given Data :

$$m = 500 \text{ g}$$

$$\text{Molecular mass of } \text{NH}_3 = 17$$

$$\text{No. of moles } n = \frac{500}{17} = 29.41 \text{ mol}$$

$$V = 30,000 \text{ cm}^3 = 30,000 \times 10^{-6} = 0.03 \text{ m}^3$$

$$T = 65^\circ\text{C} = 65 + 273.15 = 338.15 \text{ K}$$

$$\text{Molar Volume } v = \frac{V}{n} = \frac{0.03}{29.41} = 1.02 \times 10^{-3} \frac{\text{m}^3}{\text{mol}}$$

$$T_c = 405.7 \text{ K} ; P_c = 112.8 \text{ bar} = 112.8 \times 10^5 \frac{\text{N}}{\text{m}^2}$$

(i) Ideal gas equation:

$$P = \frac{RT}{v} = \frac{8.314 \times 338.15}{1.02 \times 10^{-3}} = 2756254.02$$

$$P = 27.56 \times 10^5 \text{ N/m}^2 = 27.56 \text{ bar}$$

(ii) Van der Waals eqn:

$$\left(P + \frac{a}{v^2}\right)(v-b) = RT$$

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$a = \frac{27R^2T_c^2}{64P_c} = \frac{27 \times 8.314^2 \times 405.7^2}{64 \times 112.8 \times 10^5} = 0.4255$$

$$b = \frac{RT_c}{8P_c} = \frac{8.314 \times 405.7}{8 \times 112.8 \times 10^5} = 3.738 \times 10^{-5}$$

$$P = \frac{8.314 \times 338.15}{1.02 \times 10^{-3} - 3.738 \times 10^{-5}} - \frac{0.4255}{(1.02 \times 10^{-3})^2}$$

$$= 2861105.107 - 408977.316$$

$$= 2452127.791 = 24.52 \times 10^5 \text{ N/m}^2$$

$$P = 24.52 \text{ bar}$$

(iii) Redlich Kwong Equation

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5} V(V+b)}$$

$$a = \frac{0.4278 R^2 T_c^{2.5}}{P_c} = \frac{0.4278 \times 8.314^2 \times 405.7^{2.5}}{112.8 \times 10^5}$$

$$a = 8.691$$

$$b = \frac{0.0867 R T_c}{P_c} = \frac{0.0867 \times 8.314 \times 405.7}{112.8 \times 10^5}$$

$$b = 2.593 \times 10^{-5}$$

$$P = \frac{8.314 \times 338.15}{1.02 \times 10^{-3} - 2.593 \times 10^{-5}} - \frac{8.691}{338.15^{0.5} + 1.02 \times 10^{-3} (1.02 \times 10^{-3} + 2.593 \times 10^{-5})}$$

$$= 2828150.03 - 443008.707$$

$$= 2385141.32 = 23.85 \times 10^5 \text{ N/m}^2$$

$$P = 23.85 \text{ bar}$$

7. (a) $Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} ; B = ? ; C = ?$

Vander waals equation $(P + \frac{a}{V^2})(V-b) = RT$ — (1)

The Vander waals equation can be expanded as

$$PV - Pb + \frac{a}{V} - \frac{ab}{V^2} = RT$$

$$PV = RT - \frac{a}{V} + Pb + \frac{ab}{V^2} \quad \text{--- (2)}$$

$$\textcircled{2} \Rightarrow PV - Pb = RT - \frac{a}{V} + \frac{ab}{V^2}$$

$$P(V-b) = RT - \frac{a}{V} + \frac{ab}{V^2}$$

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2} \frac{(V-b)}{(V-b)}$$

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2} \quad \text{--- (3)}$$

Replace P from the R.H.S of eqn (2) using eqn (3).
Noting that $a = RT$, the resulting equation

$$\textcircled{2} \Rightarrow PV = RT - \frac{a}{V} + \left(\frac{RT}{(V-b)} - \frac{a}{V^2} \right) b + \frac{ab}{V^2} \quad \textcircled{3}$$

$$PV = RT - \frac{a}{V} + \frac{RTb}{(V-b)} - \frac{ab}{V^2} + \frac{ab}{V^2}$$

$$PV = RT - \frac{a}{V} + \frac{RTb}{V-b} \quad \textcircled{4}$$

$\div \textcircled{4}$ by $RT \Rightarrow$

$$\frac{PV}{RT} = 1 - \frac{\cancel{RT}}{\cancel{RT} \cdot V} + \frac{\cancel{RT}}{\cancel{RT}} \cdot \frac{b}{(V-b)} \quad \left[\because a = RT \right]$$

$$Z = \frac{PV}{RT} = 1 + \frac{b}{(V-b)} - \frac{1}{V}$$

$$Z = 1 + \frac{b}{V} \left(1 - \frac{b}{V} \right)^{-1} - \frac{1}{V} \quad \textcircled{5}$$

$$\therefore \left(1 - \frac{b}{V} \right)^{-1} = 1 + \frac{b}{V} + \frac{b^2}{V^2} + \dots$$

Eqn $\textcircled{5}$ may be simplified as

$$Z = 1 + (b-1) \frac{1}{V} + \frac{b^2}{V^2} + \frac{b^3}{V^3} + \dots \quad \textcircled{6}$$

$$Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} \quad \textcircled{7}$$

On comparing eqn $\textcircled{6}$ & eqn $\textcircled{7}$

$$B = b-1; \quad C = b^2; \quad D = b^3$$

(b) The virial equation truncated to three terms is $Z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2}$

which can be rearranged as

$$V = \frac{RT}{P} \left(1 + \frac{B}{V} + \frac{C}{V^2} \right)$$

$$V = \frac{8.314 \times 500}{10 \times 10^5} \left(1 - \frac{2.19 \times 10^{-4}}{V} - \frac{1.73 \times 10^{-8}}{V^2} \right)$$

Volume is determined by trial and error method.

Using the ideal gas volume $V = \frac{RT}{P} = 4.157 \times 10^{-3} \text{ m}^3$

as the initial guess value. $V \equiv 3.92 \times 10^{-3} \text{ m}^3$

$$\text{Compressibility factor } Z = \frac{PV}{RT} = \frac{10 \times 10^5 \times 3.92 \times 10^{-3}}{8.314 \times 500}$$

$$Z = 0.943$$

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