

8

(18) Thermodynamics Processes

- (1) Isothermal process
- (2) Isobaric process
- (3) Isochoric process
- (4) Adiabatic process
- (5) Cyclic process
- (6) Reversible process
- (7) Irreversible process

- Work done in Isothermal process

Consider a ideal gas in a cylinder with conducting walls.

$$\text{Work done} = \text{Force} \times \text{displacement}$$

$$dW = Fdx$$

$$dW = PAdx$$

$$dW = PdV$$

Now,

Integrate on both side if volume change from V_1 to V_2

$$\int dW = \int_{V_1}^{V_2} \int_{V_1}^{V_2} PdV = RT [\log V_2 - \log V_1]$$

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

$$= RT \int_{V_1}^{V_2} \frac{dV}{V} = RT [\log V]_{V_1}^{V_2}$$

$$\Rightarrow W = RT \log \frac{V_2}{V_1} = 2.303 RT \log \frac{V_2}{V_1}$$

OR

$$W = RT \log \frac{P_1}{P_2} = 2.303 RT \log \frac{P_1}{P_2}$$



(18)

$$= RT \left[\log \frac{V_2}{V_1} \right]^{V_2}$$

$$= RT \left[\log V_2 - \log V_1 \right]$$

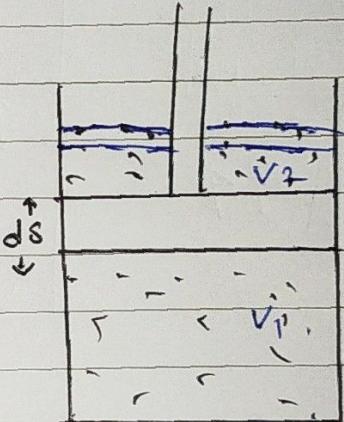
$$\boxed{W = RT \log \frac{V_2}{V_1}}$$

OR

$$\boxed{W = RT \log \frac{P_1}{P_2}}$$

- Work done in Adiabatic process

Consider an ideal gas in a Cylinder with non conducting walls.



Work done = Force \times displacement

$$dw = F dx$$

$$dw = P A dx$$

$$dw = P dV$$

Now, Integrate on both sides

Volumes changes from V_1 to V_2

$$\int dw = \int_{V_1}^{V_2} P dV$$

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

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

$$\begin{aligned}
 &= K \int_{V_1}^{V_2} V^{-r} dV \\
 &= K \left[\frac{V^{-r-1}}{-r+1} \right]_{V_1}^{V_2} \\
 &= K \left[\frac{V^{1-r}}{1-r} \right]_{V_1}^{V_2} \\
 &= \frac{K}{1-r} [V_2^{1-r} - V_1^{1-r}]
 \end{aligned}$$

$$W = \frac{1}{1-r} [P_2 V_2 - P_1 V_1]$$

for 1 mole os
gas $PV = RT$

$$W = \frac{1}{1-r} [RT_2 - RT_1]$$

$$W = R [T_2 - T_1]$$

$$W = \frac{R [T_2 - T_1]}{1-r}$$

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

$$W = \frac{1}{1-r} [K V_2^{1-r} - V_1^{1-r}] \quad \text{--- (1)}$$

As we know

$$\begin{aligned}
 PV^r &= K \\
 P_1 V_1^r &= P_2 V_2^r = K \\
 P_2 V_2^r &= K \\
 P_2 V_2^r \cdot \frac{V_2}{V_2} &= K
 \end{aligned}$$

$$\begin{aligned}
 P_2 V_2 V_2^{r-1} &= K \\
 P_2 V_2 = \frac{K}{V_2^{r-1}} &\text{ or } P_2 V_2 = K V_2^{-(r-1)} \\
 &= K V_2^{1-r}
 \end{aligned}$$

$$P_2 V_2 = K V_2^{1-r} \quad \text{--- (2)}$$

$$\begin{aligned}
 \text{Similarly } P_1 V_1 &= K V_1^{1-r} \quad \text{--- (3)} \\
 \text{Now, (2) and (3) in (1)}
 \end{aligned}$$

(5)

(6)

Dilute Clausius - Clapeyron equation, Derivation

(19)

The equation which deals with the change in the boiling point or the freezing point of a substance with increase in pressure is called Clausius - Clapeyron equation and is given by

$$\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)}$$

This is the application of Maxwell's second thermodynamical relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Multiplying both sides by T we have

$$= T \left(\frac{\partial S}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V$$

$$\text{But } T dS = \partial Q$$

$$\therefore \left(\frac{\partial Q}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V$$

The quantity $\left(\frac{\partial Q}{\partial V}\right)_T$ represent the quantity of heat absorbed or liberated per unit change in volume at constant temperature. As there is a change in volume due to the heat absorbed at constant temperature, the heat represent the latent heat used when the temperature remains constant during the

(2)

(19) Change of state.

If L is the quantity of heat required to change the state of a unit mass of the substance, v_2 and v_1 the corresponding specific volumes (volumes per unit mass), then

$$\delta Q = L \text{ and } \delta V = v_2 - v_1$$

$$\therefore \left(\frac{\delta Q}{\delta V} \right)_T = \frac{L}{v_2 - v_1}$$

Hence

$$\frac{L}{v_2 - v_1} = T \left(\frac{\delta P}{\delta T} \right)_V$$

$$\text{Or} \quad \boxed{\frac{\delta P}{\delta T} = \frac{L}{T(v_2 - v_1)}}$$

Where δT is the change in melting point or boiling point due to change in pressure δP .

This is a Clapeyron's equation.

(1)

~~(2)~~

Q) Derive Value of C_p , C_v and γ for monoatomic and diatomic gases.

Energy available /molecule/degree of freedom =

$$\frac{1}{2} k_B T, \quad k_B = \frac{R}{N_A}$$

Energy available /molecule = $\frac{n}{2} \frac{R}{N_A} T$

$$\text{Energy/mole} = \frac{n}{2} \frac{R}{N_A} \times N_A = \frac{nRT}{2} \Rightarrow U = \frac{nRT}{2}$$

$$\text{for constant vol.} \quad \therefore dQ = dU + dW \Rightarrow \boxed{dQ = dU} + PdV$$

$$\frac{dV}{dT} = 0, \quad dQ = (1) C_V dT \Rightarrow C_V = \frac{dQ}{dT}$$

$$\therefore dQ = dU$$

$$\therefore C_V = \frac{dU}{dT} = \frac{d}{dT} \left(\frac{nRT}{2} \right) \quad \boxed{\gamma = \frac{C_P}{C_V} = \frac{R \cdot \frac{n+2}{2}}{nR}}$$

$$C_V = \frac{n}{2} R \frac{dT}{dT}$$

$$\boxed{C_V = \frac{nR}{2}}$$

$$= \frac{n+2}{n} \Rightarrow \boxed{\gamma = 1 + \frac{2}{n}}$$

* Monoatomic gas

$$n = 3$$

$$C_V = \frac{3R}{2}, \quad C_P = \frac{3R+R}{2} = \frac{5R}{2}, \quad \gamma = \frac{C_P}{C_V} = \frac{5}{3}$$

* diatomic gas $n = 5$

$$C_V = \frac{5R}{2}, \quad C_P = \frac{5R}{2} + R = \frac{7R}{2}, \quad \gamma = \frac{7}{5} = 1.4$$

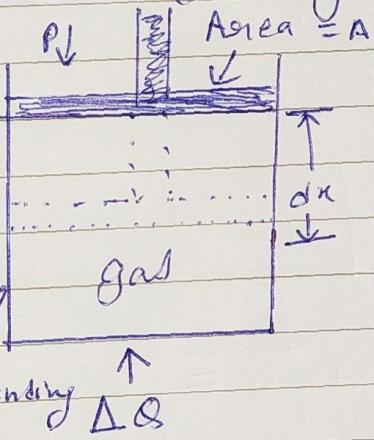
$$C_P = R \left(n + \frac{n+2}{2} \right)$$

$$\Rightarrow \boxed{C_P = R \left(\frac{n}{2} + 1 \right)}$$

(1)

First law of thermodynamics

(2) It is simply the law of conservation of energy applied to any system in which energy transfer (in the form of heat or work) from or to the surroundings is taken into consideration. According to the first law of thermodynamics, if some heat is supplied to a system which is capable of doing work, then the quantity of heat absorbed by the system will be equal to the sum of the increase in its internal energy and the external work done by the system on the surrounding.



Let

 ΔQ = heat supplied to the system by the surrounding

 ΔW = work done by the system on the surrounding

 ΔU = change in internal energy of the system

 Then according to the First law of thermodynamics $\Delta Q = \Delta U + \Delta W$

As shown in figure, suppose the system is a gas contained in a cylinder provided with a movable piston. Then the gas does work in moving the piston. The work done by the system against a constant pressure ~~P~~ P is

$$\Delta W = \text{Force} \times \text{Displacement}$$

$$= \text{Pressure} \times \text{Area} \times \text{Distance}$$

$$\text{or } \Delta W = P \Delta V$$

where $\Delta V = A \Delta x =$ the change in the volume of the gas. So the first law of thermodynamics takes the form, $\Delta Q = \Delta U + P \Delta V$

(i)

Prove of $C_p - C_v = R$

(2)

$C_p - C_v$ for an ideal gas. Making use of Maxwell's second thermodynamical relation.

$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ and definition of C_p and C_v first prove the relation

$$C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \dots \textcircled{1}$$

for a perfect gas, if V is the gram molecular volume, then

$$PV = RT$$

$$P = \frac{RT}{V} \text{ and } V = \frac{RT}{P}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \text{ and } \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

Substituting in $\textcircled{1}$, we have

$$\begin{aligned} C_p - C_v &= T \frac{R}{V} \times \frac{R}{P} = \frac{TR^2}{PV} \\ &= \frac{TR^2}{RT} = R \end{aligned}$$

Or $C_p - C_v = R$

As R is positive quantity $C_p > C_v$

* Thermodynamic Potentials :- The thermodynamics can be discussed by knowing thermodynamic variables or thermodynamics co-ordinates (P, V, T, U, S).

(23) Thermodynamics ~~is~~ is a scalar function used to thermodynamic state of a system thermodynamic Potential are introduced by Pierre Duhem in 1886.

There can four thermodynamics potentials -

- (1) Internal energy (U)
- (2) Helmholtz free energy (f)
- (3) Enthalpy (H)
- (4) Gibbs functions (Gibbs free energy) (G)

1) Internal energy (U) :- It is defined as the total energy of the system. The sum of total kinetic energy and potential energy of the atom and molecules of the system that can be transformed directly as heat.

According to first law of thermodynamic

$$dQ = dU + dW \quad (\because dW = PdV)$$

$$dQ = dU + PdV$$

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

Again from second law of thermodynamic

$$dQ = Tds \quad \text{--- (2)} \quad (\because ds = dQ/T)$$

put $dQ = Tds$ in eqn (1)

$$\therefore dU = Tds - PdV \quad \text{--- (3)}$$

This gives the change in internal energy of the system in terms of thermodynamic variables.

(2)

(2)

Helmholtz free energy (Helmholtz function (f))

it is the thermodynamic property of the system denoted by s as given by

$$F = U - TS \quad (4)$$

According to the equation

$$dU = Tds - dw$$

At Constant temperature

$$Tds = d(TS)$$

$$\therefore dU = d(TS) - dw$$

$$d(U - TS) = -dw$$

$$df = -dw \quad (5)$$

from eqn (4)

$$df = d(U - TS)$$

$$df = dU - Tds - SdT$$

$$\text{But } dU = Tds - PdV \quad (\text{from eqn (3)})$$

$$\therefore df = Tds - PdV - Tds - SdT$$

$$\therefore df = -PdV - SdT \quad (6)$$

equation (6) gives the change in helmholtz free energy during the reversible process.

(3) Enthalpy (H) : It is the energy (total heat) needed to create a system and the work needed to space

(3)



(22)

$$H = U + PV - \textcircled{7}$$

If the system undergoes a reversible process then the change in enthalpy.

$$dH = dU + PdV + Vdp$$

but

$$dU = Tds - Pdv$$

putting the value of $dU = Tds - Pdv$

$$dH = Tds - Pdv + Pdv + Vdp$$

$$dH = Tds + Vdp - \textcircled{8}$$

it is the change in enthalpy which measures the heat absorbed during a process at constant temperature.

4) Gibbs function (Gibbs free energy) (G_f) :-

It is a energy released in a reversible process at constant pressure and constant temperature it is given by.

$$\boxed{G_f = H - TS} - \textcircled{9}$$

∴ putting the value of $H = U + PV$ in eqn - 9

$$G_f = U + PV - TS - \textcircled{10}$$

Since we know that helmoltz

$$\therefore F = U - TS$$

$$\boxed{G_f = F + PV} - \textcircled{11}$$

This gives function G_f remains constant in isothermal and isobaric process.

①

Thermodynamics Processes



1) Isothermal Process → This is the process where temperature remains constant. i.e $T=0$, $T=\text{Constant}$.
e.g. → ① Water boils at 100°C

② Reaction gain on refrigerator.

2) Isochoric → Isochoric process it is the process where volume is Constant. i.e $V=0$
e.g. → Cooking food in pressure cooker.

3) Reversible → This is the process in which substance can get back to original form or which can reverse in its original condition.
e.g. → ① ice to water or water to ice.

② Vaporization.

③ Water cycle.

4) Irreversible process → This is the process which the system and surroundings can be returned to the original condition.
e.g. → Slow adiabatic compression or expansion of gases.

5) Isobaric → This is the process where pressure is constant. i.e., $P=0$

6) Adiabatic → This is the process where there is no exchange of heat inside or outside the environment / surrounding.
e.g. → Thermal flask.

7) Irreversible → This is the process which can not reverse to its original form.
OR This is the process in which substance cannot get back to its original form in its original condition.

e.g. → ① Burning of Coal.
② Cook food.

8) Cyclic process → This is the process which repeats starting to end.
e.g. → ① Function of refrigerator.
② Air Conditioner.

(1)

(24)

Transport Phenomena

3- Those phenomena which can be explained on the basis of movement of gas atoms or molecules are known as Transport phenomena. According to the kinetic theory of gases, molecules of a gas are in a constant state of thermal-agitation. The gas, therefore, has a tendency to come to steady state or equilibrium state. When a gas is not in a steady state, the following three cases arises.

i) Transport of momentum :- The different layers of the gas may have different velocities.

In such a case there will be a relative motion of the layers of the gas with respect to each other and to bring about a steady state the layers moving faster will transfer momentum to the layers moving slower. This is the phenomenon of ~~res~~ Viscosity and arises due to transport of momentum.

ii) Transport of energy : The different layers of the gas may be at different temperatures. The molecules at a higher temperature will have greater energy. To bring about a steady state the molecules will transfer energy from regions of higher temperature to regions of lower temperature. The energy is in the form of heat and gives rise to phenomenon of thermal conductivity. Thus the phenomenon of thermal conductivity is due to transport of energy.

iii) Transport of mass : The different layers of the gas may have different concentrations. In such a case the molecules of the gas will move from regions of higher concentration (no. of molecules per unit

Q
24)

(2)

Volume) to regions of lower Concentration to come to a steady state, thereby transferring mass from regions of higher concentration to regions of lower concentration.

This is the Phenomenon of diffusion and arises due to transport of mass.

Thus viscosity, conduction and ~~and~~ diffusion represent the transport of momentum, energy and mass respectively and are called transport Phenome Phenomena.