Ch-11- Thermodynamics

→ any system consists of radiation & matter.

* System = The part which will be studied in thermodynamics is called thermo- system.

* Surrounding = The rest part of system is called surrounding. (other than system)

⇒ Universe = System + Surrounding

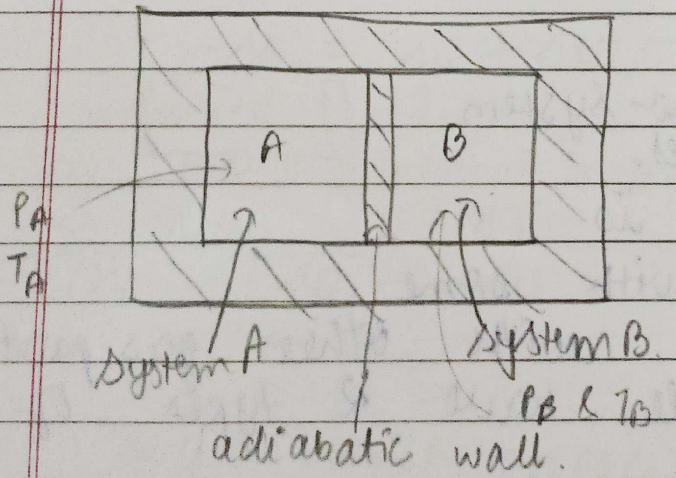
* Boundary = The imaginary wall that separates system & surrounding.

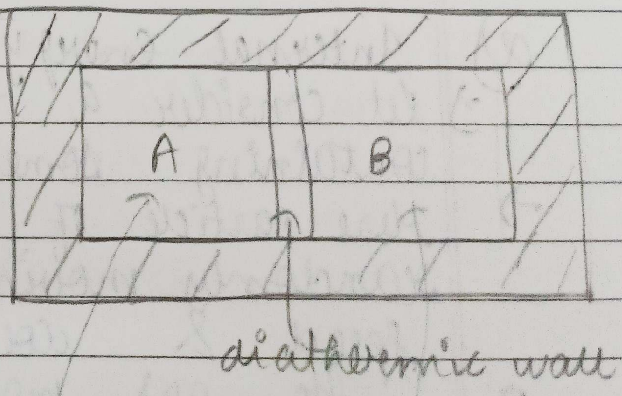
→ Two types of boundary

(i) Adiabatic wall :- there is no heat flow b/w system & surrounding through this wall.

(ii) Diathermic wall :- There is heat exchange b/w system & surrounding through this type of wall.

* Thermal equilibrium :-





$T_A' = T_B'$

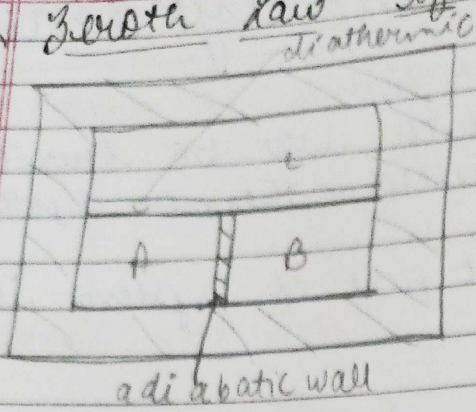
P_A' P_B'

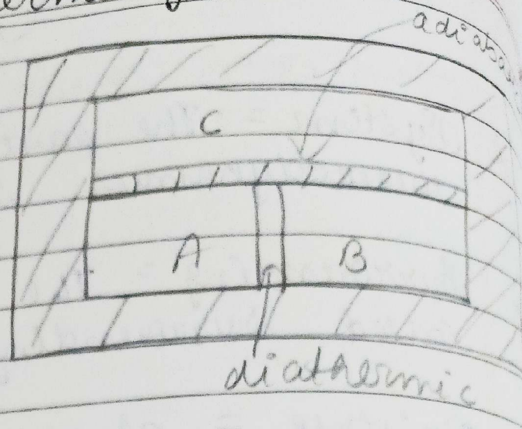
→ equilibrium

→ State variables don't change.

R H Fowler

* Zeroth Law of Thermodynamics :-





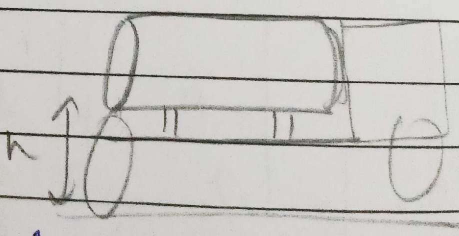
→ $T_A = T_C$
$T_B = T_C$ } $T_A = T_B$

→ Two systems in thermal equilibrium with a third system separately are in thermal equilibrium with each other.

* Heat, Internal energy & Work

1) Heat → The energy transported due to temp. difference from high temp. to low temp. is called heat.

2) Internal energy
→ Let us consider a thermo-system containing some gases.



→ Here particle of gas is randomly moving with some speed & collide with other gas particles.
→ So gas molecule have 2 types of associated energy.

if t. const. T K.E. (internal) const. → associated with temp.

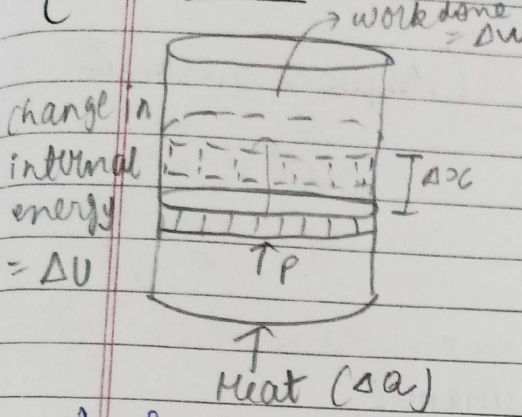
(i) Kinetic energy :- due to random motion.
(ii) Potential energy :- due to intermolecular forces

1 cal = 4.186 J

- extra :- Internal energy of ideal gas :

⇒ For ideal gas, no inter-forces act b/w gas particle. So, there is no P.E. Only K.E.

3) Work :-



→ Let we give heat to thermo-cylindrical system with piston.

→ So piston move by Δx due to inside pressure P.

→ Here force exerted on piston due to P pressure is

$F = PA$ ← area of piston

⇒ So, work done

$w = F\Delta x$

$= \underbrace{PA\Delta x}_{\text{change of volume} = \Delta V}$

$\boxed{W = P\Delta V}$

$\boxed{W = \int P dV}$

* First law of thermodynamics :-

$$\underbrace{\Delta Q}_{\text{exchanged heat}} = \underbrace{\Delta U}_{\text{change in internal energy}} + \Delta W \leftarrow \text{work done}$$

Now $\Delta W = P\Delta V$

So, $\boxed{\Delta Q = \Delta U + P\Delta V}$

* Specific heat capacity of water :-

⇒ Heat required to rise temp. of water from ~~1°C~~ 14.5°C to 15.5°C is called 1 calorie.

⇒ 1cal = 4.186 J.

⇒ Heat capacity of water is 1 cal/gK or $4.186 \frac{J}{gK}$

⇒ Specific heat capacity of water is not const. It depends on temperature.

IMP

* **Prove that $C_p - C_v = R$.** (Mayer's Formula)

$\Delta Q = \mu C \Delta T$

$C_p = \left(\frac{\Delta Q}{\Delta T}\right)_P$

⇒ For 1 mol ideal gas ΔQ

$$C_p = \left(\frac{\Delta Q}{\Delta T}\right)_P \quad \& \quad C_v = \left(\frac{\Delta Q}{\Delta T}\right)_V$$

⇒ From 1st law of thermodynamic.

$$\Delta Q = \Delta U + P\Delta V \quad —①$$

For const. volume. $(\because \Delta V = 0)$

$$\Delta Q = \Delta U$$

So, $\left(\frac{\Delta Q}{\Delta T}\right)_V = \left(\frac{\Delta U}{\Delta T}\right)_V$

So, $C_v = \left(\frac{\Delta Q}{\Delta T}\right)_V = \left(\frac{\Delta U}{\Delta T}\right)_V$

⇒ For ideal gas eq^n

$$PV = \mu RT \quad (\mu = 1)$$

$$\therefore PV = RT$$

at const. pressure.

$$P\Delta V = R\Delta T$$ ↓ put in ①

⇒ From ①

$$\Delta Q = \Delta U + R\Delta T$$

$$\left(\frac{\Delta Q}{\Delta T}\right)_P = \left(\frac{\Delta U}{\Delta T}\right)_P + R$$

⇒ but $\left(\frac{\Delta Q}{\Delta T}\right)_P = C_p$

So, $C_p = \left(\frac{\Delta U}{\Delta T}\right)_P + R$ — ②

⇒ Internal energy only depends on temperature
So,

$$\left(\frac{\Delta U}{\Delta T}\right)_V = \left(\frac{\Delta U}{\Delta T}\right)_P = C_V \quad — ③$$

→ from ② & ③

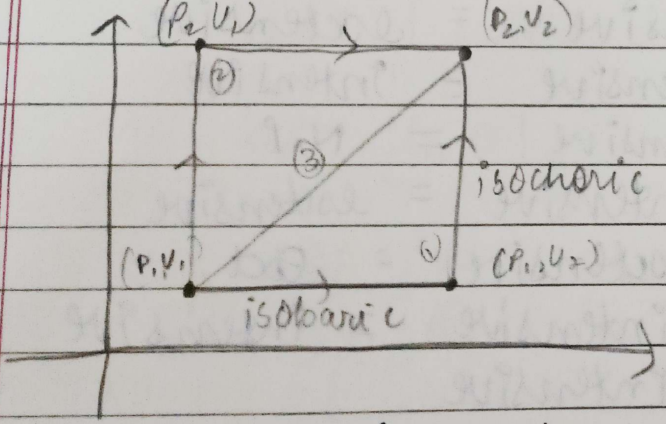
$C_p = C_v + R$

∴ $\boxed{C_p - C_v = R}$

* Thermodynamic State variables :-

→ The variables which describe thermodynamic state is called thermo. state variables.
eg. Pressure, volume, Temp., internal energy.

→ These variables are also called state funⁿ which depends on initial & final state & not on how the state is gained.



in all the 3 cases Internal energy is equal.

⇒ Path dependent function :-

⇒ The thermo-dynamic variable which depends on path to attain new thermo-dynamic state that variable is path dependent...
eg :- Heat & work.

⇒ The eqⁿ which represent inter relation b/w thermo-variable is called thermo-state equation.
eg :- $PV = \mu RT$.

* extensive state variable :

⇒ The state variable which depends on size of thermo. system.

ex :- volume, mass, internal energy, no. of moles

* Intensive state variable :-

⇒ The state variable which does not depend on size of system.
eg :- Temp., pressure, density.

⇒ To remember :-
extensive ± extensive = extensive
intensive ± intensive = intensive
extensive ± intensive = N.P
extensive × Intensive = extensive
extensive × extensive = ext.
intensive × intensive = intensive

$$\frac{\text{extensive}}{\text{extensive}} = \text{Intensive}$$

$$\frac{\text{intensive}}{\text{intensive}} = \text{intensive}$$

- * Isothermal process } Temp. remains const.
- * Adiabatic process } There is no heat exchange.
- * Isobaric process } const. pressure
- * Isochoric process } const. volume
- * Cyclic process } ex:- carnot cycle.

* Isothermal process:-

→ Temp. remains constant

→ $P_1, V_1, T \longrightarrow P_2, V_2, T$

→ During this process

work $W = \int_{V_1}^{V_2} P\,dV$

From ideal gas eq^n. $PV = \mu RT$

So, $P = \frac{\mu RT}{V}$

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

$$= \mu RT \int_{V_1}^{V_2} \frac{1}{V}\,dV$$

$$= \mu RT \left[\ln V\right]_{V_1}^{V_2}$$

$$= \mu RT \left(\ln V_2 - \ln V_1\right)$$

So, $\boxed{\mu RT \ln \frac{V_2}{V_1}}$

From ① $P_1V_1 = P_2V_2$

So, $\frac{V_2}{V_1} = \frac{P_1}{P_2}$

So, $\boxed{W = \mu RT \ln\left(\frac{P_1}{P_2}\right)}$

⇒ For Isothermal process

$\Delta U = 0$ $(\because \text{Temp.} = \text{const})$

⇒ So, from 1st law of thermodynamic,

$$\Delta Q = \Delta U + \Delta W$$

OR

$$Q = \Delta U + W \quad (\because \Delta U = 0)$$

$$\therefore \boxed{Q = W}$$

- **Isothermal expansion :-**

$V_2 > V_1$

$\ln \frac{V_2}{V_1} > 0$

$W > 0$ } work done by system

$Q > 0$ } ~~work done on~~ system
Heat absorb by

compression

- **Isothermal expansion :-**

$V_2 < V_1$

$\ln \frac{V_2}{V_1} < 0$; $Q < 0$

$W < 0$ } work done on system

$Q < 0$ } Heat lose by system.

* Adiabatic process :-

→ No heat exchange

→ $P_1, V_1, T_1 \longrightarrow P_2, V_2, T_2$

→ Work done is $W = \int_{V_1}^{V_2} P\,dV$ — ①.

⇒ For adiabatic process

$PV^r = \text{constant}$. ⇒ $P = \frac{\text{const}}{V^r}$ (put in ①)

where $r = \frac{C_P}{C_V} > 1$

So, $P_1 V_1^r = P_2 V_2^r = \text{const.}$ — ②

So, $W = \int_{V_1}^{V_2} \frac{\text{const}}{V^r}\,dV$

$= \text{const.} \int_{V_1}^{V_2} V^{-r}\, dV$

$= \text{const.} \left[\frac{V^{-r+1}}{-r+1}\right]_{V_1}^{V_2}$

$= \frac{\text{const.}}{-(r-1)} \left[\frac{1}{V^{r-1}}\right]_{V_1}^{V_2}$

$= \frac{\text{const}}{-(r-1)} \left[\frac{1}{V_2^{r-1}} - \frac{1}{V_1^{r-1}}\right]$

$= \frac{1}{r-1} \left[\frac{\text{Const.}}{V_1^{r-1}} - \frac{\text{const.}}{V_2^{\gamma-1}}\right]$

from ②

$= \frac{1}{\gamma-1} \left[\frac{P_1 V_1^{r}}{V_1^{r-1}} - \frac{P_2 V_2^{r}}{V_2^{\gamma-1}}\right]$

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

from ideal gas eq^n.

$P_1 V_1 = \mu R T_1$ & $P_2 V_2 = \mu R T_2$

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

So, $\boxed{W = \frac{\mu R}{r-1} [T_1 - T_2]}$

⇒ from 1st law of thermo.

$Q = \Delta U + W$

(but $Q = 0$ ∵ adiabatic

$\therefore \Delta U = -W$.

(i) if $T_1 > T_2$	(ii) If $T_2 > T_1$
$W > 0$	$W < 0$
$\Delta U < 0$	$\Delta U > 0$

* Isochoric process

→ Volume is constant in this process
→ $P_1, V_1, T_1 \rightarrow P_2, V_2, T_2$
∴ $V = \text{const.}$
∴ $P_1, V, T_1 \rightarrow P_2, V, T_2$

→ work done
$W = \int P dV$ but $dV = 0$
so, $W = 0$.

→ From 1st law of thermo.
$Q = \Delta U + W$
So, $\boxed{Q = \Delta U}$

(i) If $T_1 > T_2$ } temp decrease
$\Delta U < 0$ } heat lose
$Q < 0$ } by system

(ii) If $T_1 < T_2$ } temp. increase
$\Delta U > 0$ } heat gain
$Q > 0$ } by system.

* Isobaric Process :-

→ Pressure → constant.
→ $P, V_1, T_1 \rightarrow P, V_2, T_2$
So, work done

$$W = \int_{V_1}^{V_2} P dV = P \int_{V_1}^{V_2} dV$$

$$= P [V]_{V_1}^{V_2}$$

$$\boxed{W = P(V_2 - V_1)}$$

So, $W = PV_2 - PV_1$

from ideal gas eqn :
$PV_1 = \mu R T_1$ & $PV_2 = \mu R T_2$
So, $W = \mu R T_2 - \mu R T_1$

So, $\boxed{W = \mu R (T_2 - T_1)}$

→ From I^{st} law of thermo.

$Q = \Delta U + W$

Let $T_1 > T_2$ } temp. decrease

$\Delta U < 0$

work done on system } $W < 0$

heat loose by system } $Q < 0$

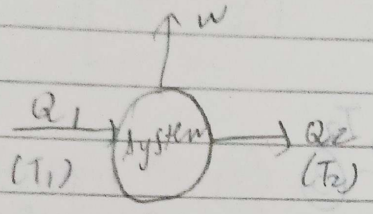
Let $T_2 > T_1$ } temp. increase

$\Delta U > 0$

$W > 0$ } work done by the system

$Q > 0$ } heat gain by system.

* Heat engine (vehicle)



$Q_1 = W + Q_2$

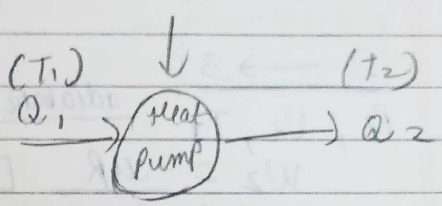
$W = Q_1 - Q_2$

efficiency $\eta = \frac{W}{Q_1}$ $0 < \eta < 1$

$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$

never greater than 100%.

* Heat pump (A.C)



$Q_1 + W = Q_2$

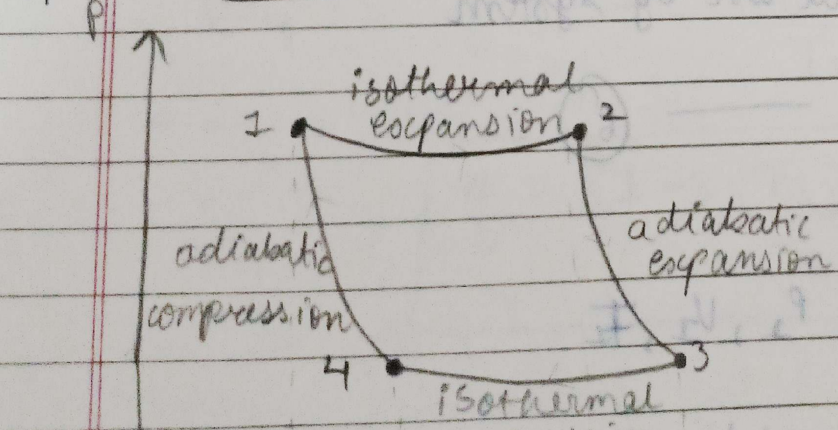
$W = Q_2 - Q_1$

may be greater 0

Performance coefficient $\alpha = \frac{Q_1}{W} > 0$

$= \frac{Q_1}{Q_2 - Q_1}$

* Carnot Engine :-



$\Delta Q = \Delta U + \Delta W$

$\Delta Q = \Delta W$

- $\boxed{1 \rightarrow 2}$

$\rightarrow P_1, V_1, T_1 \xrightarrow{\text{iso. exp.}} P_2, V_2, T_1$

$W_1 = \mu R T_1 \ln\left(\frac{V_2}{V_1}\right)$, And, $P_1V_1 = P_2V_2$ —— ②

But for isothermal process

$Q_1 = W_1 = \mu R T_1 \ln\left(\frac{V_2}{V_1}\right)$ —①

Here $V_2 > V_1$

so, $Q_1 > 0$ } Heat absorb by system

- $\boxed{2 \rightarrow 3}$

$P_2, V_2, T_1 \xrightarrow{\text{adiabatic exp.}} P_3, V_3, T_2$

$W_2 = \frac{\mu R}{\gamma - 1}\left[T_1 - T_2\right]$ —— ③

And $P_2V_2^{\gamma} = P_3V_3^{\gamma}$ —— ④

- $\boxed{3 \rightarrow 4}$

$P_3, V_3, T_2 \xrightarrow[\text{comp.}]{\text{isothermal}} P_4, V_4, T_2$

$W_3 = \mu R T_2 \ln\left(\frac{V_4}{V_3}\right)$

But for isothermal process

$Q_2 = W_3 = \mu R T_2 \ln\left(\frac{V_4}{V_3}\right)$ —— ⑤

Here $V_4 < V_3$

so, $Q_2 < 0$ } heat lose by system

And, $P_3V_3 = P_4V_4$ —— ⑥.

- $\boxed{4 \rightarrow 1}$

$P_4, V_4, T_2 \xrightarrow[\text{comp.}]{\text{adiabatic}} P_1, V_1, T_1$

$W_4 = \frac{\mu R}{\gamma - 1}\left[T_2 - T_1\right] = -W_2$

And. $P_4V_4^{\gamma} = P_1V_1^{\gamma}$ — ⑦

Here total work done

$$W = W_1 + W_2 + W_3 + W_4$$
$$= W_1 + W_2 + W_3 - W_2$$
$$= W_1 + W_3$$
$$= \mu R T_1 \ln\left(\frac{V_2}{V_1}\right) + \mu R T_2 \ln\left(\frac{V_4}{V_3}\right)$$

⇒ So, efficiency η

$$\eta = \frac{W}{Q_1} = \frac{\mu R T_1 \ln\left(\frac{V_2}{V_1}\right) + \mu R T_2 \ln\left(\frac{V_4}{V_3}\right)}{\mu R T_1 \ln\left(\frac{V_2}{V_1}\right)}$$

$$\eta = 1 + \frac{T_2 \ln(V_4/V_3)}{T_1 \ln(V_2/V_1)} \quad \text{———} \quad ⑧$$

⇒ From ②, ④, ⑥ & ⑦

$$P_1V_1 \, P_2V_2^{r} \, P_3V_3 \, P_4V_4^{r} = P_2V_2 \, P_3V_3^{r} \, P_4V_4 \, P_1V_1^{r}$$

$$V_2^{r-1} \, V_4^{r-1} = V_1^{r-1} \cdot V_3^{r-1}$$
$$V_2 V_4 = V_1 V_3$$
$$\frac{V_4}{V_3} = \frac{V_1}{V_2} \quad \text{———} \quad ⑨$$

Now from ⑧ & ⑨

$$\eta = 1 + \frac{T_2 \ln(V_1/V_2)}{T_1 \ln(V_2/V_1)}$$

So, $$\eta = 1 - \frac{T_2 \ln(V_2/V_1)}{T_1 \ln(V_2/V_1)}$$

$$\therefore \quad \boxed{\eta = 1 - \frac{T_2}{T_1}}$$ //