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THERMODYNAMICS (deals with energy and transformation)

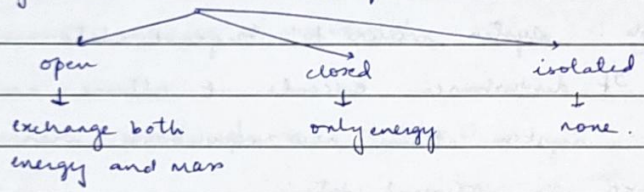
→ Microscopic :- start at molecular level

→ Macroscopic :- don't consider microscopic

Heat :- Energy transfer due to finite temperature difference

→ heat ≠ work

System :- refers to definite quantity of matter enclosed by a boundary on which we focus.



→ Intensive property → independent of mass. Eg:- BP, MP, P, T

→ Extensive property → depends on mass Eg:- V

Energy

Microscopic mode

↓

Internal energy (U)

molecules move with independent velocities at random.

Energy possessed by random motion of molecules i.e translational energy ($\frac{mv^2}{2}$), rotational energy ($\frac{I\omega^2}{2}$).

Individual atoms vibrates - vibrational energy. In atoms electrons orbit around the nucleus and some energy associated with coloumbic interactions.

→ All of these contribute to U

Macroscopic mode

PE, KE → macroscopically

↙ mgz ↘ $\frac{1}{2}mv^2$

Work done on the body in raising its elevation (or) Compressed spring → due to its location or configuration

Energy possessed by the virtue of its motion.

PE + KE = mechanical energy

$E = PE + KE + U$

Heat and work are energies in transit → capable of crossing system boundaries __/__/____

Equilibrium → absence of driving force.

- Thermal ↓ no further change in the thermal state → no temp gradient
- Mechanical ↓ no imbalance of forces on the system → no pressure gradient
- Chemical ↓ no tendency for chemical reaction or mass transfer → Equality of chemical potential

→ Meta stable: system returns to original state when subjected to small change. If disturbance exceeds, it attains new equilibrium

→ Unstable: system attains new equilibrium when disturbed. Does not return to original state.

→ Stable: reaches to original state when disturbed.

Work done: Work done by a system if by manipulating the surrounding a mass can be lifted against gravity. It can be electrical, mechanical. (transfer of energy through some forces measurable.)

Free expansion: $W = 0$, $dV \neq 0$

→ $W \neq 0$, $dV = 0$ possible (cyclic process)

→ $W = pdV$ Expansion work done = −ve

1st law of thermodynamics (closed system) Work done by the system = +ve. heat given = +ve.

In a cyclic process, the amount of work done on the system is equal to the energy transferred as heat from the system (nothing about spontaneity or feasibility)

$$\oint dQ = \oint dW$$

(Perpetual motion machine of first kind)

Consequence: $dE = dQ - dW$ (net energy transfer; net change in energy of a system)

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Reversible process:-

→ Change from one stable equilibrium state to another stable equilibrium state.

→ Both the system and surroundings can be restored to their respective original states by reversing the direction of process

→ quasi static process:- takes very slowly and with infinitesimal driving force

→ Every reversible process is quasi static but vice versa is not true.

→ spontaneous changes → irreversible

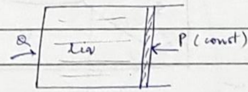
→ isomeric → const volume → $dV = 0$

→ $Q = 0$, $W_e \neq 0$ (electrical) → $\Delta U = W_e$; $\Delta U = Q - W$

$\Delta U = nC_v\Delta T$ (heat capacity at const volume.)

→ Vigorously stirred → T↑ W increases T no Q

→ Isobaric → const P.

→ 

If energy is added as heat to the liq, temp and pressure of system remains const. (Vapourisation occurs) just phase change.

→ $W = P(\Delta V)$

$dU = dQ - dW = dQ - PdV$.

$H = U + PV$ → at const P → $Q = H$ → enthalpy

$dH = -dW_s$ → shaft work or electrical → $dQ = 0$ (enthalpy)

$\Delta H = C_p\Delta T$ (ideal gas)

Adiabatic system → no change in thermal energy across the boundary.
It can be achieved by insulation.

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Adiabatic process

enclosed by an insulated boundary.

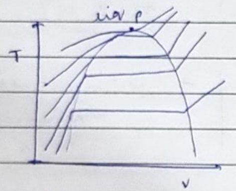
$dU = -dW$

Work done by the gas decreases internal energy.

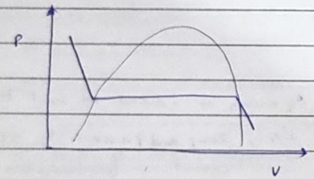
→ $\gamma = \frac{C_p}{C_v}$ = ratio of specific heats PV^{γ} = const
↳ adiabatic

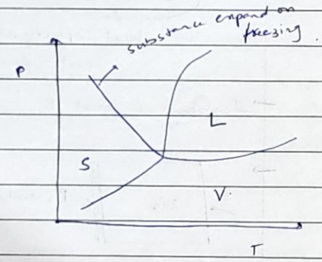
→ Isothermal - const temp
↓
If we are compressing a gas, its temp will tend to increase. So we need to arrange a cold source. So the system attains its original temp.
(Isothermal compression) ✓

For pure liquids



P = critical point





→ -ve slope for H_2O → P v/s T
↳ regelation → P↑, melting of ice ↓
$d_{H_2O} > d_{ice}$ ↳ when we press two ice cubes, they join

adiabatic v/s insulation

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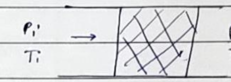
Throttling process (irreversible adiabatic process)

check
Why P↓
Velocity ↑, P↓
↳ check ??

When a fluid flows steadily from high pressure to low pressure, through a porous plug or partially opened valve inserted in a long horizontal pipe and insulated pipe, the enthalpy remains constant (isoenthalpic process)



obstruction to the flow
↳ Area ↓, velocity ↑
∴ P↓

$\dot{Q} = 0$ / $\dot{W}_s = 0$

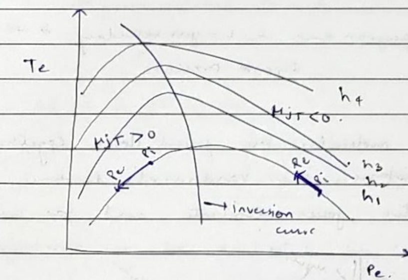
→ ignoring the change in velocity. $\Delta KE = 0$

→ One can generate isenthalpic curve → T_{exit}, P_{exit} → diff
($P_i > P_e$) ✓
($T_i > T_e$) ✓

$\dot{m} h_i = \dot{m} h_o$

$h_i = h_o$

→



P_i, T_i are fixed.
→ curve

→ $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_h$
↓
Joule Thomson expansion coeff

at very high P → $\mu_{JT} < 0$ → $T_i < T_e$, $P_i > P_e$
→ repulsive forces dominate
internal energy ↑, T↑

at moderate pressure → $\mu_{JT} > 0$
attractive forces dominate
↳ gas uses its own energy and frictional losses to overcome attractive forces
∴ gas cools down

temp ↓
$T_i > T_e$
$P_i > P_e$

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Critical point :- end pt of phase equilibrium diagram i.e co-existence of vapor - liq.

① Critical temp.
The temperature above which whatever pressure is applied, a gas cannot be cooled

② Critical Pressure
Pressure at critical temp

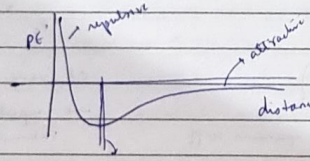
→ Inversion temp :-

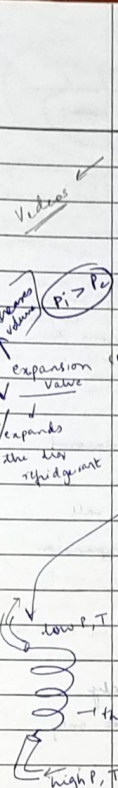
→ Supercritical fluid :- above the critical point where liq, gas distinction is difficult.

→ Stokis fluid → internal energy = internal KE

→ clausius clapeyron eqn → L-gas boundary ⇒ to calculate Vapour Pressure

→ gas to liq :- molecules are forced closer together at some point in distance, the vanderwaal's distance is reached. The attractive forces dominate and gas will change to liq





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Properties of refrigerant : low BP, non-corrosive, high conductivity, low freezing pt

Refrigerator cycle

HVAC → heating, ventilation and air conditioning

→ throttling :- fluid is passed through narrow channel. Provided no interaction

$\dot{W}_s = 0$

$dQ = 0 \Rightarrow dU = -dW$

$U_2 - U_1 = -(P_2 V_2 - P_1 V_1)$

$U_2 + P_2 V_2 = U_1 + P_1 V_1$ $\quad h_2 = h_1$

→ performance can be evaluated by coeff of performance (COP)

$COP = \frac{\text{heat absorbed} \rightarrow \text{output}}{\text{Power in}}$

→ Frost might form in the refrigerator coil (evaporator) → Efficiency to heat transfer ↓

(no heating coil is present to defrost → that is why we have water droplets)

→ capacity of refrigerator is measured in terms of Litre
↳ shows how much food can be stored.
↳ total interspace.

Freon — refudgerant
↳ dangerous for environment
↳ depletes ozone layer
CFCs
↳ green house gas

variable speed
motor ~~speed~~

AC cycle — same as refudgerator

→ ~~Warm air enters~~ ~~in with the help of blower.~~ compressor speed, flow rate
→ It absorbs heat from surroundings → evaporator and cooling capacity
→ rotating evaporator blower → ✓

expansion valve — some part of the liq ~~evapor~~ evaporates and this energy is supplied by the liq itself
∴ temp drops

→ TON = capacity → how much heat is absorbed from the room

→ evaporator → Temp < room Temp

→ Temp of air is low ∴ we will require pipe for removal
↳ water will condense on the evaporator

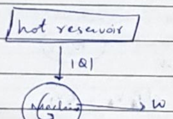
→ Compressors cannot handle liq ∴ to make sure all the liq is converted to vapour → Thermostatic expansion valve is used

Second law of thermo

Kelvin-planck statement

It is impossible to devise a cyclic machine, which solely absorbs energy in the form of heat and converts it to only work

doesn't violate 1st law

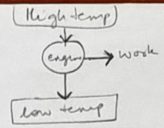


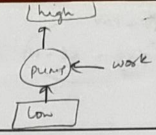
(perpetual motion machine of second kind)

→ Heat engine requires min 2 reservoirs
to absorb energy as heat from source and convert it into work and reject heat to sink

→ heat cannot be only taken to do work, without cooler reservoir

PMMFK → first kind
impossible
produce work indefinitely without any input of energy
Violates 1st law → as energy can neither be created nor destroyed.





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Carnot ?? heat engine

Clausius statement

Heat energy cannot be transferred from cold body to hot without any work done/effect

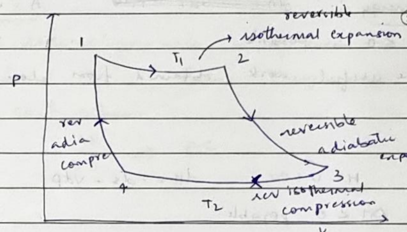
→ Work done$|_{rev}$ ≥ W_{irr}
↳ slow and more no. of steps.

↗ No cycle is as efficient as carnot cycle.

Carnot cycle → Ideal reversible closed thermodynamic cycle with 4 operations
reverse carnot cycle → refridgerator

① isothermal expansion
② adiabatic expansion
③ isothermal compression
④ adiabatic compression

heat engine
↓
converts thermal energy to mechanical work.



(each step is reversible ↳ so overall cycle is reversible)

Heat pump

$\sum \frac{\delta Q_i}{T_i} = 0$ → cyclic reversible process

2nd law spontaneity
↓
whether a particular engine/pump is possible or not
by introducing entropy

→ Clausius inequality :- $\oint \frac{\delta Q_{irr}}{T} < 0$.

$\frac{\sum dQ}{T} = 0$ → reversible

$\eta_{irr} < \eta_{rev}$

→ Entropy → associated with state of disorder, randomness or uncertainty

→ state function → $ds = \left(\frac{dQ}{T}\right)_R$ → reversible

$\Delta S_{sys} = \int \frac{\delta Q}{T}$ → reversible

$\Delta S > 0$ → process is feasible and spontaneous } universe
$\Delta S = 0$ → reversible
$\Delta S < 0$ → not feasible

Gibbs free energy $G = H - TS$ $dG = Vdp - SdT$ tells about
$(\Delta G)_{sys} \leq 0$ → spontaneous Quantity which spontaneity (non PV)
It tells us about max amount of non-expansion work that can be extracted from a thermodynamically closed system at const T,P (reversible work).
It is minimized when a sys reaches equilibrium.
at equilibrium $\Delta G_{sys} = 0$ $\Delta G < 0$ → if process is spontaneous

Helmholtz energy :- ~~$dA = -SdT - PdV$~~ $A = U - TS$
$\Delta A \leq 0$ → possible
measures the useful work obtained from closed system at const T (const T,V)

MAGU Thermodynamic potential

Enthalpy :- $H = U + PV$ $dH = Tds + Vdp$
$\Delta H \leq 0$ possible
heat absorbed or evolved during a process at const P

→ Mollier chart → H v/s S
→ chemical potential :- Gibbs free energy or chemical energy per mole of substance.
(depends on T, P (conc.))
molar gibbs free energy
↓ It defines change of gibbs free energy when particles corresponding to component change
equilibrium relationship, mass transfer properties

$dU = TdS - PdV$

Third law :- (perfect crystal)
entropy of the system approaches to a const value 0 as its temp approaches to absolute 0
→ It is impossible to bring the entropy of a given system to zero in a finite no: of operations

$$\Rightarrow \Delta S = \int \frac{dQ}{T}$$

Zeroth law
If two thermodynamic systems are each in equilibrium with third one, Then they are in thermal equilibrium with each other
A B, B C ⇒ A C

→ VLE :- No change in macroscopic properties with time
equilibrium ⇒ thermal, mechanical, chemical between two phases

$ds \geq \int \frac{dQ}{T}$ closed system

Entropy is a state function. does not depend on whether the process is reversible or not