Thermodynamics GATE

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1. Basic Concepts & Zeroth Law of Thermodynamics

Macroscopic Approach

- Average molecular behaviour considered
- **Continumm** concept should be valid
    - Matter is continuously distributed
    - In case of gases, the **Mean Free Path** (average distance travelled by molecule between two successive collisions) should be less than system dimensions.

Quasistatic process - Infinitely slow process.

- All reversible processes are quasistatic, but not all quasistatic processes are reversible.
- Frictionless quasistatic process is reversible
- Properties of a system are Exact differentials

Intensive properties

- Independent of mass
- All specific properties like, specific volume, specific heat are Intensive properties.
- Density is also an intensive property.
- Intensive properties when divided will still be the same.

Extensive properties

- Dependent on mass
- When divided will be half as before.

Temperature Scales :-

$$\boxed{\frac{t_c - 0}{100 - 0} = \frac{t_F - 32}{212 - 32}}$$

- Converting Degree Celcius to Fahrenheit $\implies$ $\boxed{t_f = \frac{9}{5}t_c + 32}$

- **Note:** $\boxed{\Delta t_F = 1.8\Delta t_C}$

Gibbs Phase rule :-

- $\boxed{P + F = C + 2}$

→ P = Number of Phases
→ F = Degree of Freedom
→ C = Number of chemical components

→ Mixture of Refrigerants which behave as pure substance is called **Azeotrope**

→ Mixture of Air and Liquid air is not a pure substance

→ **Extensive properties are additive**, meaning extensive property's whole is the sum of parts of the extensive property.

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2. Energy and Energy Interactions

→ The molecular weight of air is approximamtely taken as 29. Air is approx 77% of N_2 and 23% O_2 by weight. So,

$$\boxed{0.77 * 28 + 0.23 * 32 = 28.92 \approx 29}$$

Ideal Gas Equation

- $PV = mRT$ Where,
  - P = Pressure
  - V = Volume
  - m = Mass
  - R = Characteristic Gas Constant
  - T = Temperature
- Also $PV = n\bar{R}T$ Where,
  - n = Number of Kilo moles
  - $\bar{R}$ = Universal Gas Constant = 8.314 $^{KJ}/_{KmolK}$

- Now, R for Air is calculated as: $R_{Air} = \dfrac{\bar{R}}{m_{Air}} = \dfrac{8.314}{29} = 0.287^{KJ}/_{KmolK}$

→ $\boxed{mass(m) = number\ of\ moles(n) * Molecular\ mass(M)}$

Work - (+ve = Done by system, -ve = Done on system)
- The work done by a **reversible process or closed system process** is the area under the curve in a P-V diagram.
- The work done in a **reversible cycle or closed system cycle** is the area enclosed by the curve in a P-V diagram.
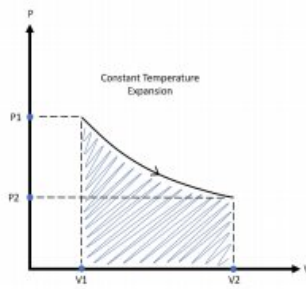

Work in various Quasi-static processes

1. Constant Volume - Isochoric - Isometric process $\implies$ $\boxed{W_{1-2} = 0}$
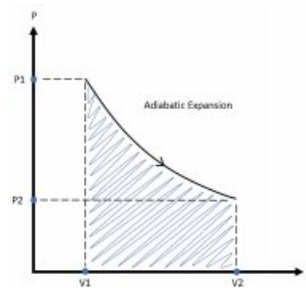
2. Constant Pressure - Isobaric - Isopiestic process $\implies$ $\boxed{W_{1-2} = \int_1^2 PdV = P(V_2 - V_1)}$
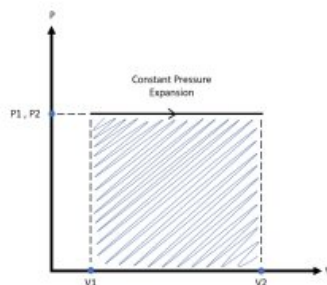
3. Constant Temperature - Isothermal - Hyperbolic process $\implies$ $\boxed{W_{1-2} = P_1 V_1 \ln \dfrac{V_2}{V_1} = P_1 V_1 \ln \dfrac{P_1}{P_2}}$

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4. Adiabatic process - $\boxed{W_{1-2} = \dfrac{P_1 V_1 - P_2 V_2}{\gamma - 1}}$ $\boxed{\dfrac{T_2}{T_1} = \left(\dfrac{P_2}{P_1}\right)^{\frac{\gamma}{\gamma - 1}} = \left(\dfrac{V_1}{V_2}\right)^{\gamma - 1}}$

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5. Polytropic process - $\boxed{W_{1-2} = \dfrac{P_1 V_1 - P_2 V_2}{n - 1}}$ $\boxed{\dfrac{T_2}{T_1} = \left(\dfrac{P_2}{P_1}\right)^{\frac{n}{n - 1}} = \left(\dfrac{V_1}{V_2}\right)^{n - 1}}$

Heat - (+ve = Transferred to system, -ve = Rejected from system)

- The Heat transfer in a **reversible process** is the area under the curve in a T-S diagram
- The Heat transfer in a **reversible cycle** is the area enclosed by the curve in a T-S diagram.
- The specific heats (Cp and Cv) of monoatomic gas is constant with temperature. They vary for Di and tri atomic gases
- We know $\boxed{\dfrac{C_P}{C_V} = \gamma}$. But γ can also be calculate in another way: $\boxed{\gamma = 1 + \dfrac{2}{n}}$

    - n = Degree of freedom, T = Translational, R = Rotational
    - n = 3 for mono atomic gases [3T]
    - n = 5 for di atomic gases [3T+2R]
    - n = 6 for tri atomic gases [3T+3R]
- Heat capacity of the substance = Mass * Specific Heat
- LATENT HEAT

    - It is the Amount of Heat required to cause phase change in unit mass of any substance. It is of three types:
    - **Latent heat of fusion** (L_f) $\rightarrow$ Not much affected by pressure

    – **Latent heat of vapourization** $(L_V) \to$ Highly sensitive to pressure.

    – **Latent heat of sublimation**

    – **Very important thing to note is that, in these phase change scenarios, even when heat transfer is taking place, the temperature of the system remains constant**

    – consider the scenario where a solid at temperature T_1 is to be converted into vapour at temperature T_2. The freezing temperature is T_f and the boiling temperature is T_V. The total heat required for this conversion to occur is calculated as follows: Here $(T_1 < T_f)$, $(T_2 > T_V)$

      * Heat added to rasie temp from T_1 to T_f: $\boxed{Q_1 = mC_1(T_f - T_1)}$

      * Heat added for phase change from Solid to Liquid: $\boxed{Q_2 = mL_f}$

      * Heat added to raise temp from T_f to T_V: $\boxed{Q_3 = mC_2(T_V - T_f)}$

      * Heat added for phase change from Liquid to Vapour: $\boxed{Q_4 = mL_V}$

      * Heat added to raise temp from T_V to T_2: $\boxed{Q_5 = mC_3(T_2 - T_V)}$

      * Here, C_1, C_2, C_3 are specific heats of the substance in Solid, Liquid and Gaseous phases respectively.

      * Total heat required for the aforementioned conversion is the sum of all the above heats from Q_1 to Q_5

- Increasing of order of slopes for the following processes in P-V diagram:

$$\boxed{\textbf{Isothermal} < \textbf{Polytropic} < \textbf{Adiabatic}}$$

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3. First Law of Thermodynamics

First Law :-

- $dE = dU + dK.E. + dP.E.$

- $\delta W = \delta W_{PdV} + \delta W_{shaft} + \delta W_{elec}$

- $\delta Q = dE + \delta W$ for process

  $\implies$ $\boxed{\delta Q = dU + \delta W}$ for stationary process

- $\delta Q = \delta W \impliedby$ [for cycle $(dU = 0)$]

- $U(Internal\ energy), H(Enthalpy) = f(T)$ only for an ideal gas.

Heat Transfer in Various processes :-

CONSTANT VOLUME

- from first law, $\delta Q = dU + \delta W \implies dU + PdV \implies dU + 0$

- $\implies \delta Q = dU = mC_V \Delta T$

CONSANT PRESSURE

- **Enthalpy**(H) = U + PV

- In constant pressure proces, from First law, $\delta Q = dU + \delta W \implies dU + PdV \implies dU + dPV \implies d(U + PV) = dH$

- $\implies \delta Q = dH = mC_p \Delta T \impliedby$ applicable in cases of constant pressure process or Ideal gas involving any process

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CONSTANT TEMPERATURE

- In case of constant temperature, dU = 0. So, $\delta Q = \delta W$

- **NOTE:** The above is not possible due the limitations of second law.

- Since, its adiabatic, $\delta Q = 0 \implies W = -dU = U_1 - U_2$

Polytropic Heat transfer

- $Q_{poly} = W_{poly} * \left(\dfrac{\gamma - n}{\gamma - 1} \right) \implies \boxed{\dfrac{P_1 V_1 - P_2 V_2}{n - 1} * \left(\dfrac{\gamma - n}{\gamma - 1} \right)}$

- Specific heat for polytropic process, $\boxed{C_{poly} = -C_V * \left(\dfrac{\gamma - n}{n - 1} \right)}$

- the above is derived using the first law and Meyer's equation: $C_P - C_V = R$. This relation is derived from the definition of enthalpy as H = U + PV $\implies mC_P dT = mC_V dT + mR dT$

  $\implies C_V = \dfrac{R}{\gamma - 1}$ and $C_P = \dfrac{\gamma R}{\gamma - 1}$

- Polytropic specific heat being negative implies that even though heat is added to the gas, its temperature decreases because the work done by the gas exceeds the heat supplied to the gas and the additional work is done at the expense of the internal energy

- Generally $1 < n < \gamma$

Free Expansion of gases

- The free expansion process is **highly irreversible**

- When partition is removed the internal energy of the fluid gets used as Kinetic energy

- When the particles hit the walls of the container and reaches the equilibrium, the Kinetic energy gets converted back into Internal energy

- Even though the Initial and final internal energy is same, meaning Initial and final temperature is same, the process is not isothermal, because when the fluid is expanding with Kinetic energy, the temperature varies.

- **Note:** Instead of partition, if there is movable frictionless piston, it is **not the case of free expansion**, as the fluid is doing work on the piston. here also the final and initial temperature will be same.

4. Open System Analysis by First Law

$$\boxed{\textbf{SFEE} \implies U_1 + P_1 V_1 + \dfrac{C_1{}^2}{2} + gZ_1 + Q = U_2 + P_2 V_2 + \dfrac{C_2{}^2}{2} + gZ_2 + W_{CV}}$$

Steady Flow systems

- Fluid properties can change from point to point within the control volume, but they don't change with respect to time

- The volume, mass and total energy of the control volume remain constant. As a result, the displacement work is zero as V is constant.

- Mass balance equation: Mass incoming = Mass outgoing. That is $\boxed{\displaystyle\sum_{inlet} \dot{m}_i = \sum_{outlet} \dot{m}_e}$

- **NOTE:** In case of Air as the fluid, the continuity equation is $\boxed{\rho_1 A_1 V_1 = \rho_2 A_2 V_2}$

- **NOTE:** But in case of Liquids(Incompressible fluids), the continuity equation is $\boxed{A_1 V_1 = A_2 V_2}$

Nozzle & Diffusers

- Assumptions:

    - $\Delta PE = 0$ i.e $Z_1 - Z_2 = 0$
    - Adiabatic process (Nozzle is insulated) $\implies$ Q=0;
    - $W_{CV} = 0$

- So, SFEE = $\boxed{h1 + \dfrac{C_1{}^2}{2} = h2 + \dfrac{C_2{}^2}{2}}$

- **NOTE:** Generally the enthalpies in the sum will be given in KJ/kg which has to be converted to J/Kg to get the velocities in m/s.

Turbine and Compressors

- Assumptions:

    - Insulated $\implies$ Q = 0;
    - Flow velocities are negligible $\implies$ C1 = C2 = 0;
    - $Z_2 - Z_1$ also negligible $\Delta PE = 0$

- So, SFEE = $\boxed{h_1 = h_2 + W_{CV}}$

- For Turbines, W_{CV} is positive. For compressor, its negative.

Throttling (Pressure drop)

- Assumptions

    - Adiabatic $\implies$ Q = 0;
    - No workdone $\implies$ $W_{CV} = 0$
    - K.E. = 0 & P.E. = 0

- So, SFEE $\implies$ $\boxed{h_1 = h_2}$ - Since the enthalpy at inlet and outlet are same, the throttling valves are referred to as **Isenthalpic valves**

- Dryness friction(x)

    - SFEE $\implies$ $\boxed{h_1 = h_f + x(h_g - h_f)}$

Heat Exchangers

- Assumptions

    - Heat exchange is within the CV. So, no heat interactions with the surroundings. $\implies$ Q = 0;
    - No workdone $\implies$ $W_{CV} = 0$
    - K.E. = 0 & P.E. = 0

- So, SFEE for (non-contact type - hot and cold fluid do not mix)

$$\implies \boxed{\dot{m}_c h_1 + \dot{m}_h h_2 = \dot{m}_c h_3 + \dot{m}_h h_4}$$

- So, SFEE for (contact type - hot and cold fluid mix) $\implies$ $\boxed{\dot{m}_1 h_1 + \dot{m}_2 h_2 = \dot{m}_3 h_3}$

Comparison of SFEE with Euler and Bernoulli's equation

$$\textbf{SFEE} \implies U_1 + P_1 V_1 + \frac{C_1{}^2}{2} + gZ_1 + Q = U_2 + P_2 V_2 + \frac{C_2{}^2}{2} + gZ_2 + W_{CV}$$

$$\implies H_1 + \frac{C_1{}^2}{2} + gZ_1 + Q = H_2 + \frac{C_2{}^2}{2} + gZ_2 + W_{CV}$$

$$\implies h_1 + \frac{C_1{}^2}{2} + gZ_1 + \delta q = h_2 + \frac{C_2{}^2}{2} + gZ_2 + \delta w_{CV}$$

where $h_1, h_2 \ \delta q$ and δw_{CV} are specific quantities, i.e., they are divided by mass(m)

$$\implies \delta q = -h_1 + -\frac{C_1{}^2}{2} + -gZ_1 + h_2 + \frac{C_2{}^2}{2} + gZ_2 + \delta w_{CV}$$

$$\implies \delta q = (h_2 - h_1) + \frac{C_2{}^2 - C_1{}^2}{2} + g(Z_2 - Z_1) + \delta w_{CV}$$

- $(h_2 - h_1) = dH$

- $(z_2 - z_1) = dz$

- $\dfrac{C_2{}^2 - C_1{}^2}{2} = CdC$

- **Assumptions:**

  - Insulated. $\implies \delta q = 0$
  - No Work done $\implies \delta w_{CV} = 0$
  - Temperature remains constant $\implies du = 0$
  - Fluid is incompressible $\implies dv = 0$

$$\implies 0 = dh + CdC + gdZ + 0$$
$$= du + Pdv + vdP + CdC + gdZ$$
$$= 0 + 0 + \boxed{vdP + CdC + gdZ} --- Euler's\ form\ of\ SFEE$$

Integration of the above between two section will give the Bernoulli's form of SFEE:

$$\boxed{\frac{P_1}{\rho} + \frac{C_1{}^2}{2} + gZ_1 = \frac{P_2}{\rho} + \frac{C_2{}^2}{2} + gZ_2}$$

Unsteady flow

- The rate at which mass of fluid within the control volume is accumulated is equal to the net rate of mass flow across the control surface $\implies \dfrac{dm_{cv}}{dt} = \dot{m}_i - \dot{m}_e$

- Similarly $\implies \dfrac{dE_{cv}}{dt} = \dot{E}_i - \dot{E}_e$

- So, $\boxed{\dfrac{dE_{cv}}{dt} = \left\{ \dot{m}_i \left(h_i + \frac{C_i{}^2}{2} + gZ_i \right) + \dot{Q} \right\} - \left\{ \dot{m}_e \left(h_e + \frac{C_e{}^2}{2} + gZ_e \right) + \dot{W}_{CV} \right\}}$

- The above is called the **First law of thermodynamics for an open system with Unsteady flow**

- If the above system is stationary, then $\implies \boxed{\dfrac{dE_{cv}}{dt} = \dfrac{dU_{cv}}{dt} = \dot{m}_i h_i + \dot{Q} - \dot{m}_e h_e - \dot{W}_{CV}}$

Charging of tank

- a supply line carrying a fluid in connected to a **rigid, isolated and evacuated** tank.

- No changes in K.E. and P.E.

- No Work done

- No heat interactions (as Insulated)

- Since there is no exit, the rate of change of mass inside the tank is given by:

$$\implies \frac{dm_{CV}}{dt} = \dot{m}_i \quad \implies \frac{dU_{CV}}{dt} = \dot{m}_i h_i$$

- Assuming h_i as constant and integrating will give us:

$$\implies (U_f - U_i)_{CV} = h_i (m_f)_{CV} \quad (U_i = 0, \ U_f = u_f * m_f)$$

$$So, \ \boxed{u_f = h_i} \quad (u_f = c_v * T_f, \ \ h_i = c_p * T_f)$$

$$\implies \boxed{T_f = \gamma * T_i}$$

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5. Second Law of Thermodynamics

Thermal Energy Reservoir (TER)

- A hypothetical body with large heat capacity (mass * SpecificHeat) that can supply or absorb large amounts of heat with not much change in its temperature. Example: The air in a room with a TV as a heating source can be considered as a TER

Heat engines

- Rotating a paddle shaft in water will increase the internal energy of the water, which will later leave the water as heat. So, work gets converted into heat naturally.

- But the reverse requires usage of special devices called **Heat engines** which takes in heat as input and produce work.

- There are different types of heat engines, but they have common charateristics like, they absorb heat from a source, **convert a part of it as work and reject remaining** to the sink

- **Example:** Steam powerplant is a heat engine. It has five major components: Furnace, Boiler, Turbine, Condenser, Pump. The boiler takes in heat from the furnace, heats up the water to convert it to steam, the steam runs the turbine and generate work, then gets condensed back to water by the condenser and the pump pushes the water back into the boiler.

Thermal Efficiency (η)

- The ratio of fraction of heat that gets converted as work, to the total heat input to the boiler is called as the Thermal efficiency of the Heat engine.

- $\boxed{\eta = \dfrac{W_{net}}{Q_{supplied}}}$

- δQ_{net} = Amount of heat supplied to boiler(Q_1) - Amount of heat rejeted from condenser(Q_2)

- δW_{net} = Amount of Work produced by Turbine(W_1) - Amount of work required by pump to get water back to boiler pressure(W_2)

- In a cyclic process, $\Delta U = 0$. So, according to first law, $\delta Q = \delta W \implies \delta Q_{net} = \delta W_{net}$

- So, $\eta = \dfrac{W_{net}}{Q_1} \implies \dfrac{Q_{net}}{Q_1} \implies \dfrac{Q_1 - Q_2}{Q_1} \implies \boxed{1 - \dfrac{Q_2}{Q_1}}$

- Thermal efficiency of 100 percent is impossible in reality. For $\eta = 100\%$ Q_2 has to be Zero. I.e., There must be zero heat loss and all of heat input should be converted to work.

Kelvin-Planck Statement

- *" It is impossible for a system to operate in a thermodynamic cycle and deliver a net amount of energy by work to its surroundings while receiving energy by heat transfer from a single reservoir "*

- In simple terms, Thermal efficiency can never be 100%.

Perpetual Motion Machine

- **PMM - I**: A machine that violates first law of thermodynamics - Producing work without Heat. $\implies \delta Q \neq \delta W$

- **PMM - II**: A machine that violates second law of thermodynamics (Kelvin-planck) - 100% Thermal efficiency

- **PMM - III**: A machine that works continuously without any heat or work interaction with the surrounding. This is possible only in the complete absence of all forms of irreversibitlies.

Refrigerators and Heat pumps

- Heat tranfer from high temp to low temp can occur naturally. But for the reverse to occur, special devices like **Refrigerator or Heat pump** is required.

  - REFRIGERATOR
    * Like Heat engine which uses water as the working fluid, refrigerators use refrigerants as working fluid. **Vapor compression refrigeration** is one of the most commonly used process.
    * It has four main components: Compressor, condensor, expansion valve (capillary tube) and evaporator.
    * The refrigerant enters the compressor (the compressor requires external work) and gets its pressure increased. Then it enters the condensor where its temperature decreases by rejected heat to the surrounding. Then it goes through an expansion valve, where due to throttling its pressure and temperature drop significantly. Then the refrigerant enters the evaporator where it absorbs heat from the surrounding and re-enters the compressor.
    * Q_L - Amount of heat removed from refrigerated space which is at temperature T_L
    * Q_H - Amount of heat rejected from condensor to surrounding which is at a temperature of T_H
    * W_{net} - Work input to the compressor.
    * $Q_H - Q_L = W_{net} \implies \boxed{Q_H = W_{net} + Q_L}$
    * $\boxed{COP_R = \dfrac{Desired\ effect}{Work\ input} \implies \dfrac{Q_L}{W_{net}} \implies \dfrac{Q_L}{Q_H - Q_L}}$

  - HEAT PUMPS
    * Heat pump is another device that transfers heat from low temp to high temp. But the operation objective of heat pump is different from that of refrigerator as it is used to make the place warmer than surroundings whereas refrigerator makes a space colder than surroundings.
    * $\boxed{COP_H = \dfrac{Q_H}{W_{net}} \implies \dfrac{Q_H}{Q_H - Q_L}}$ **NOTE:** $\boxed{COP_H = COP_R + 1}$

Clausius Statement :-

- Heat pumps and refrigerators are based on clausius statement of second law of thermodynamics

- *" It is immpossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to a higher temperature body "*

- In simple terms, Transfer of heat from low temperature to high temperature without the aid of an external agency is impossible.

- According to Clausius statement, **NOTE:** COP_H and COP_R can never be ∞

Reversible process :-

- They do not occur in nature due to second law of thermodynamics.

- They need to be carried out infinitely slowly (Quasi-static)

- Since they don't occur in nature, devices imagined to be performing reverible processes have the best efficiency compared to the ones performing Irreversible processes. It applies to both work-producing as well as work-consuming devices.

- concept of reversibility leads to **Second Law efficiency** for actual processes which tells by what percent the process is like a reversible process.

- **Internally Reversible**: If in a process, the system can be brought to its original state, then its called Internally Reversible

- **Externally Reversible**: If in a process, the surrounding can be brought to its original state, then its called Externally reversible

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Irreversible process :-

- Factors like friction, free expansions, inelastic deformation, etc., create irreversibilites in processes.

- **Friction** - a brick is in contact with the floor. Moving the brick requires force which should be greater than the friction force between the brick and the floor. When applied force is higher than the firctional force, the brick will start moving. But since there is friction, heat will be generated due to motion, and this in turn will rasie the temperature of the body. Now if we try to bring back the body to its original position, still some more amount of heat will be generated since frictional force is always opposite to the direction of motion. Those heats that were generated will get dissipated into the surrounding (considereing the brick to be the system).
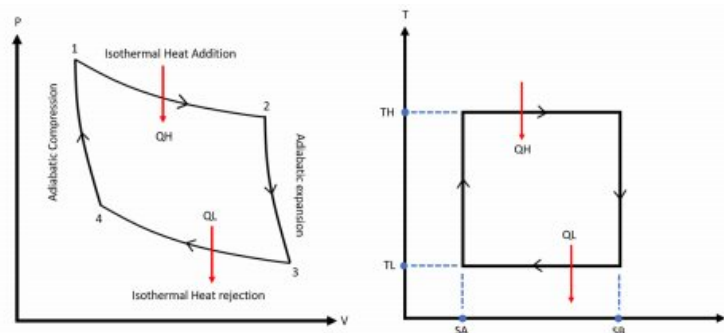

Carnot Cycle :-

- Carnot cycle is composed of an **adiabatic piston cyclinder with gas inside**

- Processes:

    - (1-2) Reversible isothermal heat addition: $\boxed{Q_H = (U_2 - U_1) + W_{1-2}}$

    - (2-3) Reversible adiabatic expansion: $\boxed{0 = (U_3 - U_2) + W_{2-3}}$

    - (3-4) Reversible isothermal heat rejection: $\boxed{-Q_L = (U_4 - U_3) - W_{3-4}}$

    - (4-1) Reversible adiabatic compression: $\boxed{0 = (U_1 - U_4) - W_{4-1}}$

- Carnot cycle cannot be used in actual devices because it becomes impractical to have a reversible isothermal heat transfer process, cause the heat transfer has to occur between infinitesimally small temperature difference and infinitely slowly.

- A practical and slightly modified version of the carnot cycle is the **Rankine cycle** used in Steam plants.

Reversed Carnot Cycle :-

- If all the process in carnot cycle is reversed, we obtain what is called a reversed carnot cycle or **Carnot Refrigeration cycle** which can be used for Heat pumps and refrigerators

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Carnot Principles :-

- **Principle I:** $\boxed{\eta_{Rev} > \eta_{Irr}}$ for operation between the same temperature range

- **Principle II:** Efficiencies of all reversible engines working between the same temperature range are equal

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Thermodynamic Temperature scale :-

- A temperature scale independent of the properties of the substances that are used to measure the temperature.

- From carnot's principle II, the efficiency is dependent on the operating temperature range only, i.e,. $\boxed{\eta_{REV} = f(T_H, T_L)}$

- We know $\eta = 1 - \dfrac{Q_L}{Q_H}$. This can be written as: $\eta = 1 - \dfrac{\Phi(T_L)}{\Phi(T_H)}$. Kelvin suggested, $\Phi(T) = T$.

- So, $\boxed{\eta = 1 - \dfrac{T_L}{T_H}}$

- And since η cannot be 1, the lowest possible temperature for T_L is Zero. Hence the Kelvin scale is called as absolute scale.

- **NOTE:** We now know $\boxed{\dfrac{Q_L}{Q_H} = \dfrac{T_L}{T_H}}$ So, inorder to reach absolute zero, we would need heat rejected to the sink to be zero which would violate the Kelvin-planck statement of second law.

Maximum performance measures for cycles operating between two reservoirs :-

- EFFECT OF TEMPERATURE ON PERFORMANCE OF **reversible** DEVICES

  - **Heat engine** $\implies \boxed{\eta = 1 - \dfrac{T_L}{T_H}} \implies \eta \uparrow$ for $T_L \downarrow$ (or) $T_H \uparrow$.

  - Decreasing the $T_L \downarrow$ is more effective than increasing the $T_H \uparrow$

  - **Refrigerator** $\implies \boxed{COP_R = \dfrac{T_L}{T_H - T_L} = \dfrac{1}{\left(\dfrac{T_H}{T_L} - 1\right)}} \implies COP_R \uparrow$ for $T_L \uparrow$ (or) $T_H \downarrow$

  - **Heat Pump** $\implies \boxed{COP_H = \dfrac{T_H}{T_H - T_L} = \dfrac{1}{\left(1 - \dfrac{T_L}{T_H}\right)}} \implies COP_H \uparrow$ for $T_L \uparrow$ (or) $T_H \downarrow$

  - For Refrigerator and Heat pump, increasing the $T_L \uparrow$ is more effective rather than decreasing the $T_H \downarrow$
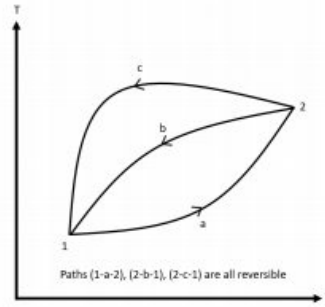
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6. Entropy

Clausius Inequality :-

- Entropy is a measure of Irreversibility

- Clausius inequality $= \boxed{\oint \dfrac{\delta Q}{T} \leq 0} \implies \boxed{\oint \dfrac{\delta Q}{T} = 0} \quad \boxed{\oint \dfrac{\delta Q}{T} < 0} \quad \boxed{\oint \dfrac{\delta Q}{T} > 0}$

  $\qquad\qquad\qquad\qquad\qquad\qquad\quad$ Reversible $\qquad$ Irreversible $\qquad$ Impossible

<u>**The property of Entropy :-**</u>

- Just like how energy was defined using first law, entropy can be defined using clausius inequality.

Paths (1-a-2), (2-b-1), (2-c-1) are all reversible

- So, $\int\limits_{2b1} \dfrac{\delta Q}{T} = \int\limits_{2c1} \dfrac{\delta Q}{T}$, which means $\left(\dfrac{\delta Q}{T}\right)_{rev}$ must represent a property, which we are defining as Entropy(S).

- $S_2 - S_1 = \Delta S = \int\limits_{1}^{2} dS = \int\limits_{1}^{2} \left(\dfrac{\delta Q}{T}\right)_{rev}$ (Only for Reversible processes)

- **NOTE:** We have defined change in entropy instead of entropoy just like how we defined change in energy instead of energy itself.

- Entropy is **Extensive** property

<u>**Entropy Increase :-**</u>

- If in the above diagram, **had the path C been irreversible**, Then

- $\oint\limits_{1a2b1} \dfrac{\delta Q}{T} = 0$ but, $\oint\limits_{1a2c1} \dfrac{\delta Q}{T} < 0$ as it is irreversible.

- $\int\limits_{2b1} \dfrac{\delta Q}{T} > \int\limits_{2c1} \dfrac{\delta Q}{T} \implies \int\limits_{1}^{2} dS > \int\limits_{2c1} \dfrac{\delta Q}{T}$

- Which can be generalized as: $\boxed{dS \geq \dfrac{\delta Q}{T}}$

- The entropy change is equal to heat transfer in case of reversible process and in case of irreversible process, it is greater than it, which implies that **some entropy is generated during an irreversible process**.

- So, $\boxed{\Delta S_{sys} = S_2 - S_1 = \int\limits_{1}^{2} \dfrac{\delta Q}{T} + \boldsymbol{S_{gen}}}$ S_{gen} is always ≥ 0. S_{gen} is a measure of magnitude of irreversibilities

- **NOTE:** Unlike entropy, which doesn't depend on the path, the $\boldsymbol{S_{gen}}$ is a path function so it depends on the path.

- In case of an **Isolated system**, $\boxed{\Delta S_{sys} = S_{gen}}$ and since S_{gen} is always positive, the entropy of the universe always increases or incase of the never naturally occuring reversible process, it could remain constant, **but it could never decrease**. This is called **Increasing entropy principle**

- **NOTE:** The above principle does not mean that change in entropy cannot be negative. It only means that entropy generation can never be negative.

- **NOTE:** Since entropy is an extensive property, total entropy = sum of parts of entropies of the system.

$$\implies \boxed{S_{gen} = \Delta S_{univ} = \Delta S_{isolated} = \Delta S_{total} = (\Delta S_{Sys} + \Delta S_{Surr}) \geq 0}$$

T-S diagram :-

- We know $\boxed{dS = \left(\dfrac{\delta Q}{T}\right)_{rev}}$. So, $\boxed{\delta Q_{rev} = TdS}$ $\impliedby$ **Very important!!**

- $\implies$ $\boxed{Q_{rev} = \int\limits_{1}^{2} Tds}$. Therefore, we can say area under the curve on a T-S diagram represent the heat transfer during a reversible process.

- In case of an adiabatic process, there is no heat transfer, so
  - i. Reversible adiabatic $\implies$ dS = 0. $\impliedby$ Isentropic process
  - ii. Irreversible adiabatic $\implies$ dS = S_{gen}

- From first law, $\delta Q = dU + \delta W$ and now we know, for a reversible process, $\delta Q = TdS$ & $\delta W = PdV$. So, $\boldsymbol{TdS = dU + PdV}$

- And for a reverible cyclic process, $\boldsymbol{TdS = PdV}$ as dU is zero in a cyclic process. So, for a cyclic process, **net heat interaction = net work interaction**

T-dS Relations :-

1. $\boxed{TdS = dU + PdV}$

2. $\boxed{TdS = dH - VdP}$ $\impliedby$ ($H = U + PV \implies dH = dU + PdV + VdP \implies dH = TdS + VdP$)

- **NOTE:** Even though the above relation is developed based on reversibility, since entropy is a point function, the above relations hold good for irreversible processes as well.

- They can be applied to both closed / open systems as well.

Slopes of Isobaric and Isochoric processes in T-S diagram :-

- For an Isochoric / Constant volume process, V = Constant. So, $TdS = dU + PdV \implies TdS = dU + 0 \implies TdS = mC_V dT$

  $\implies$ $\boxed{\dfrac{dT}{dS} = \dfrac{T}{C_V}}$ $\impliedby$ $\left(\dfrac{dT}{dS} = Slope\ of\ a\ curve\ in\ TS\ diagram.\right)$

- For an Isobaric / Constant pressure process, P = Constant, So, $dH = TdS + VdP \implies dH = TdS + 0 \implies mC_p dT = TdS$

  $\implies$ $\boxed{\dfrac{dT}{dS} = \dfrac{T}{C_P}}$

- Since, $C_P > C_V \implies \boxed{\dfrac{T}{C_P} < \dfrac{T}{C_V}}$ $\implies$ Slope of Constant Pressure < Slope of Constant Volume in TS diagram.

Entropy Change for an Ideal gas :-

- $\boxed{S_2 - S_1 = C_V \ln \dfrac{P_2}{P_1} + C_P \ln \dfrac{V_2}{V_1}}$

- Derived using TDS equations, $dH = mC_P dT$, $dU = mC_V dT$ and $PV = mRT$

Entropy Change for an imcompressible substance :-

- For most liquids and solids the density does not change and hence $dv \approx 0$

- On the above pretext, $Tds = du + Pdv = du = 0$

- $du = cdT$ where, for incompressible substance, $c_p = c_v = c$

- So, $\boxed{Tds = cdT} \implies ds = \dfrac{cdT}{T} \implies s_2 - s_1 = \int\limits_1^2 ds = \int\limits_1^2 \dfrac{cdT}{T} \implies c\ln\dfrac{T_2}{T_1}$

- Total Change in Entropy$(dS) = m(s_2 - s_1) = \boxed{S_2 - S_1 = mc\ln\left(\dfrac{T_2}{T_1}\right)}$

- From the above, **NOTE:** The change in entropy for an imcompressible substance is zero in case of an isothermal process.

Finite Body analysis :-

Mixing of two incompressible fluids or solids brought into contact

- An adiabatic enclosure with two subsystems each with an incompressible fluid separated by a partition.
    - Subsystem 1: m_1, C_1, T_1
    - Subsystem 2: m_2, C_2, T_2

- Partition removed, the two fluids mix and attain a final temperature(T_f)

- Applying first law to the whole system: $Q = \Delta U + W$. But here, Q=0 and W=0. As the system is adiabatic and no boundary work.

    $\implies \Delta U = 0 \implies \Delta U_1 + \Delta U_2 = 0 \implies m_1 C_1(T_f - T_1) + m_2 C_2(T_f - T_2) = 0$

    $\implies \boxed{T_f = \dfrac{m_1 C_1 T_1 + m_2 C_2 T_2}{m_1 C_1 + m_2 C_2}}$

- and Since, the system is adiabatic, $S_{gen} = \Delta S_{Sys} + \Delta S_{Surr} \implies \Delta S_{Sys} + 0$ (as no heat goes to the surrounding)

- $S_{gen} = \Delta S_{univ} = \Delta S_1 + \Delta S_2$ and since they are assumed incompressible $\implies \boxed{m_1 C_1 \ln\left(\dfrac{T_f}{T_1}\right) + m_2 C_2 \ln\left(\dfrac{T_f}{T_2}\right)}$

- **Special Case:** $\boxed{m_1 = m_2 = m}$ and $\boxed{C_1 = C_2 = C}$

    $\implies \Delta S_{Sys} = mC\ln\left(\dfrac{T_f^2}{T_1 T_2}\right) = 2mC\ln\left(\dfrac{T_f}{\sqrt{T_1 T_2}}\right) = 2mC\ln\left(\dfrac{A.M}{G.M.}\right) = nmC\ln\left(\dfrac{A.M}{G.M}\right)$

    $\implies$ A.M $= \boxed{T_f = \dfrac{T_1 + T_2 + ...T_n}{n}}$ and G.M. $= \boxed{\sqrt[n]{T_1 T_2 ...T_n}}$

Maximum work obtainable from two finite bodies operating between T_1 and T_2 :-

- **Body 1:** m_1, C_1, T_1 and **Body 2:** $m_2, C_2, T_2 (T_2 < T_1)$

- Heat exchange through a reversible heat engine and heat exchange only till they both attain T_f - common Final Temperature

- Q_1 - Heat rejected from body 1 and Q_2 - Heat gained by body 2 $\boxed{W = Q_1 - Q_2}$

- From first law, $Q = dU + W$ and W $= 0$ (no boundary work)

- $Q_1 = m_1 C_1(T_1 - T_f)$ and $Q_2 = m_2 C_2(T_f - T_2) \implies W = m_1 C_1(T_1 - T_f) - m_2 C_2(T_f - T_2)$ ... **Eqn(1)**

- Here $\Delta S_{Surr} = 0$ since no heat interaction with the surrounding (But work interaction is present)

- So, $\Delta S_{Univ} = \Delta S_1 + \Delta S_2 + \Delta S_{Engine} \impliedby (\Delta S_{engine} = 0\ as\ it\ is\ a\ cyclic\ device)$

- $\Delta S_{Univ} \implies \boxed{m_1 C_1 \ln\left(\dfrac{T_f}{T_1}\right) + m_2 C_2 \ln\left(\dfrac{T_f}{T_2}\right)}$ and for $W_{max} \implies \Delta S_{Univ} = 0$

- Solving for T_f in the above and plugging it in Eqn(1) will give W_{max}

- **Special Case:** $\boxed{m_1 = m_2 = m}$ and $\boxed{C_1 = C_2 = C}$ $\implies$ $\boxed{T_f = \sqrt{T_1 T_2}}$ $\implies$ $\boxed{W_{max} = mC\left(T_1 + T_2 - 2\sqrt{T_1 T_2}\right)}$

$\rightarrow$ CASE A: Two incompressible body exchanging energy and no work extracted

$\rightarrow$ CASE B: Two incompressible body exchanging energy and max work extracted.

* The $(T_f)_A > (T_f)_B$ and if there was another CASE C: in which due to irregularities only a part of the maximum work was extracted then $(T_f)_C$ will be between that of A and B

Reversible Steady Flow Work :-

- We know that the differential form of SFEE is $\boxed{\delta q = dh + CdC + gdZ + \delta W_{CV}}$

- For a reversibible process, from clausius inequality and entropy definition, $\delta q = Tds$ and from TdS relations, $Tds = dh - vdP \implies \delta q = dh - vdP$

- $\implies dh - vdP = dh + CdC + gdZ + \delta W_{CV} \implies -vdP = CdC + gdZ + \delta W_{CV}$

- if $\Delta K.E = \Delta P.E = 0 \implies \delta W_{CV} = -vdP \implies W_{CV} = -\int vdP$

- The term $-\int vdP$ represents **the area under between the P-axis and the curve on a P-V diagram** and gives us the value of reversible adiabatic work in a steady flow system for both work producing and work consuming devices

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Open system work for various reversible processes:-

- Constant volume - Isochoric - Isometric

$\implies \boxed{W_{CV} = v(P_2 - P_1)}$

- Constant Pressure - Isobaric - Isopiestic

$\implies \boxed{W_{CV} = 0}$ since, dP is 0.

- Constant Temperature - Isothermal - Hyperbolic

$\implies \boxed{W_{CV} = P_1 v_1 \ln \frac{P_2}{P_1}}$

- Adiabatic

$\implies \boxed{W_{CV} = \frac{\gamma\left(P_1 v_1 - P_2 v_2\right)}{\gamma - 1}} = \gamma * W_{closed} \impliedby W_{CV} = -\int_1^2 \left(\frac{P_1 v_1}{P}\right)^{1/\gamma} dP \impliedby \boxed{P_1 v_1^\gamma = P v^\gamma}$

- Polytropic

$\implies \boxed{W_{CV} = \frac{n\left(P_1 v_1 - P_2 v_2\right)}{n - 1}} = n * W_{closed} \impliedby W_{CV} = -\int_1^2 \left(\frac{P_1 v_1}{P}\right)^{1/n} dP \impliedby \boxed{P_1 v_1^n = P v^n}$

Second Law analysis of a control volume :-

- $\left(\dfrac{dS}{dt}\right)_{CV} = \dot{S}_{in} - \dot{S}_{out} + \dot{S}_{gen}$

Steady-state steady flow process :-

- The above equation can be simplified to $\left(\dfrac{dS}{dt}\right)_{CV} = 0$ in case of steady flow.

- $\implies 0 = \left(\dot{m}s_i + \dfrac{\dot{Q}}{T} \right) - \dot{m}s_e + \dot{S}_{gen} \implies \boxed{\dot{m}(s_e - s_i) = \dfrac{\dot{Q}}{T} + \dot{S}_{gen}}$

- For more than one inlet and exit: $\boxed{\sum \dot{m}_e s_e - \sum \dot{m}_i s_i = \sum \dfrac{\dot{Q}}{T} + \dot{S}_{gen}}$

Available energy (Exergy) :-

- **Availability** - The maximum useful work that can be obtained.

- **Dead state** - Thermodynamic equilibrium with the surrounding

- If a reversible process is carried out that takes the system to a dead state, then the work output / required of that process is maximum / minimum.

- So the available energy is a function of:

    i. Total energy of the system
    ii. State of the system
    iii. State of the surrounding

- CLASSIFICATION OF SOURCE OF ENERGY

    - **High Grade:** High grade energy is totally available for work and is exempt from the limitation of second law. Eg.Work
    - **Low Grade:** Only a part of low grade energy can be converted to useful work due to the limitation of second law and this is called availability. Eg.Heat

- Exergy$(W) = Q\eta = Q \left[1 - \dfrac{T_0}{T} \right] = Q - T_0 \Delta S = \boxed{(T - T_0)\Delta S} \impliedby$ carnot engine operating between T and T_0

Heat transfer through a finite temperature difference :-

- Exergy decreases when heat transfers through a finite temperature difference

- Consider the following:

    - **CASE 1:** A carnot engine operating between two reservoirs at temp T_1 and T_2. $(T_1 > T_2)$
    $\implies$ Available work $(W_1) : Q_1 - Q_{R1} = (T_1 - T_2) * \Delta S_1$
        * $Q_1 =$ Amount of heat absorbed from reservoir at T_1
        * $Q_{R1} =$ Amount of heat rejected to reservoir at T_2

    - **CASE 2:** Now same carnot engine operating between two reservoirs at temp T_2 and T_3 $(T_2 > T_3)$ and the reservoir at T_2 is receiving heat(Q_1) from another reservoir at a temperature T_1 $(T_1 > T_2)$
        * Still the heat input the engine is Q_1
        * $Q_1 = T_1 \Delta S_1 = T_2 \Delta S_2 \impliedby$ but $T_1 > T_2$
        * So, $\Delta S_2 > \Delta S_1$. Also, $Q_{R1} = T_0 \Delta S_1$ and $Q_{R2} = T_0 \Delta S_2 \implies \boxed{Q_{R2} > Q_{R1}}$
        * $W_2 = Q_1 - Q_{R2}$ and $W_1 = Q_1 - Q_{R1} \implies \boxed{W_2 < W_1}$

- Thus due to irreversibilities in heat transfer between finitie temperature difference, exergy decreases

- Loss of A.E. $= W_1 - W_2 = Q_{R2} - Q_{R1} = T_0(\Delta S_2 - \Delta S_1) \impliedby$ here, $\boxed{(\Delta S_2 - \Delta S_1) = S_{gen}}$

- $\boxed{Loss\ of\ A.E.\ or\ U.A.E\ = T_0(S_{gen})}$

- According to First law, Thermal energy at higher temperature is same as compared to thermal energy at lower temperature. That's what this means: $Q_1 = T_1 \Delta S_1 = T_2 \Delta S_2$. Hence the first law is called **Quantitative law**

- But, Accordign to Second law, Thermal energy at higher temperature is more significant than thermal energy at lower temperature. This is evident from Q_{R1} being lesser than Q_{R2} as we want the heat rejection to be as minimal as posisble. Hence second law is called **Qualitative law**

Availability and Availability Function :-

- Consider:
  - Ambient Pressure (P_0)
  - Ambient Temperature (T_0)
  - Initial Volume of system (V_1)
  - Final Volume of system (V_0)
  - Final Pressure of system (P_0)

- Available work: $W_{max} - P_0(V_0 - V_1)$

- From first law, $\delta Q = dU + \delta W \implies \delta W = TdS - dU \impliedby$ since $\boxed{\dfrac{\delta Q}{T} = dS}$ for reversible process

- $W_{max} = T_0(S_0 - S_1) - (U_0 - U_1) \implies T_0S_0 - T_0S_1 - U_0 + U_1 \implies \boxed{W_{max} = (U_1 - T_0S_1) - (U_0 - T_0S_0)}$

- Available work: $(U_1 - T_0S_1) - (U_0 - T_0S_0) - P_0V_0 + P_0V_1 \implies (U_1 + P_0V_1 - T_0S_1) - (U_0 + P_0V_0 - T_0S_0)$

- Available work or Availability: $\Phi_1 - \Phi_0 \impliedby \boxed{\Phi = (U + P_0V - T_0S)}$

- Change in Availaility $= \Phi_1 - \Phi_2$ for a system that undergoes a state change from 1 to 2.

- We know from SFEE, $\boxed{\dot{m}\left(h_i + \dfrac{C_i{}^2}{2} + gZ_i\right) + \dot{Q} = \dot{m}\left(h_e + \dfrac{C_e{}^2}{2} + gZ_e\right) + \dot{W}_{CV}}$

- $\implies \dot{W}_{CV} = \dot{m}\left(h_i + \dfrac{C_i{}^2}{2} + gZ_i\right) + \dot{Q} - \dot{m}\left(h_e + \dfrac{C_e{}^2}{2} + gZ_e\right)$

- $S_{gen} = 0 = \dot{m}(s_e - s_i) - \dfrac{\dot{Q}}{T} \implies \dot{Q} = \dot{m}T_0(s_e - s_i)$

- $\implies \dot{W}_{CV} = \dot{m}\left(h_i + \dfrac{C_i{}^2}{2} + gZ_i\right) - \dot{m}\left(h_e + \dfrac{C_e{}^2}{2} + gZ_e\right) - \dot{m}T_0(s_i - s_e)$

- $\dot{W}_{CV} = \dot{m}\left[(h_i - h_e) + \dfrac{C_i{}^2 - C_e{}^2}{2} + g(Z_i - Z_e) - T_0(s_i - s_e)\right]$

- Here, Availability function $(\Phi) = h + \dfrac{C^2}{2} + gZ - T_0s \implies \dot{W}_{CV_{max}} = \dot{m}(\Phi_i - \Phi_e)$

- **NOTE:** For open system, Maximum work = Maximum useful work

- **NOTE:** For closed system, Maximum work = Maximum useful work + Atmospheric work

Irreversibility :-

- $I = W_{rev} - W_{actual} = W_{max} - W_{actual}$

- For non-flow processes, $I = (\Phi_1 - \Phi_2) - W_{actual}$

- Upon deriving we obtain, for both flow and non-flow processes: $\boxed{I = T_0(\Delta S_{Univ}) = T_0 S_{gen}}$ and $I \geq 0$

- **Gouy-Stodola Theorem:** $\dot{I} = T_0\left(\dot{S}_{gen}\right) \implies$ rate of loss of availability is proportional to the rate of entropy generation

- The performance of Heat engines and Regfrigerators or Heatpumps have been measured using the Efficiency and Coefficient of performance quantitites. They are also called **First law efficiencies**

- But they make no reference to how best the machine is performing vs how the machine is possible to perform as best.

- Consider: Heat engine operating between 500K and 450K, withdrawing 100KJ and producing work ouptut of 9.5KJ. Now, $\eta = \dfrac{W}{Q_{in}} = \dfrac{9.5}{100} = 9.5\%$ $\Longleftarrow$ This may seem very low. But,

- $\eta_{max} = 1 - \dfrac{T_l}{T_H} = 1 - \dfrac{450}{500} = 10\%$ $\Longleftarrow$ Best efficiency possible for the given temperature range.

- Now, The second law efficiency $\boxed{\eta_{II} = \dfrac{\eta_{actual}}{\eta_{max}}} = \dfrac{9.5}{10} = 95\%$ $\Longleftarrow$ as you can see the engine is performing quite the best.

- similarly, for work consuming devices, $\boxed{\eta_{II} = \dfrac{\eta_{rev}}{\eta_{actual}}}$

- For Heat pumps and refrigerators, $\boxed{\eta_{II} = \dfrac{COP_{actual}}{COP_{rev}}}$

7. Properties of Pure Substance

__Introduction :-__

- **Pure substance:** has fixed chemical composition throughout. It does not have to be a single component. for eg. Air is a mixture of many gases and is considered a pure substance and on the other hand, a mixture of liquid air and air is not a pure substance, because different gases have different condensing point.

__Phase change of a pure substance :-__

- Consider 1 kg of liquid water at 25°C in a vertical piston cylinder arrangement. This setup is heated to 100°C at atmospheric pressure.

- After the water reaches 100°C, if the heating is continued, the water begins to change phase to vapor while the temperature is still 100°C. That amount of heat that was added to convert a unit mass of liquid to a unit mass of vapor is called **Latent heat of vapourization**.

- The corresponding temperature and pressure at phase change is called **saturation temperature** and **saturation pressure**

- For a pure substance, there exists a definite relationship between the saturation temperature and pressure. The curve of that relation is called **Vapor pressure curve** (drawn in a PT diagram)

- **Subcooled liquid:** For a given pressure, if the temperature of the liquid drops below the saturation temperature, then the liquid is said to be subcooled.

    $\Longrightarrow$ **Degree of subcooling:** $T_{sat} - T$

- **Saturated Liquid:** Just before the boiling starts, the liquid is said to be saturated.

- **Saturated Vapour:** After all the liquid has undergone the phase change.

- **Superheated Vapour:** If the saturated vapour is heated, then its called superheated vapour.

    $\Longrightarrow$ **Degree of Superheating:** $T - T_{sat}$

- **NOTE:** As pressure is increased, the Latent heat of vapourization decreases.

- **Critical pressure:**   The pressure for which the Latent heat of vapourization becomes zero. For water, the critical pressure is 225 bar. At critical pressure, the specific volume of saturated liquid and saturated vapour becomes equal. i.e.,($v_f = v_g$). **Above critical pressure, Liquid water directly converts to superheated steam**

- **Wet region:**   Region where saturated liquid and vapour coexist in equilibrium.
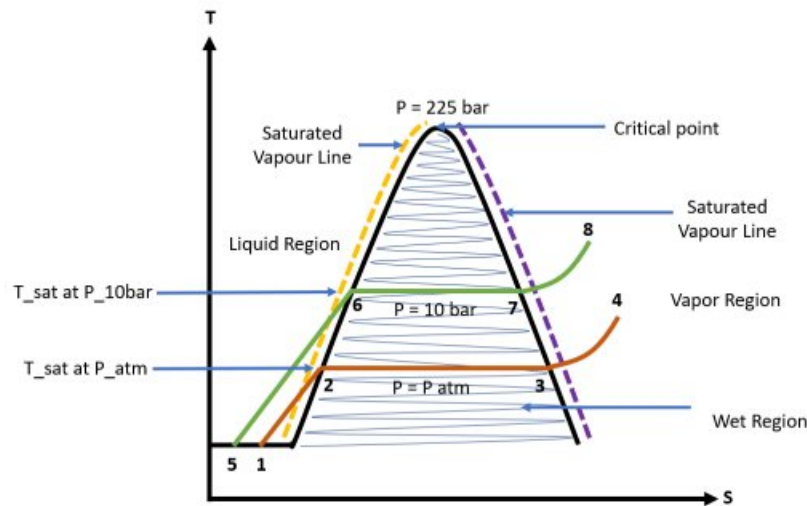
- Terms:

  - s_f = Specific entropy of saturated water
  - s_g = Specific entropy of saturated vapor
  - $s_{fg} = s_g - s_f$ = Specific entropy change during the phase change $\Longleftarrow$ (becomes zero at Critical point)

Property Diagrams

P-T DIAGRAM

- Also called Phase diagram

- Three lines separates the three phases

  - **Sublimation line:** separates Solid and vapour
  - **Vapourization line:** separates Liquid and Vapour
  - **Melting (or) Fusion line:** separates Solid and Liquid
    * Substances that expand or contract on freezing differ only in the Melting line of the PT diagram.

- The above three lines meet at **Triple Point**.**NOTE:**   Only in P-T diagram, there is no phase change region and as a result, the triple point exists as point. In all other diagrams, there is phase change region and the triple point exists as a line and so its called as **Triple line**

- But critical point is a point in all the diagrams, no exceptions.

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h-s DIAGRAM (OR) MOLLIER DIAGRAM

- We know, $Tds = dh - vdP \implies Tds = dh$ (at Constant pressure $dP = 0$) $\implies \boxed{\left(\dfrac{dh}{ds}\right)_P = T}$

- In wet region of h-s diagram, isotherms and isobars are same and they start deviating when they enter the superheated region.

- The slope of an isobar on the h-s coordinate is equal to the absolute temperature at that pressure

- Terms:

- h_f = Specific enthalpy of saturated water at a given pressure
- h_g = Specific enthalpy of saturated vapor at a given pressure
- h_{fg} = Latent heat of vaporization at a given pressure. As the pressure increases, h_{fg} decreases and becomes zero at critical point.

Quality and Saturated Liquid-Vapor Mixture :-

- **Dryness fraction(x)** $= \dfrac{mass\ of\ saturated\ vapor}{total\ mass} \implies \boxed{x = \dfrac{m_g}{m_f + m_g}}\ (0 \leq x \leq 1)$

  $\implies$ x=0 for saturated liquid
  $\implies$ x=1 for saturated vapor
  $\implies$ If x > 1 in any problem, then it's in Superheated region.
  $\implies$ If x < 0 in any problem, then it's in Subcooled region.
  - x is undefined at critical point.
  - Consdier:
    * A mixture of saturated liquid and saturated Vapor
    * Total Mass (m) $= m_f + m_g$
    * Total Volume (V) $= V_f + V_g \implies m_f v_f + m_g v_g \implies v = \dfrac{V}{m} \implies \dfrac{m_f v_f}{m} + \dfrac{m_g v_g}{m}$
    * $v = (1-x)v_f + x v_g \impliedby \boxed{\dfrac{m_f}{m} = \dfrac{m - m_g}{m} = 1 - \dfrac{m_g}{m} = 1 - \dfrac{m_g}{m_f + m_g} = 1 - x}$
    * $v = v_f - x v_f + x v_g \implies v_f + x(v_g - v_f) \implies \boxed{\boldsymbol{v = v_f + x v_{fg}}}$
    * Now instead of volume, had any other property been taken, they all would end with the similar result as above, meaning: The value of any specific-extensive property(y) in the wet region is $y = y_f + x(y_{fg})$
  $\implies \boxed{h = h_f + x(h_{fg})}\ \boxed{s = s_f + x(s_{sg})}\ \boxed{u = u_f + x(u_{ug})}$
    * $\boxed{\boldsymbol{Lever\ Rule:}\ \ x = \dfrac{y - y_f}{y_{fg}}}$

Enthalpy and Entropy of Pure substances :-

ENTHALPY AT VARIOUS POINTS

- Wet region: $\boxed{h = h_f + x(h_{fg})}$

- Superheated region: $\boxed{h = h_g + C_{pv}(T - T_{sat})} \impliedby C_{pv} =$ Specific heat of superheated vapor at Const P

- Subcooled region: $\boxed{h = h_f + C_{pl}(T_{sat} - T)} \impliedby C_{pl} =$ Specific heat of subcooled liquid at Const P

ENTROPY AT VARIOUS POINTS

- Wet region:

  $\to s = s_f + x(s_f g) \impliedby s_{fg} = (s_g - s_f) =$ Entropy of Vapourization

  $\to$ Evaporation is an Isothermal process and we know $ds = (s_g - s_f) = \dfrac{\delta Q}{T}$

  - When a liquid evaporates, the heat absorbed is the latent heat of vaporization (h_{fg}) and thus heat goes into water without showing any rise in temperature $\implies Q = h_{fg} \implies \boxed{s_{fg} = s_{evap} = \dfrac{h_{fg}}{T_{sat}}}$

- Supherheated region:

  $\to$ We know $Tds = dh - vdP \implies Tds = c_{pv}dT \impliedby (dp = 0$ at constant pressure and $dh = c_{pv}dT)$

  $\to ds = \dfrac{c_{pv}dT}{T}$ Integrating, $s_2 - s_g = \int\limits_{g}^{2} \dfrac{c_{pv}dT}{T} \implies c_{pv}\ln\left(\dfrac{T_2}{T_g}\right)$

$\rightarrow \implies \boxed{s_2 = s_g + c_{pv} \ln\left(\dfrac{T_2}{T_{sat}}\right)}$ as $(T_f = T_g = T_{sat})$

- Subcooled region:

    $\rightarrow$ Similar to the above derivation. So, $\boxed{s_3 = s_f + c_{pl} \ln\left(\dfrac{T_{sat}}{T_3}\right)}$

Points to remember :-

- Always remember to taken in account the mass when dealing with pure substance problems

- Energy supplied in constant volume will be the change in Internal energy

- Energy supplied in constant pressure will be the change in Enthalpy

- The values u,h, and s cannot be measured directly and they are calculated from measurable properties using the relations between thermodynamic properties. But those relations give the changes in properties and not the actual values of the properties at specified state. Therefore a reference state is chosen and that property is assigned a value of zero at that state.

    $\rightarrow$ For water, a state of saturated liquid at 0.01°C is taken as reference

    $\rightarrow$ Some properties may have negative values as a result of the chosen reference state. It should be noted that different tables list different values for some properties at the same state as a result of using different reference state.

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8. Thermodynamic Relations

Mathematical Theorems :-

- $\left(\dfrac{\delta P}{\delta v}\right)_T \left(\dfrac{\delta T}{\delta P}\right)_v \left(\dfrac{\delta v}{\delta T}\right)_P = -1 \impliedby$ by Chain rule

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Maxwell Relations :-

- The equations that relate the partial derivatives of properties P,v,T and s of a simple compressible system to each other are called Maxwell relations.

- They are obtained from 4 Gibbs equations in which 2 of them we have already seen by the name of TdS equations.

$$du = Tds - Pdv \tag{1}$$
$$dh = Tds + vdP \tag{2}$$

- The other 2 gibbs functions are derived from:

$$f = u - Ts \tag{a}$$
$$g = h - Ts \tag{b}$$

- Here f is calld **Helmholtz function** and g is called **Gibbs function** and for any natural process, both these values decrease and attain a minimal value.

- By differentiating (a) and (b), we get, $df = du - Tds - sdT$ and $dg = dh - Tds - sdT$. using $du - Tds = -Pdv$ and $dh - Tds = vdP$ from (1) and (2) we get the remaining 2 gibbs relations:

$$df = -sdt - Pdv \tag{3}$$
$$dg = -sdT + vdP \tag{4}$$

- Using the exact differential, $\left(\dfrac{\delta M}{\delta z}\right)_y = \left(\dfrac{\delta N}{\delta y}\right)_z$ on the four relations we'll obtain:

- $$\left(\frac{\delta T}{\delta v}\right)_s = -\left(\frac{\delta P}{\delta s}\right)_v \quad \left(\frac{\delta T}{\delta P}\right)_s = \left(\frac{\delta v}{\delta s}\right)_P \quad \left(\frac{\delta s}{\delta v}\right)_T = \left(\frac{\delta P}{\delta T}\right)_v \quad \left(\frac{\delta s}{\delta P}\right)_T = -\left(\frac{\delta v}{\delta T}\right)_P$$

- The above 4 are the Maxwell relations which are extremely important as they provide a mean to determine the change in entropy which is not possible by simply measuring the properties P, v and T

Tds Partial Differential Equations :-

- $$Tds = C_v dT + T\left(\frac{\delta P}{\delta T}\right)_v dV$$

- $$Tds = C_p dT - T\left(\frac{\delta V}{\delta T}\right)_P dP$$

- The above two are derived by writign s $= f(T,v)$ and s$=f(T,P)$ and then applying Maxwell relations

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Specific Heats C_p and C_v

- $$\beta = \frac{1}{v}\left(\frac{\delta v}{\delta T}\right)_P \qquad K_T = \frac{-1}{v}\left(\frac{\delta v}{\delta P}\right)_T \qquad C_p - C_v = \frac{Tv\beta^2}{K_T}$$

- K_T = Isothermal Compressibility

- β = Volume expansivity

Energy and Enthalpy Equations :-

- $$du = C_v dT + \left[T\left(\frac{\delta P}{\delta T}\right)_v - P\right]dv \qquad dh = C_p dT - \left[T\left(\frac{\delta v}{\delta T}\right)_P - v\right]dP$$

Joule Thomson Coefficient :-

- When a fluid passes through a restriction such as a porous plug, a capillary tube or an ordinary valve, its pressure decreases due to throttling. Although this **throttling is Isenthalpic**, the temperature behaviour of the fluid during the throttling is described by the Joule-thomson coefficient(μ)

- $$\mu = \left(\frac{\delta T}{\delta P}\right)_h$$

  - $\rightarrow \mu > 0 \implies$ Temperature increases during throttling
  - $\rightarrow \mu < 0 \implies$ Temperature decreases durign throttling
  - $\rightarrow \mu = 0 \implies$ Temperature remains constant durign throttling
  - $\rightarrow$ There will be no change in temperature when Ideal gas is throttled.

Clausius - Clapeyron Equation :-

- Clausius clapeyron gives the relation between the P_{sat}, T_{sat}, Enthalpy of evaporation and the specific volume of the two phases involved.

$$\implies \left(\frac{\delta P}{\delta T}\right)_{sat} = \frac{h_{fg}}{T_{sat}v_g} = \frac{h_{fg}P_{sat}}{RT_{sat}^2}$$

Compressibility Factor(z) :-

- $Z = \dfrac{Actual\ Volume}{Ideal\ Gas\ Volume} = \dfrac{V_a}{V_i} = \dfrac{Pv_a}{RT}$

- If a gas behaves like an ideal gas then Z=1 at all temperatures and pressures.

- Z is used to quantify the deviation of gases from ideal gas behaviour.

- Reduced Pressure($P_r = \dfrac{P}{P_C}$) is the ratio of existing pressure to Critical pressure. Similarly, $T_r = \dfrac{T}{T_C}$ and $v_r = \dfrac{v}{v_C} = \dfrac{Z}{Z_C}\dfrac{T_r}{P_r}$

- The deviation is highest in the vicinity of critical point.

- At very low pressure or very high temperature Ideal gas behaviour can be assumed.

Van der Waal's Equation of state :-

- $\boxed{\left(P_C + \dfrac{a}{V_c^2}\right)(V_c - b) = RT_C}$

  $\rightarrow v_c = 3b$

  $\rightarrow T_C = \dfrac{8}{27Rb}$

  $\rightarrow P_C = \dfrac{a}{27b^2}$

  $\rightarrow a = \dfrac{27R^2T_C^2}{64P_C}$

  $\rightarrow b = \dfrac{RT_C}{8P_C}$

  $\rightarrow$ At critical point, $\dfrac{P_C v_c}{RT_C} = \dfrac{3}{8}$