THERMODYNAMICS

CHAPTER 1

1. BASIC CONCEPTS

SYSTEM AND SURROUNDING :

A system is a matter or region on which analysis is done.

System is separated from the surrounding by ***boundary***.

Everything external to the system is called surrounding. System & surrounding together is called ***universe***.

➢ ***Boundary:***

It seperate system and surrounding

It can be fixed or movable

Fixed boundary e.g. rigid box containing gas

Movable boundary e.g. cylinder with piston

TYPE OF SYSTEM :

Types of System	Mass Transfer	Energy Transfer	Example
Closed	No	Yes	Piston cylinder without valves
Open	Yes	Yes	Turbine, pump, compressor
Isolated	No	No	Universe, hot coffee in a perfectly Insulated thermoflask

PROPERTY OF SYSTEM :

Properties are point function and are **exact** or perfect differentials e.g. internal energy, enthalpy, entropy.

Intensive properties :

These properties are independent of mass e.g. pressure, temperature density, specific volume, specific heat (c_p, c_v), specific enthalpy.

Extensive properties :

These properties are dependent on mass. e.g., volume, energy, Heat capacity (C_V, C_P), enthalpy. All specific properties are intensive properties.

Point Functions	Does not depend on path history (T, P, V)
Path Functions	Depend on path history (work, heat)

PROCESS : Change of state is known as process.

Reversible process :

A process when reversed in direction follows the same path as that of the forward path without leaving any effect on system and surrounding.

Irreversible process :

The process which is not reversible is known as irreversible. All actual process are irreversible process.

Zeroth Law of Thermodynamics / Temperature Measurement:

When a body A is in thermal equilibrium with a body B & also separately with a body C then body B & C will be in thermal equilibrium with each other.

Remember :

- *A system is said to have undergone a cycle when the initial and final properties are same.*
- *For a cycle change in property is zero.*
- *A frictionless Quasi static process is called a reversible process.*
- *Zeroth law of thermodynamics is the basis of temperature measurement.*

Conversion of Temperature Unit :

$$\frac{{}^{o}C}{5} = \frac{{}^{o}F - 32}{9} = \frac{T - 273.15}{5}$$

Where,
^{o}C = Temperature in degree celsius
^{o}F = Temperature in degree Fahrenheit
T = Temperature in Kelvin

Triple point of water :

It is the point where all the three phases co-exist. For water its value is

$$273.16\text{ K} = 0.01^{o}\text{C}$$

2. ENERGY INTERACTION :

WORK :

Work is said to be done by the system if the sole effect on the things external to the system can be reduced in raising of weight (weight may not actually be raised)

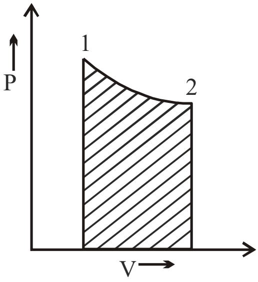
Sign Convention :

Work done by the system is positive & vice versa.

Remember :

Work is a path function and inexact or imperfect differential work is not a property of the system.

Only for quasistatic (reversible) process work done is calculated by $\int pdV$.



Conditions for Applying Above Equation :

Work should cross the boundary

System must be closed system

Process must be reversible process

REPRESENTATION OF VARIOUS PROCESS ON P-V DIAGRAM :

$$PV^K = \text{Constant}$$

Process	**K**
Adiabatic	$K = \gamma$
Polytropic	$K = n$
P = const.	$K = 0$
V = const.	$K = \infty$
T = const.	$K = 1$

CLOSED SYSTEM WORK IN VARIOUS PROCESS :

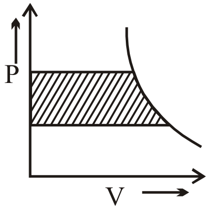
PROCESS	WORK DONE
Constant pressure (isobaric)	$W_{1-2} = p(v_2 - v_1) = mR(T_2 - T_1)$
Constant volume (isochoric)	$W_{1-2} = 0$
Constant temperature (isothermal)	$w_{1-2} = p_1 v_1 \ln\left(\frac{p_1}{p_2}\right)$ $= mRT_1 ln\left(\frac{p_1}{p_2}\right) = mRT_1 ln\left(\frac{v_2}{v_1}\right)$
Adiabatic (isentropic)	$w_{1-2} = \frac{(p_1 v_1 - p_2 v_2)}{(\gamma - 1)} = \frac{mR(T_1 - T_1)}{\gamma - 1}$
Polytropic	$w_{1-2} = \frac{(p_1 v_1 - p_2 v_2)}{(n - 1)} = \frac{mR(T_1 - T_1)}{n - 1}$

Where, 1 = Initial state

2 = Final state

OPEN SYSTEM WORK :

$$\boxed{\int dw = \int_{\text{Initial pressure}}^{\text{final pressure}} v.dp}$$



Remember :

The closed system work is obtain by plotting it on volume axis and open system work is obtain by plotting it on pressure axis on a P-V diagram.

HEAT, SPECIFIC HEAT RATIO :

Heat : $Q = mC\Delta t$

Here, $Q \rightarrow$ Heat

$m \rightarrow$ Mass

$C \rightarrow$ Specific heat

Heat flow out of a system is taken as negative while heat flow into a system is taken as positive.

Heat like work is also a path function so it is also inexact or imperfect differential.

SPECIFIC HEAT RATIO (γ)

$$\gamma = \frac{C_p}{C_v}$$

Where, $C_p \rightarrow$ Specific heat at constant pressure

$C_v \rightarrow$ Specific at constant volume

For Air : $\gamma = 1.4$

$C_p \rightarrow 1.005$ kJ/kg-K

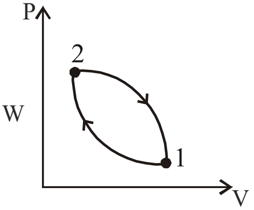
$C_v \rightarrow 0.718$ kJ/kg-K

$R \rightarrow 0.287$ kJ/kg-K

3. FIRST LAW OF THERMODYNAMICS :

For a cycle (Closed System)

$\Sigma Q = \Sigma W$



For a process $\delta Q = dE + \delta W$

$\delta Q = dU + \delta W$

If Kinetic energy and Potential energy changes are zero.

Heat transfer for Closed System:

Heat transfer at constant volume :

$$Q_V = (\Delta u) = \int_{T_1}^{T_2} C_v dT$$

$C_V \rightarrow$ Specific heat at constant volume

Heat transfer at constant pressure :

$$Q_P = (\Delta u) = \int_{T_1}^{T_2} C_p dT$$

$C_p \rightarrow$ Specific heat at constant pressure

For isothermal process :

$dU = 0$ (internal energy)

$\therefore$ U is a function of temperature only, for ideal gas

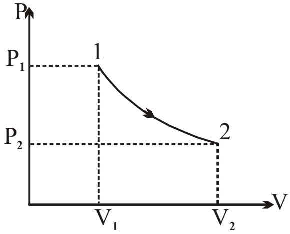
$dQ = dW = C_v T$

In adiabatic process :

Heat transfer $= 0$

$dQ = 0$

In polytropic process :



$$dQ = dQ = \frac{P_1V_1 - P_2V_2}{n-1}\left(\frac{\gamma - n}{\gamma - 1}\right)$$

$$= \text{(Polytropic work)}\left(\frac{\gamma - n}{\gamma - 1}\right)$$

Remember :

For isolated system energy (E) is always constant.

Energy is a point function and a property of the system.

Energy is an extensive property while specific energy is an intensive property.

*Heat transfer to the system at constant volume increases the **internal energy** of the system.*

*Heat transfer to the system at constant pressure increase the **enthalpy** of the system.*

In polytropic process, heat transfer is not zero.

ENTHALPY (H) :

It is the heat content of a body. Its unit is Joule.

$$H = U + PV$$

POLYTROPIC SPECIFIC HEAT :

$$C_{\text{polytropic}} = \frac{\gamma - n}{1 - n} \times C_v$$

1 – n is always –ve and hence $C_{\text{polytoropic}}$ is always –ve

Here, $n \rightarrow$ Polytropic index

$$\gamma \rightarrow \frac{C_p}{C_v}$$

Remember :

Polytropic specific heat is always negative.

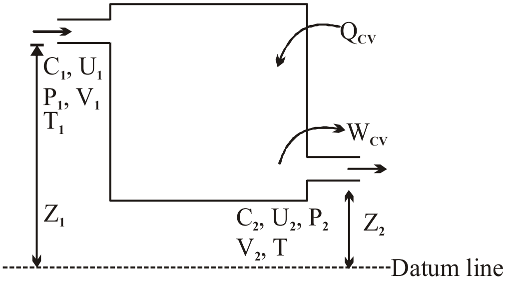
PERPETUAL MOTION MACHINE OF FIRST KIND (PMM1)

There can be no machine which would continuously supply mechanical work without some other form of energy disappearing simultaneously. Such a fictitious machine is called perpetual motion machine of first kind.

4. STEADY FLOW PROCESS / STEADY FLOW ENERGY EQUATION :

In a flow if thermodynamic properties do not change with time at different locations, the process is steady flow process.

In steady flow process there is no accumulation of mass or energy in control volume.



Steady flow energy equation (S.F.E.E.)

$$= H_1 + \frac{1}{2}mC_1^2 + mgz_1 + Q_{cv}$$

$$= H_2 + \frac{1}{2}mC_2^2 + mgz_2 + w_{CV}$$

For per Unit Mass

$$= h_1 + \frac{1}{2}C_1^2 + gz_1 + q_{cv}$$

$$= h_2 + \frac{1}{2}C_2^2 + gz_2 + w_{CV}$$

Were,
$H \rightarrow$ Enthalpy
$C \rightarrow$ Velocity
$Z \rightarrow$ Height
$m \rightarrow$ Mass flow rate
$h \rightarrow$ Specific enthalpy
$Q_{CV} \rightarrow$ Heat given to control volume
$W_{CV} \rightarrow$ Work done

APPLICATION OF S.F.E.E. IS STEADY FLOW PROCESS :

Nozzle : $C_2 = \sqrt{2(h_1 - h_2)}$

$= \sqrt{2C_p(T_1 - T_2)}$

Work done = 0

$C_1 <<<< C_2$

Were, T → Temperature

h → Enthalpy

C_2 → Velocity at outlet

Turbine : $W_{C_V} = h_1 - h_2$

Where, W_{C_V} = Work obtained/unit mass

h_1 → Enthalpy at inlet of turbine

h_2 → Enthalpy at outlet of turbine

Compressor : $W_{C_V} = h_2 - h_1$

where, W_{C_V} = Work done/unit mass

h_2 → Enthalpy at inlet of compressor

h_1 → Enthalpy at outlet of compressor

Throttling Device :

$h_1 = h_2$

No heat and work transfer, irreversible process.

When a fluid flow through a narrow passage like an orifice, partially opened valve, there is an appreciable drop in pressure. The process is throttling process.

CONDITIONS :

In all devices change in potential energy and kinetic energy neglected

i.e. $C_1 \approx C_2$

Remember :

A nozzle is a device which increases the velocity or kinetic energy of fluid at the expense of its pressure drop.

A diffuser is a device which increases the pressure of fluid at the expense of kinetic energy.

FREE EXPANSION :

Expansion against vaccum is called free expansion.

For free expansion, internal energy is same and if it is an ideal gas then.

$$T_1 = T_2$$

$T_1 \rightarrow$ Initial temperature

$T_2 \rightarrow$ Final temperature but not an isothermal process.

5. SECOND LAW OF THERMODYNAMICS

Work is said to be high grade energy and heat is a low grade energy.

The complete conversion of low grade energy into high grade energy in a cycle is impossible while the complete conversion of high grade energy into low grade energy is possible.

Heat energy is a low grade energy.

SECOND LAW OF THERMODYNAMICS :

Kelvin Plank Statement :

It is impossible for a heat engine to produce net work in a complete cycle if it exchange heat only with bodies from a single fixed temperature.

The machine which violate Kelvin plank statement is called PMM2.

Two reversible adiabatic path cannot intersect each other because that violates the Kelvin-Plank's statement.

Clausis Statement :

It is impossible to construct a device which is operating in a cycle transfers heat from cooler body to a hotter body without any work input.

THERMAL ENERGY RESERVOIR (TER / HEAT ENGINE / HEAT PUMP / REFRIGERATOR)

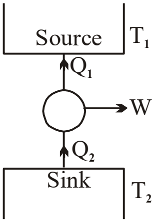
Thermal Energy Reservoir :

A thermal energy reservoir (TER) is defined as a large body of infinite heat capacity which is capable of absorbing or rejecting an unlimited quantity of heat without any appreciable changes in its thermodynamic properties.

Heat Engine :

A heat engine works on a thermodynamic cycle in which there is net heat transfer to the system and a net work transfer from the system.

Thermal Efficiency :



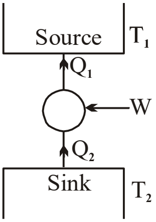
$$\eta_{th} = \frac{W_{net}}{Q_1} = \frac{Q_{net}}{Q_1} = 1 - \frac{Q_2}{Q_1} \qquad \text{...(1)}$$

$$\eta_{th(rev.\ cyc)} = 1 - \frac{T_2}{T_1}$$

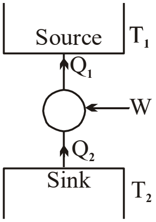
Heat Pump :

$$\text{C.O.P.} = \frac{Q_1}{Q_1 - Q_2} \qquad \text{...(ii)}$$

$$\text{C.O.P.}_{(rev.\ cyc)} = \frac{T_1}{T_1 - T_2}$$



Refrigerator :



$$\text{C.O.P.} = \frac{Q_2}{Q_1 - Q_2} \qquad \text{...(iii)}$$

$$\text{C.O.P.}_{(rev.\ cyc)} = \frac{T_2}{T_1 - T_2}$$

Remember :

$$(C.O.P.)_{H.P} = 1 + (C.O.P.)_R$$

The above formulae (i), (ii) and (iii) are applicable for both reversible and irreversible cycles.

6. ENTROPY :

Second law of thermodynamics leads to entropy.

ENTROPY / ENTROPY CHANGE :

$$\boxed{ds \geq \frac{dQ}{T}}$$

$$\boxed{ds = \left(\frac{dQ}{T}\right)_{rev.}}$$

$$(ds)_{universe} \geq 0$$

Here,
ds → Entropy change
dQ → Change in heat
T → Temperature

Remember :

Entropy change in reversible process is a point function and exact differential.

It is an extensive property.

Reversible adiabatic process is an isentropic process but reverse is not always true.

When the system is at equilibrium, any conceivable change in entropy would be zero.

INEQUALITY OF CLAUSIUS :

Inequality of Clausius :

It provides the criterion of irreversibility of cycle.

$\boxed{\oint \frac{dQ}{T} = 0}$ the cycle is reversible

$\boxed{\oint \frac{dQ}{T} < 0}$ the cycle is irreversible and possible

$\boxed{\oint \frac{dQ}{T} > 0}$ the cycle is impossible

CHANGE IN ENTROPY OF SYSTEM :

Change in entropy of a system is due to heat transfer and internal irreversiblity (entropy generation)

$$\boxed{S_2 - S_1 = \underbrace{\int_1^2 \frac{dQ}{T}}_{\text{Due to heat transfer}} + \underbrace{S_{gen}}_{\text{Due to interna irreversibility}}}$$

Entropy generation is a path function.

Twin Equation of Entropy :

$$T.ds = du + P.dv$$

$$T.ds = dh - v.dP$$

Above equations are applicable for reversible and irreversible process and for open and closed system both.

Entropy Change (Δs) for Finite Body :

$$\Delta S = mc \ln (T_f / T_i)$$

Here, $C \rightarrow$ Specific heat

$T_f \rightarrow$ Final temperature

$T_i \rightarrow$ Initial temperature

$m \rightarrow$ Mass of body

Entropy Change for an ideal gas between state '1' and state '2'

Where, $2 =$ Final

$1 =$ Initial

$$\boxed{S_2 - S_1 = C_p \ln \frac{V_2}{V_1} + C_v \ln \frac{P_2}{P_1}}$$

$$\boxed{S_2 - S_1 = C_v.\ln \frac{T_2}{T_1} + R.\ln \frac{V_2}{V_1}}$$

$$\boxed{S_2 - S_1 = C_p \ln \frac{T_2}{T_1} - R \ln \frac{P_2}{P_1}}$$

Here, $S \rightarrow$ Entropy

$P \rightarrow$ Pressure

$V \rightarrow$ Volume

$T \rightarrow$ Temperature

$R \rightarrow$ Characteristic gas constant

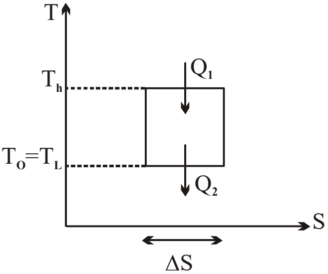
7. AVAILABLE ENERGY, AVAILABILITY AND IRREVERSIBILITY :

The part of low grade energy which is available for conversion to high grade energy is referred as available energy, which is also know as exergy while the part of low grade energy which, according to second law, must be rejected is called unavailable energy. Unavailable energy is known as anergy or exergy.

Available energy (cycle) :

$T_o =$ Ambient temperature

$$W_{max} = Q_1.\ \eta_{max}$$



$$\Rightarrow \qquad = Q_1\left(1-\frac{T_o}{T_H}\right)$$

$$W_{max} = Q_1 - Q_2 = Q_1 - (\Delta S)T_o$$

Here, $(\Delta S)T_o \rightarrow$ Unavailable energy

The maximum work can be obtain when the lower temperature would be ambient temperature.

Remember :

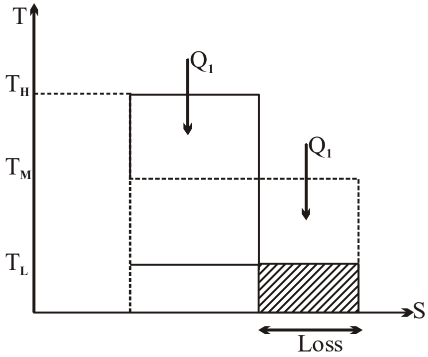
Decrease in available energy take place due to irreversible process when heat is transferred through a finite temperature difference.

Same amount of heat has more available energy when it is transferred from higher temperature body than when it is transferred from lower temperature body.

The degradation is more for energy loss at a higher temperature than that at a lower temperature.

The first law states that the energy is always conserved quantity wise while the second law emphasizes that energy always degrades quality wise.

LOSS OF AVAILABLE ENERGY IN A CYCLE :

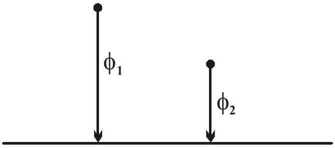


Loss of Available energy $= Q_1\left[\frac{T_L}{T_M} - \frac{T_L}{T_H}\right]$

Here, $Q_1 \rightarrow$ Heat input

AVAILABILITY (PROCESS) :

Availability (A) of a given system is defined as the maximum useful work that is obtainable in a process in which the system comes to equilibrium with its surroundings.



Availability $= \phi_1 - \phi_2$

Availability of a Closed System :

$$= \phi_1 - \phi_2 \quad (\phi = U - T_oS + P_oV)$$

$$W_{max.useful} = (U_1 - U_2) - T_O(S_1 - S_2) + P_O(V_1 - V_2)$$

Here, $U \rightarrow$ Internal energy

$T_O \rightarrow$ Surrounding temperature

Other symbol has usual meaning.

Availability of open system :

$$= \phi_1 - \phi_2 \quad (\phi = h - T_oS)$$

$$W_{(max.useful)} = (h_1 - h_2) - T_O(S_1 - S_2)$$

IRREVERSIBILITY (I):

Irreversibility is the loss of available energy due to dissipation of energy or entropy generation.

$$\text{Irreversibility} = W_{max} - W_{act}$$

$$= T_0(\Delta s)_{univ}$$

GOUY STODULA THEOREM :

$$I \propto (\dot{\delta s})_{gen}$$

8. PROPERTIES OF PURE SUBSTANCE :

A pure substance is a substance of constant chemical composition throughout its mass. It is one component system. It may exist in one or more phases.

DEFINATION:

Saturation State :

A saturation state is a state from where a change of phase may occur without a change of pressure or temperature.

Critical Temperature :

At critical temperature a liquid completely changes to vapour and vice-versa. Also above critical temperature a vapour cannot be liquefied by any amount of pressure.

Critical Pressure :

At critical temperature the minimum pressure required to transform a vapour to liquid is called critical pressure.

Triple Point :

Triple point is the fixed point (fixed temperature and pressure) at which solid, liquid and vapour phase co-exist in equilibrium

Remember :

Transformation of solid to vapour directly is called sublimation.

Transformation of vapour to solid directly is called deposition.

Degree of subcooling :

$$T_{\text{saturation}} - T_{\text{actual}}$$

Degree of superheating :

$$= T_{\text{superheat}} - T_{\text{saturation}}$$

Dryness fraction :

$$\boxed{x = \frac{m_v}{m_v + m_l}}$$

Here, $m_v \rightarrow$ mass of vapour

$m_l \rightarrow$ mass of liquid

Various properties of pure substance based on dryness fraction.

$$v = v_f + x(v_g - v_f)$$

Similarly $$h = h_f + x(h_g - h_f)$$

$$s = s_f + x(s_g - s_f)$$

Here, $v, v_f, v_g \rightarrow$ specific volume of moist vapour, liquid, vapour

$h, h_f, h_g \rightarrow$ specific enthalpy of moist vapour, liquid, vapour

$s, s_f, s_g \rightarrow$ specific entropy of moist vapour, liquid, vapour