

CHAPTER-4

Second Law of Thermodynamics

* Qualitative Law / Directional Law / Law of Degradation of Energy -

$Q \rightarrow \text{Low GrE}$

$W \rightarrow \text{High GrE}$

$Q \xrightarrow{\text{fully}} W$
 $W \xrightarrow{\text{fully}} Q$

First law of Thermodynamics simply says that Total Energy is conserved and it doesn't provide any information regarding the direction of energy conversion. It is a second law of Thermodynamics which provides the feasibility or the spontaneity of the process through the concept of entropy. Therefore it is second law of T.D. which is applied first in the numericals to find out the direction of possible energy conversion and then apply first law of thermodynamics.

→ Note: (i) Heat is a low grade energy and work is a high grade energy.

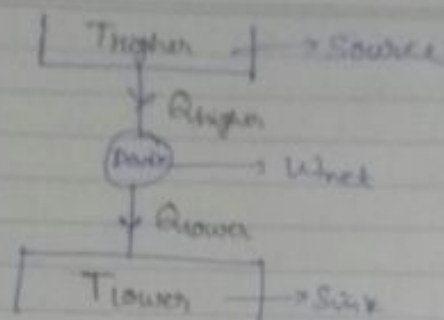
(ii) Complete conversion of heat into work is not possible but the complete conversion of work into heat is possible.

Thermal Energy Reservoir (TER) -

It is a reservoir of infinite heat capacity.

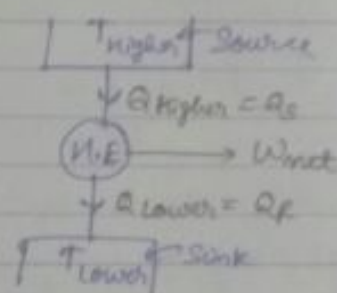
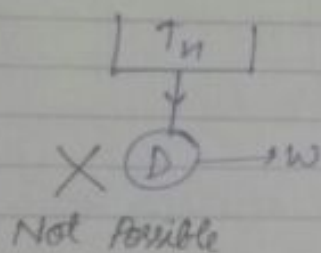
Source - Supplier of heat energy without affecting its temp.

Sink - Absorber of heat energy without any change in its temp.



Kelvin-Planck Statement -

It is impossible to construct a device which operates in a cycle produces work continuously while interacting with single thermal reservoir.



$$\eta = \frac{\text{Output}}{\text{Input}} = \frac{W_{\text{net}}}{Q_s} = \frac{Q_{\text{net}}}{Q_s} = \frac{Q_s - Q_r}{Q_s}$$

$$\eta = 1 - \frac{Q_r}{Q_s}$$

$$\boxed{\eta = 1 - \frac{Q_L}{Q_H}}$$

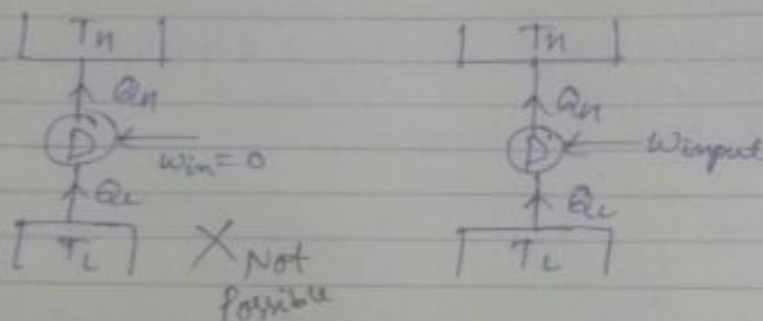
* Thermodynamic temp. scale or kelvin temp. scale $\rightarrow Q \propto T$

$$\boxed{\eta = 1 - \frac{T_L}{T_H}} \quad \text{Obj.} \quad \left\{ \frac{Q_L}{Q_H} = \frac{T_L}{T_H} \right\}$$

Note: Kelvin-Planck provides the concept of work producing device i.e., Heat Engine.

* Clausius Statement -

It is impossible to construct a device which operates on a cycle, transfer heat from low temp. reservoir to high temp. reservoir without consuming any other form of energy (work = 0).



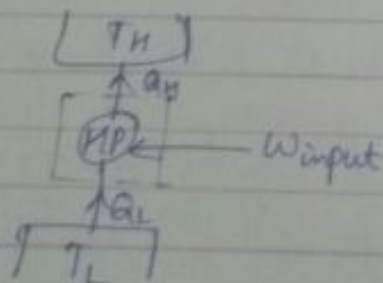
→ Note: It provides the concept of work absorbing device i.e., heat pump and refrigerator.

* C.O.P (Coefficient of Performance) - or

E.P.R (Energy Performance Ratio) -

It is defined as the ratio of desired effect to the work input.

Heat Pump



$$Q_L + W_{in} = Q_H$$

$$W_{in} = Q_H - Q_L$$

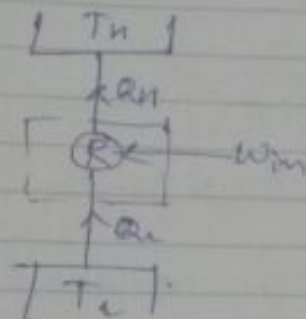
$$(COP)_{HP} = \frac{DE}{W_{input}} \quad \rightarrow \text{Desired Effect}$$

$$(COP)_{HP} = \frac{Q_H}{W_{in}}$$

$$(COP)_{HP} = \frac{Q_H}{Q_H - Q_L} \quad \text{obj.}$$

$$\boxed{(COP)_{HP} = \frac{T_H}{T_H - T_L}}$$

Refrigerator-



$$(COP)_R = \frac{DE}{W_{input}}$$

$$= \frac{Q_L}{W_{in}}$$

$$= \frac{Q_L}{Q_H - Q_L} \quad \text{obj.}$$

$$\boxed{(COP)_R = \frac{T_L}{T_H - T_L}}$$

* Relationship Between COP of HP. & COP of Refrigerator-

$$1 + COP_R = \frac{T_H}{T_H - T_L} + 1$$

$$= \frac{T_L + T_H - T_L}{T_H - T_L}$$

$$1 + COP_R = \frac{T_H}{T_H - T_L} = COP_{HP} \quad \text{obj.}$$

$$\boxed{1 + COP_R = COP_{HP}}$$

→ Note: The above expression is applicable between same temp. limits.

Q1- If the efficiency of a Reversible Engine is 40%, then what will be the COP of reversible Heat Pump?

$$\eta = 0.4$$

$$\eta = 1 - \frac{T_L}{T_H}$$

$$0.4 = 1 - \frac{T_L}{T_H}$$

$$\frac{T_L}{T_H} = 0.6$$

$$\begin{aligned} \text{COP}_{\text{HP}} &= \frac{T_H}{T_H - T_L} \\ &= \frac{1}{1 - \frac{T_L}{T_H}} \end{aligned}$$

$$= \frac{1}{1 - 0.6} = \frac{1}{0.4} = 2.5$$

obj.

$$\boxed{\text{COP}_{\text{HP}} = 1 + \text{COP}_R = \frac{1}{\eta_{\text{NE}}}}$$

→ Note: It is applicable for the same temp. limits

→ Note: Both Heat Pump and Refrigerator are known as reverse Heat Engine.

* Clausius Inequality -

According to this, the cyclic integral of $\oint \frac{dQ}{T} \leq 0$.

$$\oint \frac{dQ}{T} < 0 \rightarrow \text{Irreversible Device}$$

$$\oint \frac{dQ}{T} = 0 \rightarrow \text{Reversible Device}$$

$$\oint \frac{dQ}{T} > 0 \rightarrow \text{Impossible Device}$$

* Entropy (s) -

Entropy is the measurement of Degree of Disorder or Randomness of the gaseous molecules.

According to this principle the entropy change of universe can never have negative value.

$$(dS)_{\text{uni}} \geq 0$$

$$[(ds)_{\text{system}} + (ds)_{\text{non}}] \geq 0$$

$$(\delta S)_{\text{univ}} > 0 \rightarrow \text{Irreversible Device}$$

$$(dS)_{\text{min}} = 0 \rightarrow \text{Reversible Device}$$

$$(ds)_{uni} < 0 \rightarrow \text{Impossible Device}$$

* Entropy change of the System-

Entropy change of the system is the summation of entropy change due to internal irreversibility and entropy change due to external interaction.

$$ds = (ds)_{nr} + (ds)_{el}$$

$$p_{\text{el}} = (ds)_{\text{el}} + \frac{da}{T}$$

Sym

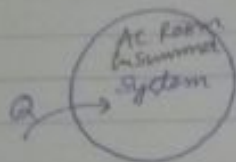
CASE 1 - If the entropy change due to internal irreversibility is zero, then the entropy change of the system is given by

$$dS_{int} = 0.$$

$$S_{gen} < 0.$$

$$dS = \frac{dQ}{T}$$

Case 1 - If the heat is supplied from the system, then the entropy change of the system is having positive value.



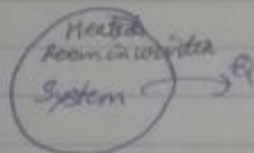
$$dQ > 0$$

$$\frac{dQ}{T} > 0$$

$$dS > 0.$$

Fig

Case 2 - If the heat is rejected from the system, then the entropy change of the system having negative value.



$$dQ < 0$$

$$\frac{dQ}{T} < 0$$

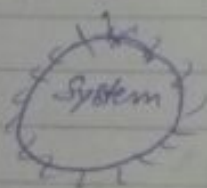
$$dS < 0.$$

Case 3 - If the system is well insulated the entropy change is zero.

$$dQ = 0$$

$$\frac{dQ}{T} = 0.$$

$$dS = 0.$$



→ Note: If the system is reversible and adiabatic then it has to be isentropic.

Qb Entropy change of the system may be positive, zero value or negative, but entropy change of the universe can never be negative.

CASE 1 - If the system is irreversible then entropy change of the system is given by,

$$dS = (dS)_{irr} + (dS)_{ext}$$

$$\boxed{dS = S_{gen} + \frac{dQ}{T}}$$

CASE 2 - If the system is adiabatic,

$$\frac{dQ}{T} = 0$$

$$\boxed{dS = S_{gen}}$$

Remember

→ Note: The value of entropy generation is always positive.

CASE 2 - Increase in internal irreversibility is compensated by decrease in external interaction then the entropy change is equal to zero.

$$dS = \uparrow (dS)_{irr} + \frac{dQ}{T} \downarrow$$

$$0 = +S$$

$$0 \neq \underline{-S} + S \rightarrow S_{gen} \text{ can never be negative}$$

TdS Equation -

$$dQ = dU + PdV$$

$$\text{for rev. process, } dS = \frac{dQ}{T} \Rightarrow TdS = dQ$$

$$dQ = TdS$$

$$\boxed{TdS = dU + PdV} \quad \text{--- (1)}$$

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

$$dH = dQ + VdP$$

$$dQ = dH - VdP$$

$$dQ = TdS \text{ for rev. process}$$

$$TdS = dH - VdP \quad \text{--- (2)}$$

Integral form of TdS,

$$TdS = dU + PdV$$

$$dS = \frac{dU}{T} + \frac{P}{T}dV$$

$$dU = C_V dT \quad \left| \begin{array}{l} PV = RT \\ \frac{P}{T} = \frac{R}{V} \end{array} \right. \quad (m=1)$$

$$\int_{S_I}^{S_F} dS = C_V \int_{T_I}^{T_F} \frac{dT}{T} + R \int_{V_I}^{V_F} \frac{dV}{V}$$

$$S_F - S_I = C_V \ln \frac{T_F}{T_I} + R \ln \frac{V_F}{V_I}$$

$$S_F - S_I = C_V \ln \frac{T_F}{T_I} + R \ln \frac{V_F}{V_I} \quad \text{--- (3)}$$

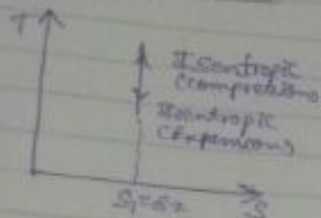
$$TdS = dH - VdP$$

$$dS = \frac{dH}{T} - \frac{V}{T}dP \quad \int_{S_I}^{S_F} dS = C_P \int_{T_I}^{T_F} \frac{dT}{T} - R \int_{P_I}^{P_F} \frac{dP}{P}$$

$$S_F - S_I = C_P \ln \frac{T_F}{T_I} - R \ln \frac{P_F}{P_I} \quad \text{--- (4)}$$

→ Note: Equation (1) & (2) are applicable for both reversible and irreversible processes because it contains all properties.

Representation of constant pressure and constant volume line of T-S curve-



$$TdS = dU + PdV$$

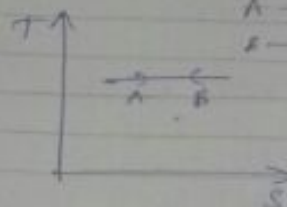
$$V = c$$

$$dV = 0$$

$$TdS = dU$$

$$TdS = C_v dT$$

$$\left(\frac{dT}{dS} \right)_V = \frac{T}{C_v}$$



$$TdS = dH - VdP$$

$$P = c$$

$$dP = 0$$

$$TdS = dH$$

$$TdS = C_p dT$$

$$\left(\frac{dT}{dS} \right)_P = \frac{T}{C_p}$$

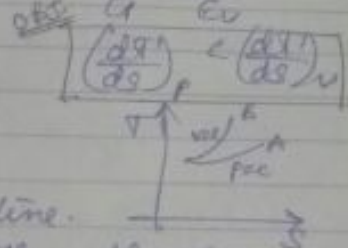
A → Isothermal heat add
B → Isothermal heat reject

$$C_p > C_v$$

$$\frac{1}{C_p} < \frac{1}{C_v}$$

$$\frac{T}{C_p} < \frac{T}{C_v}$$

$$\left(\frac{dT}{dS} \right)_P < \left(\frac{dT}{dS} \right)_V$$



Note: The slope of constant volume line on T-S curve is always greater than the slope of constant pressure line.

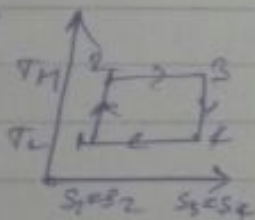
CARNOT

Process 1-2 → Isentropic Compression

Process 2-3 → Isothermal Heat Addition

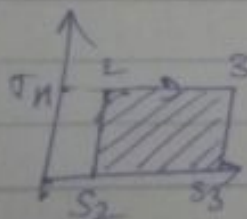
Process 3-4 → Isentropic Exp. or Perv. adiab. expansion

Process 4-1 → Heat rejection at const. temp.



$$\eta = \frac{\text{Output}}{\text{Input}} = \frac{W_{\text{net}}}{Q_S} = \frac{Q_{\text{net}}}{Q_S} = \frac{Q_3 - Q_4}{Q_3}$$

$$\eta = 1 - \frac{Q_R}{Q_S} \quad \text{--- (1)}$$



$$ds = \frac{dq}{T} \quad (\text{rev})$$

$$ds = \frac{dq}{T}$$

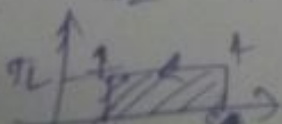
$$TdS = dQ$$

$$dQ = Q_3 = T_H (S_3 - S_2) \quad \text{--- (2)}$$

$$Q_R = T_L (S_4 - S_1) = (S_3 - S_2) T_L$$

$$\text{Use (2) \& (3) in (1)}$$

$$\eta = 1 - \frac{T_L}{T_H}$$



Q - Prove the following for an ideal gas. ^{Using this result show}
 that an ideal gas undergoing an ~~isothermal~~ ^{isobaric} change of state with
 constant specific heat is $PV^\gamma = C$.

$$ds = C_p \frac{dV}{V} + C_v \frac{dT}{T}$$

$$T ds = du + P dV$$

$$ds = \frac{du}{T} + \frac{P dV}{T}$$

$$du = C_v dT \quad \left| \quad \begin{array}{l} PV = RT \\ \frac{P}{T} = \frac{R}{V} \end{array} \right.$$

$$ds = \frac{C_v dT}{T} + \frac{R dV}{V}$$

$$ds = C_v \frac{dT}{T} + (C_p - C_v) \frac{dV}{V}$$

$$ds = C_v \frac{dT}{T} + C_p \frac{dV}{V} - C_v \frac{dV}{V}$$

$$ds = C_p \frac{dV}{V} + C_v \left(\frac{dT}{T} - \frac{dV}{V} \right) \quad \text{--- (1)}$$

$$PV = mRT$$

$$P dV + V dP = mR dT$$

$$\frac{P dV}{PV} + \frac{V dP}{PV} = \frac{mR dT}{PV} \quad (PV = mRT)$$

$$\frac{dV}{V} + \frac{dP}{P} = \frac{dT}{T}$$

$$\therefore \frac{dT}{T} - \frac{dV}{V} = \frac{dP}{P} \quad \text{--- (2)}$$

use (2) in (1), obj.

$$\boxed{ds = C_p \frac{dV}{V} + C_v \frac{dP}{P}}$$

$$\therefore ds = 0.$$

$$C_p \frac{dV}{V} + C_v \frac{dT}{T} = 0.$$

$$\frac{C_p}{C_v} \frac{dV}{V} + \frac{C_v}{C_v} \frac{dT}{T} = 0.$$

$$r \frac{dV}{V} + \frac{dT}{T} = 0.$$

$$r \ln V + \ln T = \ln C.$$

$$\ln PV^r = \ln C.$$

$$\therefore \boxed{PV^r = C}.$$

QUESTIONS

Q - The specific heat of the gas are of form $C_p = a + kT$, $C_v = b + kT$ where a, b, k are the constants and T is the temp. in K. Then derive the expression,

$$T^b e^{kT} V^{a-b} = \text{constant}.$$

For the reversible adiabatic process executed by this gas.

$$T ds = C_v \frac{dT}{T} + R \frac{dV}{V}$$

$$ds = C_v \frac{dT}{T} + R \frac{dV}{V}$$

$$T ds = C_v \frac{dT}{T} + R \frac{dV}{V}, \quad ds = 0 = C_v \frac{dT}{T} + C_p \frac{dV}{V} - C_v \frac{dV}{V}.$$

$$0 = \frac{C_p}{T} dT + (a-b) \frac{dV}{V}$$

$$= C_v \frac{dT}{T}$$

$$\boxed{C_p - C_v = a - b}$$

$$b \frac{dT}{T} + k dT + (a-b) \frac{dV}{V} = 0$$

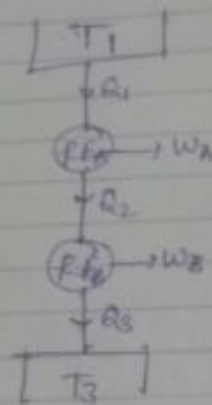
$$b \ln T + kT + (a-b) \ln V = \ln C.$$

$$\ln T^b + \ln e^{kT} + \ln V^{a-b} = \ln C$$

$$\boxed{T^b \cdot e^{kT} \cdot V^{a-b} = C}.$$

→ Note: There are 2 rev. heat engines operating in series.
The heat rejected by engine A directly to engine B. Then
find out the expression of intermediate temp. if,

- (i) Both engines are equally efficient. (Ans - Geometric Mean)
(ii) If both engines produce equal amount of work. (Ans - Arithmetic Mean).



$$(i) \eta_A = \eta_B$$

$$1 - \frac{T_2}{T_1} = 1 - \frac{T_3}{T_2}$$

$$\frac{T_2}{T_1} = \frac{T_3}{T_2}$$

$$T_2^2 = T_1 T_3$$

$$T_2 = \sqrt{T_1 T_3}$$

$$(ii) W_A = W_B$$

$$Q_1 - Q_2 = Q_2 - Q_3$$

$$2Q_2 = Q_1 + Q_3$$

$$\therefore \left[Q_2 = \frac{Q_1 + Q_3}{2} \right], \Rightarrow T_2 = \frac{T_1 + T_3}{2}$$

CHAPTER-4 W.B

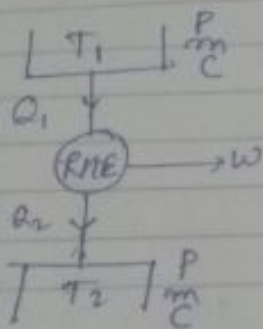
$$(a) \frac{Q_1}{T_1} + \frac{Q_2}{T_2} - \frac{Q_3}{T_3}$$

$$\frac{100}{100} + \frac{50}{500} - \frac{60}{30} = 0 \rightarrow \text{Rev. heat engine.}$$

V.V. V3-8.
 4th inst RS
 3rd inst T AS
 15th inst

Q- Two identical bodies of equal mass 'm' and specific heat 'C' initially at temp T_1 & T_2 (both in K) are used as a reservoir for a heat engine operating in a rev. cycle. The bodies may be treated as operating at const. P. If the engine interacts with the reservoirs until they attain the same final temp. then find the expression of max. final temp.

(ii) Max. work obtained.



$$\frac{W}{Q_1} = 1 - \frac{T_2}{T_1}$$

$$TdS = dH - VdP$$

$$TdS = C_p dT$$

$$TdS = dU + PdV$$

$$C_p dT = C_v dT + PdV$$

Let us assume T_f is the final temp attained by both bodies and $T_1 > T_2$.

$$T_1 > T_2$$

$$T_1 > T_f$$

$$T_2 < T_f$$

$$Q_1 = W_{\max} + Q_2$$

$$W_{\max} = Q_1 - Q_2$$

$$Q_1 = mC(T_1 - T_f)$$

$$Q_2 = mC(T_f - T_2)$$

$$\therefore W_{\max} = mc(T_1 - T_F) - mc(T_F - T_2).$$

$$= mc(T_1 - T_F - T_F + T_2)$$

$$\therefore W_{\max} = mc(T_1 + T_2 - 2T_F). \quad \text{--- (1)}$$

$$\text{Rev.} \rightarrow \oint \frac{dq}{T} = 0 \quad \text{or } (ds)_{\text{univ}} = 0.$$

$$(ds)_I + (ds)_{II} + (ds)_{F.H.E} = 0$$

$$\boxed{(ds)_I + (ds)_{II} = 0.} \quad \text{--- (2)}$$

$$Tds = dh - ydP^0$$

$$ds = mC \int_{T_2}^{T_F} \frac{dT}{T} = mc \ln \frac{T_F}{T_2} = mc \ln \left(\frac{T_F}{T_1} \right). \quad \text{--- (3)}$$

Put (3) in (2),

$$mc \ln \left(\frac{T_F}{T_1} \right) + mc \ln \left(\frac{T_F}{T_2} \right) = 0,$$

$$\text{---ve} \quad \ln \frac{T_F^2}{T_1 T_2} = 0, \quad \text{+ve}$$

(ds)_{system} can be either -ve or +ve but for universe it should be ≥ 0 .

$$\frac{T_F^2}{T_1 T_2} = 1$$

$$\boxed{T_F = \sqrt{T_1 T_2}} \quad \text{obj}$$

$$\therefore W_{\max} = mc(T_1 + T_2 - 2\sqrt{T_1 T_2}).$$

$$= mc((\sqrt{T_1})^2 + (\sqrt{T_2})^2 - 2\sqrt{T_1 T_2}).$$

$$\therefore \boxed{W_{\max} = mc(\sqrt{T_1} - \sqrt{T_2})^2}.$$

Ques 36

Ques

$$W_{\max} = mC[\sqrt{T_H} - \sqrt{T_L}]^2$$

$$T_F = \sqrt{T_{\max} T_{\min}}$$

Ques 36

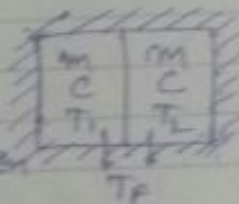
Q - A fluid of mass 'm' at temp. T_1 is mixed with equal amt. of same fluid at temp. T_2 . The specific heat of the liquid 'c', then derive the expression for total entropy change due to the mixing process.

Let us assume T_1, T_2 and T_F is the final temp. attained by both bodies.

Ans

Assumption - Assuming the system is well insulated i.e. no heat interaction

between system and surrounding.



$$\text{Heat lost by hot body} = \text{Heat gained by cold body}$$

$$\begin{aligned} T_1 &> T_2 \\ T_1 &> T_F \\ T_2 &< T_F \end{aligned}$$

$$mC(T_1 - T_F) = mC(T_F - T_2)$$

$$T_1 - T_F = T_F - T_2$$

$$2T_F = T_1 + T_2$$

Ans

$$T_F = \frac{T_1 + T_2}{2}$$

$$(dS)_{\text{univ}} = (dS)_{\text{sys}} + (dS)_{\text{sur}}$$

$$dQ = 0$$

$$(dS)_{\text{sur}} \geq 0$$

$$(ds)_{uni.} = (ds)_{sys} = (ds)_{HE} + (ds)_{LE}$$

$$T ds = \cancel{mc dT} + \cancel{pdV} \quad \text{for } T dV = 0$$

$$ds = mc \frac{dT}{T}$$

$$\therefore (ds)_{uni.} = mc \ln \frac{T_F}{T_1} + mc \ln \frac{T_F}{T_2}$$

$$= mc \ln \left(\frac{T_F^2}{T_1 T_2} \right) \quad T_F = \frac{T_1 + T_2}{2}$$

$$ds = mc \ln \frac{T_F^2}{T_1 T_2}$$

$$= mc \ln \frac{T_F^2}{(T_1 T_2)}$$

$$= 2mc \ln \left(\frac{T_F}{\sqrt{T_1 T_2}} \right)$$

$$\boxed{AS = 2mc \ln \left(\frac{AM}{GM} \right)} \quad \text{obj.}$$

→ Note:- The value of AM is always greater than GM.
 \therefore By using the above expression, we can say that mixing of fluid is a case of irreversible process.

$$AM > GM$$

$$\frac{AM}{GM} > 1$$

$$\boxed{ds > 0}$$

* Compressibility Factor -

It represents the deviation of actual gas from the behaviour of ideal gas. The value of Z is 1 for an ideal gas and for real gas >1 or <1 .

$$Z = \frac{PV}{RT}$$

$$Z = 1 \rightarrow \text{Ideal Gas}$$

$$\begin{matrix} Z > 1 \\ Z < 1 \end{matrix} \rightarrow \text{Real Gas}$$

Fig. 2.7 -

$$\begin{aligned} 32- \text{Loss} &= \frac{R_1 T_0 (T_1 - T_2)}{T_1 T_2} \\ &= \frac{2.50}{1000} \times 300 \times 200 \\ &= \frac{240000}{8} \\ &= 28000 \text{ J} \end{aligned}$$

$$33- \phi = h_1 - T_0 s_1 + \frac{1}{2} v^2$$

$$(UW)_{05} = (h_1 - h_2) - T_0 (s_1 - s_2)$$

$$= 300 - 300(0.4)$$

$$= 180 \text{ kJ/kg}$$

$$34- (dS)_{\text{universe}} = \left(\frac{-1000}{400} + \frac{1000}{300} \right) \quad \text{Maintained}$$

$$T_0 (dS)_{\text{uni}} = \left(\frac{1}{3} - \frac{1}{4} \right) \times 298$$

CHAPTER-5

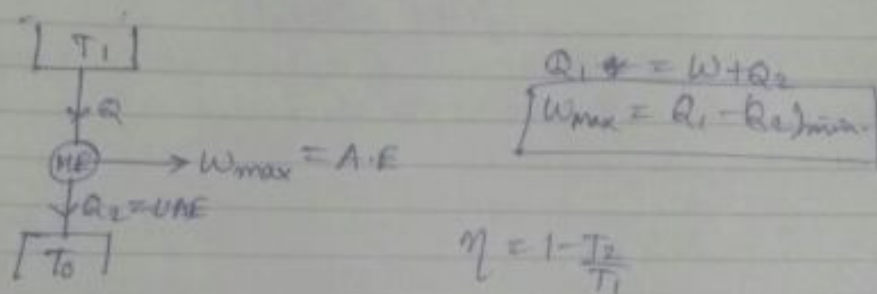
Available Energy & Unavailable Energy

* Available Energy or Exergy:-

It is the max. amount of work that can be extracted from a certain heat input in a cycle.

* Unavailable Energy:-

It is the min. amount of heat that has been rejected to the sink.

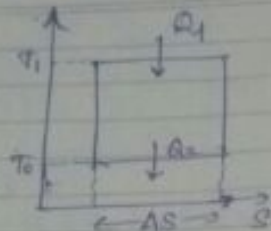


$$\eta = 1 - \frac{T_2}{T_1}$$

(a) $T_1 \uparrow, T_2 = \text{const} \Rightarrow \uparrow \eta = \left(1 - \left(\frac{T_2}{T_1 \uparrow} \right) \downarrow \right) \uparrow$

(b) $T_2 \downarrow, T_1 = \text{const} \Rightarrow \uparrow \eta = \left(1 - \left(\frac{T_2 \downarrow}{T_1} \right) \downarrow \right) \uparrow$

$T_0 = \text{Ambient Temp.} = \text{Atm. Temp.}$



$$Q_1/T_1 = T_1 AS$$

$$\frac{Q_1}{T_1} = AS$$

$$\eta = 1 - \frac{T_0}{T_1} = \frac{W_{max}}{Q_1}$$

$$W_{max} = Q_1 \left(1 - \frac{T_0}{T_1} \right)$$

$$= Q_1 - Q_1 \frac{T_0}{T_1}$$

$$= Q_1 - T_0 \left(\frac{Q_1}{T_1} \right)$$

$$W_{max} = Q_1 - T_0 AS \quad \text{obj.}$$

$$[AE = Q_1 - UAF] \quad \text{obj.}$$

$$[UAF = T_0 AS]$$

Q - 1000 kJ of heat is supplied to a reversible heat engine from a source maintained at 327°C and the sink temp. is 27°C. Then find out AE & UAF.

$$Q_1 = 1000 \text{ kJ.}$$

$$\eta = 1 - \frac{300}{600} = \frac{300}{600} \times \frac{1}{2} = 0.5$$

V. Imp.

* Loss of Available energy when the same heat is transferred through a finite temperature difference -

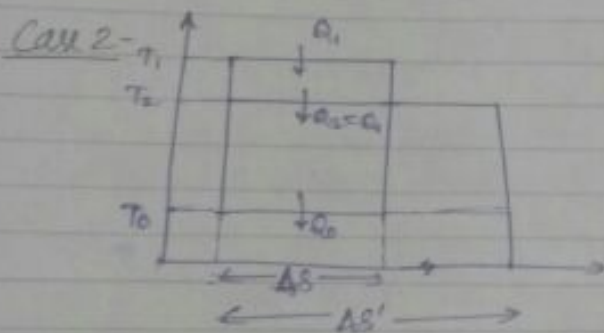
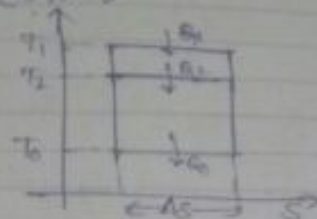
$$\eta = \frac{Q/P}{I/P} = \frac{W_{net}}{Q_s} = \frac{Q_{net}}{Q_s} = \frac{Q_s - Q_r}{Q_s} = 1 - \frac{Q_r}{Q_s}$$

Case 1- $Q_R = \text{const.}$ $\rightarrow \uparrow \eta = \left(1 - \frac{Q_R}{Q_S}\right) \uparrow$

$Q_1 = T_1 \Delta S$
 $Q_2 = T_2 \Delta S$ $\rightarrow Q_R = T_0 \Delta S$
 $Q_R = \text{const.}$

$T_1 > T_2$
 $T_1 \Delta S > T_2 \Delta S$
 $Q_1 > Q_2$

$\boxed{\eta_1 > \eta_2}$



$\eta = 1 - \frac{Q_R}{Q_S}$

$Q_S = \text{const.}$ $\rightarrow \downarrow \eta = \left(1 - \frac{Q_R \uparrow}{Q_S}\right) \downarrow$

$Q = T \Delta S$

$Q_1 = T_1 \Delta S$

$Q_2 = T_2 \Delta S'$

$$\therefore Q_1 = Q_2$$

$$T_1 > T_2$$

$$\Delta S < \Delta S'$$

$$\therefore \begin{aligned} Q_1 \text{ at } T_1 &\rightarrow Q_F = T_0 \Delta S \\ Q_2 \text{ at } T_2 &\rightarrow Q_F = T_0 \Delta S' \end{aligned}$$

$$\Delta S' > \Delta S$$

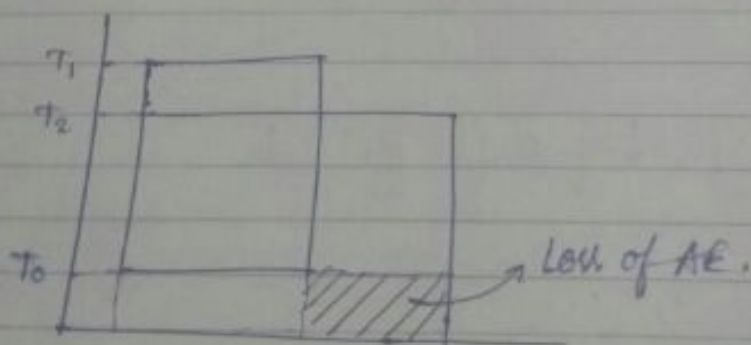
$$T_0 \Delta S' > T_0 \Delta S$$

$$(Q_F)_{Q_1 \text{ at } T_2} > (Q_F)_{Q_2 \text{ at } T_1}$$

$$(\eta)_{Q_1 \text{ at } T_2} < (\eta)_{Q_2 \text{ at } T_1}$$

$$\left(\frac{AE}{Q_1} \right)_{Q_1 \text{ at } T_2} < \left(\frac{AE}{Q_1} \right)_{Q_1 \text{ at } T_1}$$

$$\boxed{(AE)_{Q_1 \text{ at } T_1} > (AE)_{Q_1 \text{ at } T_2}}$$



$$\uparrow \text{ in CAE} = T_0 (\Delta S' - \Delta S) \quad \text{--- (1)}$$

$$\left. \begin{aligned} Q_1 \text{ at } T_1 &\rightarrow Q_1 = T_1 \Delta S \rightarrow \Delta S = Q_1 / T_1 \\ Q_1 \text{ at } T_2 &\rightarrow Q_1 = T_2 \Delta S' \rightarrow \Delta S' = Q_1 / T_2 \end{aligned} \right\} \quad \text{--- (2)}$$

Use ② in ①,

$$\uparrow \text{ in UAF} = T_0 \left[\frac{Q_1}{T_0} - \frac{Q_1}{T_1} \right],$$

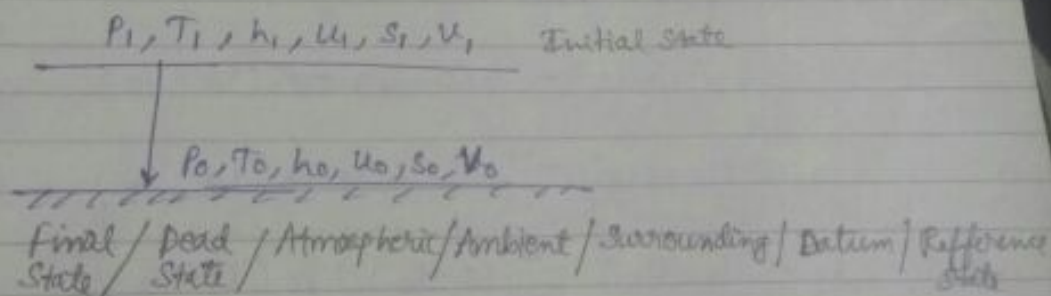
$$= Q_1 T_0 \left[\frac{1}{T_2} - \frac{1}{T_1} \right] \quad \text{obj:}$$

$$\therefore \uparrow \text{ in UAF} = \frac{Q_1 T_0 (T_1 - T_2)}{T_1 T_2}$$

→ Note: More the temp. difference, more will be the loss of Available energy. \therefore Same heat is having more importance at higher temp. in comparison to the lower temp.

* Availability -

It is a maximum useful work in which system comes into equilibrium with the dead state in a process.



* Closed System Work -

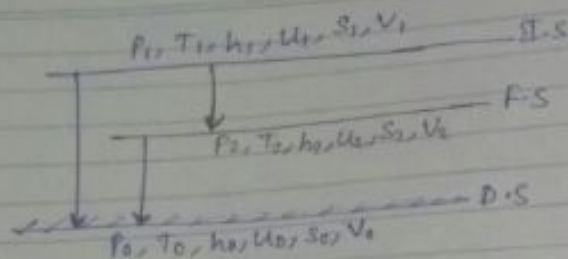
Useful work - $T_0 ds = dU + (U.W)_{es}$

$$(U.W)_{es} = T_0 ds - dU$$

$$= T_0 (s_f - s_i) - (U_f - U_i)$$

$$= T_0 (s_0 - s_1) - (U_0 - U_1)$$

$$\therefore (U.W)_{es} = \boxed{U_1 - U_0 - T_0 (s_1 - s_0)}$$



$$1-0: (u_1 - u_0) - T_0 (s_1 - s_0)$$

$$2-0: (u_2 - u_0) - T_0 (s_2 - s_0)$$

$$1-2: (u_1 - u_2) - T_0 (s_1 - s_2)$$

$$\boxed{\therefore \left(\frac{u_1}{T_0} (u_1 - u_f) - T_0 (s_1 - s_f) \right)} \quad \text{obj.}$$

$$(M.U.W)_{cs} = [(u_1 - u_f) - T_0 (s_1 - s_f)] - P_0 \Delta V.$$

$$= (u_1 - u_0) - T_0 (s_1 - s_0) - P_0 (V_f - V_2)$$

$$= (u_1 - u_0) - T_0 (s_1 - s_0) - P_0 (V_p - V_{01}).$$

$$\boxed{(M.U.W)_{cs} = (u_1 - u_0) - T_0 (s_1 - s_0) + P_0 (V_1 - V_0)} \quad \text{obj.}$$

$$\boxed{(MUW)_{cs} = (u_1 - u_f) - T_0 (s_1 - s_f) + P_0 (V_1 - V_f)} \quad \text{obj.}$$

of Open System Work-

$$\boxed{(U.W)_{os} = (h_T - h_F) - T_0 (S_T - S_F)}$$

$$\boxed{(M.U.W)_{os} = (h_T - h_F) - T_0 (S_T - S_F)}^{obj.}$$

→ Note: The expression of useful work and maximum useful work is same for the open system.
→ No resistance.

*Availability Function or Flow Availability-

Change in availability function represents the maximum useful work.

$$(i) \boxed{\phi_{os} = U + P_0 V - T_0 S}^{obj.}$$

$$(MUW)_{os} = (U_1 - U_2) - T_0 (S_1 - S_2) + P_0 (V_1 - V_2)$$

$$= (U_1 - T_0 S_1 + P_0 V_1) - (U_2 - T_0 S_2 + P_0 V_2),$$

$$= (\phi_1 - \phi_2).$$

$$(ii) \boxed{\phi_{os} = h - T_0 S}^{obj.}$$

$$(MUW)_{os} = \cancel{h_1} (h_1 - h_2) - T_0 (S_1 - S_2)$$

$$= h_1 - h_2 - T_0 S_1 + T_0 S_2$$

$$= (h_1 - T_0 S_1) - (h_2 - T_0 S_2),$$

$$= \phi_1 - \phi_2.$$

* Irreversibility -

It is defined as the difference between maximum work & Actual work.

$$I = W_{\max} - W_{\text{Actual}}.$$

1850-1860

Gouy's Stodola Theorem -

According to this theorem, rate of irreversibility is directly proportional to rate of entropy generation.

$$I \propto (ds)_{\text{universe}}$$

$$\boxed{I = T_0 (ds)_{\text{universe}}}_{\text{obj.}}$$

$$* \text{ Gibbs Function } [G] = H - TS \quad \boxed{\text{obj.}}$$

Change in Gibbs Function (dG):

$$dG = dH - Tds - SdT.$$

$$\cancel{dG = dT}$$

$$\therefore Tds = dH - VdP.$$

$$\therefore \boxed{dG = VdP - SdT}.$$

* Gibbs Helmholtz Function (F):

$$\boxed{F = U - TS} \quad \boxed{\text{obj.}}$$

Change in Gibbs Helmholtz Function (G) -

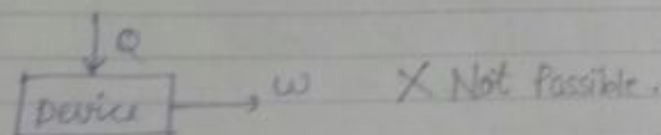
$$dG = dU - TdS - SdT.$$

$$\therefore TdS = dU + PdV.$$

$$\therefore \boxed{dG = -PdV - SdT} \quad \text{[eq]}$$

* PMM-2: Perpetual Motion Machine of Second Kind -

It is impossible because it violates second law of TDS i.e., the complete conversion of heat into work is not possible.



* PMM-3 -

Perpetual motion machine of third kind is impossible. ~~to be~~
It is impossible to construct a device which runs completely in the absence of friction.

* Third Law of Thermodynamics -

It is impossible to achieve absolute zero kelvin in a finite no. of process.

Nernst Simon Statement - The entropy of a pure ~~substance~~ crystalline substance is 0 at absolute 0 temp. (or 0K).