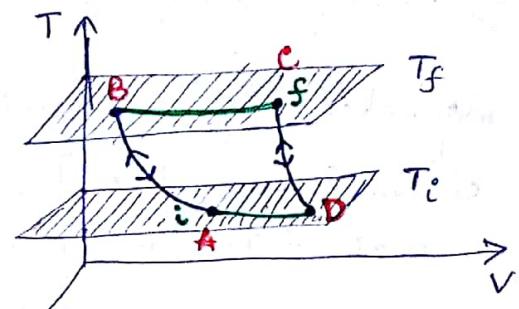
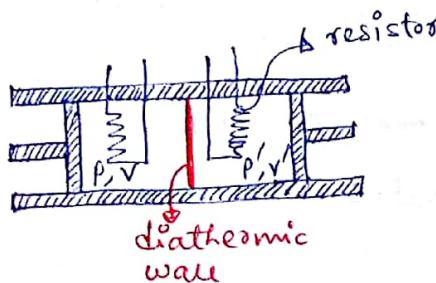


Using Curie's law  $M = C \frac{H}{T}$

$$W = \mu_0 \int_{M_i}^{M_f} \frac{MT}{C} dM = \frac{\mu_0 T}{2C} (M_f^2 - M_i^2)$$

$$= \mu_0 \int_{H_i}^{H_f} H \frac{C}{T} dH = \frac{\mu_0 C}{2T} (H_f^2 - H_i^2)$$

### Adiabatic Work



System can undergo adiabatic work with surroundings ① moving pistons quasistatically (slowly)  $W = - \int P dV$

② non-quasistatic (free expansion)  $\Rightarrow$  fast so that velocity of molecules do no work at piston. Also work can be done by dissipating electrical energy on resistors

Path ABC from  $i \rightarrow f$ , AB is reversible quasistatic adiabatic compression between two isothermal planes. BC correspond to adiabatic irreversible dissipation of electrical energy to keep  $T = \text{constant}$ , as energy can be added to resistor but cannot be extracted.

There are many such other path (e.g. ADC), meaning adiabatic work is same along all paths.

1st law of Thermodynamics: If a system is changed from initial state to final state by adiabatic work, the work done is same for all adiabatic path connecting two states.

$$W_{i \rightarrow f} (\text{adiabatic}) = U_f - U_i = dU \quad (\text{perfect differential})$$

$U$  = internal energy function

But if system change state nonadiabatically, then to conserve energy, Q heat is to be added to system (+ive)/subtracted (-ive)

from the system,  $U_f - U_i = Q + W$ .

for infinitesimal process,  $dU = dQ + dW$  & if its quasi static  
then  $dU$  &  $dW$  can be expressed in thermodynamic coordinates.

for hydrostatic system  $dU = dQ - PdV$

wire  $dU = dQ + \gamma dL$

surface film  $dU = dQ + \sigma dA$

paramagnetic Rod  $dU = dQ + \mu_0 H dM$

When  $U = U(V, T)$ ,  $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

$$\therefore dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV \quad \text{--- (1)}$$

$$\Rightarrow \frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \frac{dV}{dT}$$

(i)  $V = \text{constant}$ ,  $\left(\frac{dQ}{dT}\right)_V = \boxed{\left(\frac{\partial U}{\partial T}\right)_V} = C_V$

(ii)  $P = \text{constant}$ ,  $\left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial T}\right)_P$

$$\Rightarrow C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] V \beta \quad \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_P - C_V}{V \beta} - P}$$

Cyclic process  $dU = 0$ ,  $dQ = PdV$ . heat = work.

Also, from equation (1)  $dQ = C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV$

for ideal gas, no potential energy, free expansion do not affect heat.

$PdV = 0$ ,  $dQ = 0$  at constant temperature  $dT = 0$ ,  $\left(\frac{\partial U}{\partial V}\right)_T dV = 0$ .

$\therefore \left(\frac{\partial U}{\partial V}\right)_T = 0 \Rightarrow$  internal energy is independent of volume.

$\therefore \boxed{dQ = C_V dT + PdV}$  for ideal gas.

Equation of state  $PV = nRT \Rightarrow PdV + VdP = nRdT$  infinitesimal  
quasi static process

$$\therefore dQ = (C_V + nR)dT - VdP$$

$$\Rightarrow \frac{dQ}{dT} = C_V + nR - V \frac{dP}{dT}, P \text{ constant}$$

$$\boxed{C_P = C_V + nR}$$

$$\text{Also } \delta S = C_p dT - V dP$$

### Elasticity of perfect gas

Isothermal bulk modulus  $E_T = -V \left( \frac{\partial P}{\partial V} \right)_T$

Adiabatic bulk modulus  $E_g = -V \left( \frac{\partial P}{\partial V} \right)_g$ .

For isothermal change  $PV = RT = \text{constant}$

$$PdV + VdP = 0 \Rightarrow \left( \frac{\partial P}{\partial V} \right)_T = -\frac{P}{V}.$$

For adiabatic change  $PV^\gamma = \text{constant}$ ,  $\gamma PV^{\gamma-1} dV + dP V^\gamma = 0$

$$\therefore \left( \frac{\partial P}{\partial V} \right)_g = -\frac{\gamma P}{V}. \quad \therefore \boxed{\frac{E_g}{E_T} = \gamma.}$$

### Second law of Thermodynamics

This is an extension of first law with a direction of the process  $\rightarrow$  experimental development of engines.

#### Reversibility & Irreversibility

reversibility = system + surroundings from changed state can restore back to initial configuration without change of universe.  
The opposite to that is irreversible process.

2nd law  $\rightarrow$  Carnot's finding in ideal engine  $\rightarrow$  Clausius

statement  $\rightarrow$  Kelvin's statement  $\rightarrow$  birth of "entropy".

#### Conversion of work to heat

In previous examples, we saw how heat can be generated indefinitely at the expense of work. To study the converse process, there may be 1 or more than 1 (series of) processes.

At first it appeared that isothermal expansion may be suitable for conversion of heat into work, but it's not indefinite. Thus a cycle is required that can be taken back & forth.

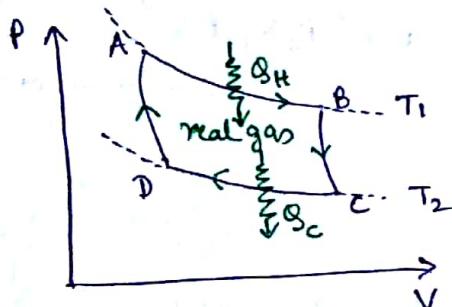
If in a cycle  $Q_H$  amount of heat is absorbed &  $Q_C$  ( $Q_C < Q_H$ ) amount of heat is radiated &  $W$  amount of work is needed then the mechanical device is a "Heat Engine." Efficiency of such engine is defined as

$$\eta = \frac{\text{work output}}{\text{Heat input}} = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$

Hot reservoir of infinite heat capacity is "source" & cold reservoir is called "sink."

### Carnot cycle

It's maximum efficient engine (nearly ideal)



AB, CD = isothermal  
BC, DA = adiabatic

Consists of four reversible steps.

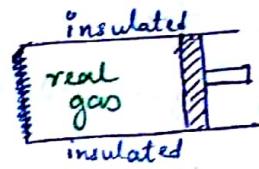
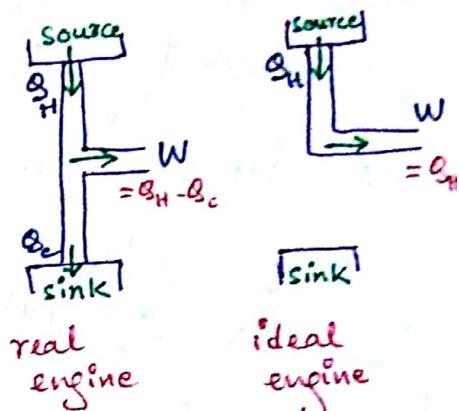
(1) Isothermal expansion  $A \rightarrow B$ :

Cylinder is placed in contact with a heat reservoir at temperature  $T_1$  & gas expands isothermally from  $(P_1, V_1, T_1)$  to  $(P_2, V_2, T_1)$ .  $Q_H$  amount of heat taken from source &  $W_1$  amount of work done "by" the gas.

(2) Adiabatic expansion  $B \rightarrow C$ : The gas is allowed to expand adiabatically in insulated environment. The temperature falls to  $T_2$  & volume changes to  $V_3$ .  $Q=0$  and work done "by" the gas is  $W_2$ .

(3) Isothermal compression  $C \rightarrow D$ : The gas at very low pressure is now reversibly compressed in sink at temperature  $T_2$  from volume  $V_3$  to  $V_4$ . Heat rejected to sink is  $Q_C$  & work done by the gas is  $-W_3$  (-ive because work done "on" gas).

(4) Adiabatic compression  $D \rightarrow A$ : Now the system is adiabatically restored to initial state from  $V_4 \rightarrow V_1$ ,  $T_2 \rightarrow T_1$ .  $Q=0$ , work done



by the gas is  $-W_4$  (-ive because workdone "on" the gas).

from first law of thermodynamics  $\oint_C dU = 0$

$$\Rightarrow \oint_C dQ - \oint_C dW = 0 \Rightarrow Q_H + 0 - Q_C + 0 = W_1 + W_2 - W_3 - W_4$$

$\therefore$  Work done by engine = difference of heat absorbed & rejected.

$$\text{Now } Q_H = \int_{V_1}^{V_2} pdV = RT_1 \ln \frac{V_2}{V_1} = W_1.$$

$$Q_C = - \int_{V_3}^{V_4} pdV = RT_2 \ln \frac{V_3}{V_1} = W_3$$

But for isothermal processes  $P_1 V_1 = P_2 V_2, P_3 V_3 = P_4 V_4$

for adiabatic processes  $P_2 V_2^\gamma = P_3 V_3^\gamma, P_4 V_4^\gamma = P_1 V_1^\gamma$

Multiplying,  $P_1 V_1 P_2 V_2^\gamma P_3 V_3^\gamma P_4 V_4^\gamma = P_2 V_2 P_3 V_3^\gamma P_4 V_4 P_1 V_1^\gamma$  (independent events)

$$\text{or } (V_2 V_4)^\gamma-1 = (V_3 V_1)^\gamma-1$$

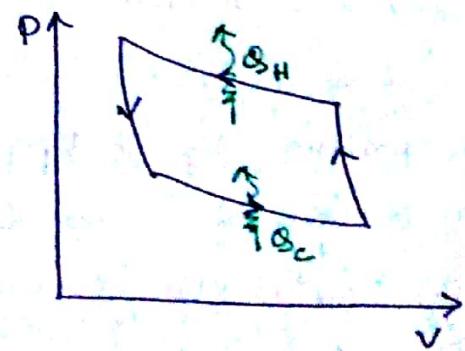
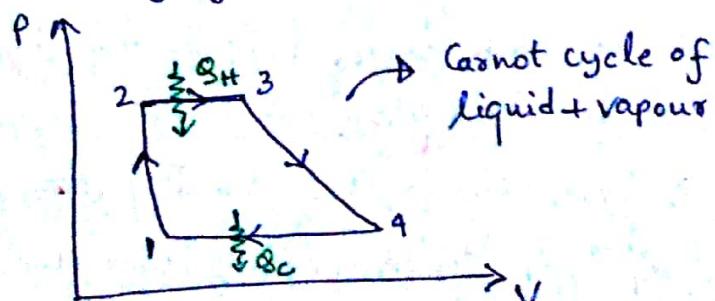
$$\text{or } V_2/V_1 = V_3/V_4$$

$$\therefore \text{Efficiency } \eta = \frac{Q_H - Q_C}{Q_H} = \frac{R(T_1 - T_2) \ln(V_2/V_1)}{RT_1 \ln(V_2/V_1)} \\ = \frac{T_1 - T_2}{T_1} \neq 100\%$$

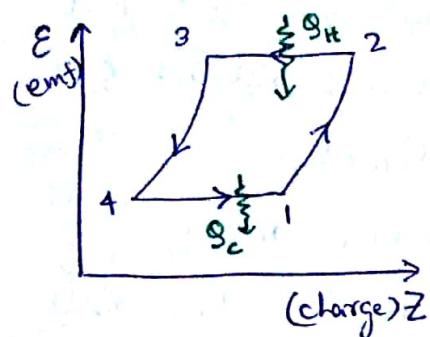
$$\therefore \boxed{\frac{Q_H}{T_1} = \frac{Q_C}{T_2}}$$

We can also reverse the cycle from any point of the indicator diagram.

In that case  $Q_C$  heat is removed from sink &  $Q_H$  is delivered to source & work must be done to the system. The system is then works as a refrigerator.



- $1 \rightarrow 2$  reversible adiabatic compression to temperature  $T_H$   
 $2 \rightarrow 3$  reversible isothermal isobaric vaporization  
 $3 \rightarrow 4$  reversible adiabatic expansion temperature falls to  $T_C$   
 $4 \rightarrow 1$  reversible isothermal isobaric condensation



- $1 \rightarrow 2$  reversible adiabatic flow of charge from - to + to temperature  $T_H$ .  
 $2 \rightarrow 3$  reversible isothermal flow of charge from + to -  
 $3 \rightarrow 4$  reversible adiabatic flow of charge to temp.  $T_C$   
 $4 \rightarrow 1$  reversible isothermal flow of charge

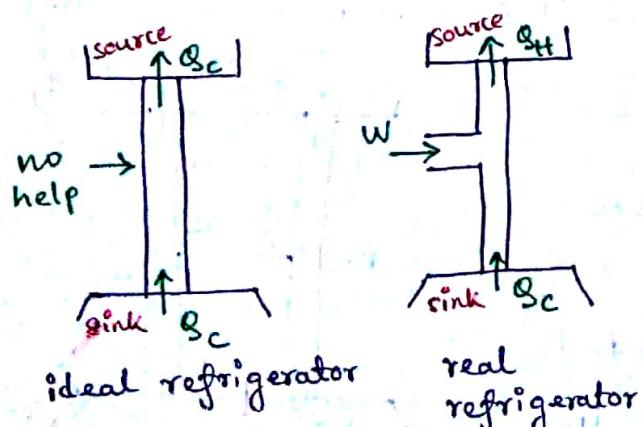
### Second law of Thermodynamics

Kelvin's Statement It is impossible by any inanimate object to derive mechanical work from any portion of the matter by cooling it below the temperature of the coldest of the surrounding objects.

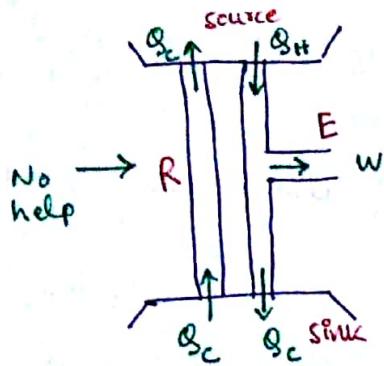
Plank's Statement It is impossible to fabricate an engine working in a complete cycle to produce no effect other than raising a weight & cooling of a hot reservoir.

P-K Statement  $\rightarrow$  It is impossible to produce an ideal engine.

Clausius Statement It is impossible for a self-acting machine unaided by any external agency to convey heat from one body at lower temperature to another at a higher temperature. Heat cannot by itself transit from a colder to a warmer body or it is impossible to construct an ideal refrigerator.



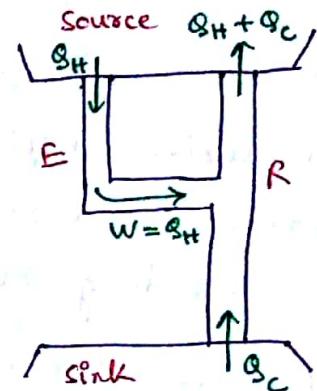
## Equivalence of Kelvin-Plank & Clausius statement



Suppose we disobey Clausius's statement & make an ideal refrigerator  $R$  that transfers  $Q_C$  from sink to source without any work. But engine  $E$  draws  $Q_H$  from source & returns  $Q_C$  to sink & delivering work  $Q_H - Q_C$ .

∴ Combined  $R-E$  system form a self-acting device drawing  $Q_H - Q_C$  heat from hot reservoir & convert fully this heat into work without change in sink → violation of K-P statement.

Consider again an ideal engine  $E$  that rejects no heat to sink & violate K-P statement.  $Q_H$  heat is fully converted to work  $W$  which is feeded to a refrigerator  $R$  to extract  $Q_C$  heat from sink. Again  $E-R$  forms a self-acting device that transfers  $Q_C$  from sink to source without any change elsewhere → violation of Clausius statement.



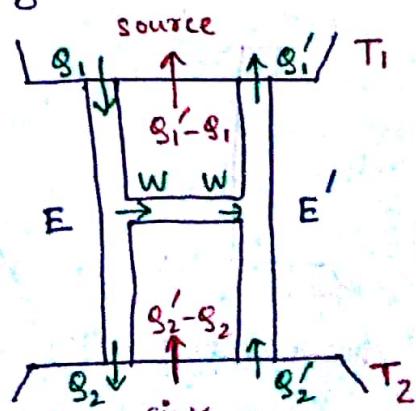
1st law of Thermodynamics = conservation of energy

2nd law of Thermodynamics = directionality (may not be true always)

## Carnot's theorem

Efficiency of all reversible engines operating between same two temperatures is equal & no irreversible engine can have a better efficiency compared to the reversible engine between same two temperatures.

Clausius & Kelvin showed that this theorem is a consequence of the 2nd law of thermodynamics.  $\eta$  is independent of working substance & depends only on  $T_1, T_2$ .



Proof Suppose engine E & E' working between  $T_1$  &  $T_2$  differ in working substance or initial pressure or length of stroke. E runs forward & E' run backward (refrigerator). The system is so made that work done by E is exact amount of work needed for E' to function. Suppose  $\eta$  (efficiency) of E  $>$   $\eta'$  of E'.

$\therefore \frac{Q_1 - Q_2}{Q_1} > \frac{Q'_1 - Q'_2}{Q'_1}$ . By construction work done per cycle be  $W = W'$   $\Rightarrow Q_1 - Q_2 = Q'_1 - Q'_2$

$$\therefore W = W' \Rightarrow Q_1 - Q_2 = Q'_1 - Q'_2$$

$$\therefore \frac{1}{Q_1} > \frac{1}{Q'_1} \quad \text{as } Q'_1 > Q_1 \quad \text{and } Q'_2 > Q_2 \text{ to satisfy } W = W'$$

Therefore hot source gains heat  $Q'_1 - Q_1$  and cold sink loses heat  $Q'_2 - Q_2$  and no work is done by the combined E + E' system. We've transferred heat from a cold to hot body without performing work is direct contradiction to Clausius statement.

$$\therefore \eta \neq \eta'$$

Similarly, by reversing the engine E backward & E' forward we can prove that  $\eta' \neq \eta$ . So the only possibility is

$$\boxed{\eta = \eta'}$$

for irreversible engine we can show by the same procedure that  $\eta_{irr} \neq \eta_{rev}$  but due to irreversibility we cannot show  $\eta_{rev} \neq \eta_{irr}$   
 $\therefore \eta_{irr}$  is either equal to or less than  $\eta_{rev}$ .

$$\therefore \boxed{\eta_{rev} \geq \eta_{irr}}$$

## Kelvin scale / Absolute scale / Thermodynamic scale of temperature

Using Carnot engine, temperature can be defined in term of energy & the scale so obtained is independent of nature of any particular substance. Efficiency of all reversible engine is a function of two temperatures only

$$\eta = \frac{W}{Q_1} = f(T_1, T_2) = \frac{Q_1 - Q_2}{Q_1} \Rightarrow \frac{Q_1}{Q_2} = \frac{1}{1-f(T_1, T_2)} = F(T_1, T_2).$$

Suppose we have three reversible engines working between the temperature  $(T_1, T_2)$ ,  $(T_2, T_3)$  &  $(T_1, T_3)$ , then

$$\frac{Q_1}{Q_2} = F(T_1, T_2), \quad \frac{Q_2}{Q_3} = F(T_2, T_3)$$

$$\therefore \frac{Q_1}{Q_3} = F(T_1, T_2) F(T_2, T_3) = F(T_1, T_3).$$

This can satisfy if & only  $F(T_1, T_3) = \frac{\psi(T_1)}{\psi(T_3)}$

∴ For any reversible engine we can write  $\frac{Q_1}{Q_2} = \frac{\psi(T_1)}{\psi(T_2)}$

Now if  $T_1 > T_2$ ,  $Q_1 > Q_2$  and therefore  $\psi(T_1) > \psi(T_2)$

∴  $\psi(T)$  is a monotonically increasing function of temperature

$$\therefore \boxed{\frac{Q_1}{Q_2} = \frac{T_1}{T_2}}$$

So we have defined a new scale of temperature whose ratio depends on heat absorbed & heat rejected in a reversible engine.

$T=0^\circ$  in this scale is when  $Q_2=0$  & ∴  $W=Q_1$  &  $\eta=100\%$  (ideal engine).  $T$  cannot be less than this as  $Q_2 < 0$  means engine would be drawing heat both from source & sink which is impossible due to direct violation of 2<sup>nd</sup> law. ∴  $T=0$  is the lowest attainable temperature when one gets an ideal engine.

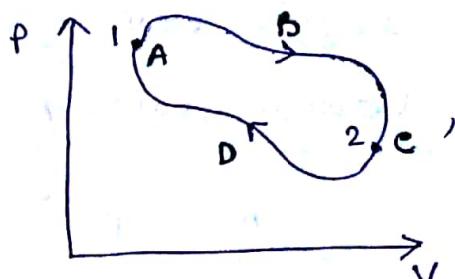
Entropy In any reversible process, if heat  $Q$  is added at temperature  $T$  and rejects  $Q'$  heat at temperature  $T'$ , then  $\frac{Q}{T} = \frac{Q'}{T'}$ .

$$\therefore \frac{Q}{T} - \frac{Q'}{T'} = 0 \quad \text{or} \quad \sum \frac{Q}{T} = 0 \quad (Q = +\text{ive heat absorbed} \\ = -\text{ive heat rejected})$$

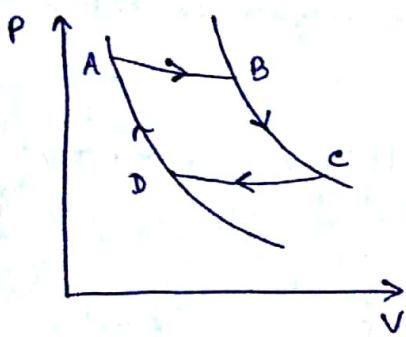
Any reversible transformation is made of a number of infinitesimal reversible isothermal & adiabatic processes.  $\therefore$  for any reversible cyclic process ABCD  $\oint_C \frac{dQ}{T} = 0$ . This is called "Clausius Theorem".

We can define a thermodynamic function "entropy"  $dS = \frac{dQ}{T}$  that has the property

$$\oint_{ABCD} \frac{dQ}{T} = 0 \quad \therefore \oint_{ABC} \frac{dQ}{T} + \oint_{CDA} \frac{dQ}{T} = 0$$



$\therefore \oint_{ABC} \frac{dQ}{T} = \oint_{ADC} \frac{dQ}{T}$ . This means that  $\int \frac{dQ}{T}$  is independent of the path and depends only on the initial & final point 1 & 2.  
 $\therefore dS = \frac{dQ}{T}$  is an exact differential. Unit cal/K.



To understand property of  $dS$ , consider a reversible cycle constituted by two adiabatic AD & BC & two isothermals AB & CD.

For AD & BC,  $dQ = 0 \therefore dS = 0$ . & hence

$$\int_A^B \frac{dQ}{T} = \int_D^C \frac{dQ}{T}.$$

Point A & B may be taken anywhere on the adiabatic AD & BC, still the integral will remain same as  $dQ = 0$  for adiabatic process. Hence it follows that if we pass from one adiabatic to other,  $\int^2 \frac{dQ}{T}$  increases by a definite amount independent of the manner of transformation. We can choose any standard state n & then  $\int_n^A \frac{dQ}{T}$  on a reversible path depends only on state n & A. If my standard reference state n is fixed, integral is a function of state A only.

and termed as  $S_A$  & can be different if we choose different  $n$ .

Thus the entropy is undetermined to the extent of an additive constant that represents entropy of an arbitrarily chosen standard state with respect to state with zero entropy.

$\therefore S_A = S_n + \int_n^A \frac{ds}{T}$ .  $S_n$  = entropy at state  $n$  which according to law of thermodynamics  $S_n$  cannot be determined & absolute value of entropy cannot be found out. But change of entropy between states A & B can be accurately determined,

$$S_A - S_B = S_n + \int_n^A \frac{ds}{T} - S_n - \int_n^B \frac{ds}{T} = \int_B^A \frac{ds}{T}$$

This is valid for equilibrium states only & for nonequilibrium states can approach equilibrium by irreversible process in which entropy increases.

Also  $ds = dU + PdV$  is an inexact differential as  $\int (dU + PdV)$  requires a knowledge of path. But  $ds = \frac{ds}{T}$  is perfect or exact differential.

Exact differential ( $ds$ )	= Inexact differential ( $ds$ )	$\times$ Integrating factor ( $YT$ )
--------------------------------	------------------------------------	---

Example  $df = 3xydx + 2x^2dy$  = inexact  $\frac{\partial^2 f}{\partial x \partial y} \neq \frac{\partial^2 f}{\partial y \partial x}$

But  $\boxed{xy} df = d\phi = 3x^2y^2dx + 2x^3ydy = d(x^3y^2) =$  exact.

I.F.

Caratheodory's Principle In the immediate neighbourhood of any arbitrary initial state, there exists neighbouring states which are not accessible from the initial state along adiabatic paths.

## Entropy of an ideal gas

If an ideal gas of  $m \text{ gm}$  at temperature  $T$  & volume  $V$  is given heat  $\delta Q$ , then change in entropy is  $ms = \int \frac{dU + PdV}{T}$

$$\text{Now } dU = mC_V dT, \quad P = \frac{mRT}{MV}$$

$$\therefore ms = m \left\{ C_V \int_{T_1}^{T_2} \frac{dT}{T} + \frac{R}{M} \int_{V_1}^{V_2} \frac{dV}{V} \right\} \text{ for } (P_1, V_1, T_1) \rightarrow (P_2, V_2, T_2)$$

In general for monoatomic gas  $C_V \neq C_V(T)$  & so

$$ms = m \left\{ C_V \ln T + \beta_M \ln V \right\} + \text{constant} \quad \therefore S = S(T, V).$$

To obtain  $S = S(T, P)$ , we use  $C_P - C_V = \beta_M$ .

$$\therefore ms = m(C_P - \beta_M) \ln T + \frac{mR}{M} \ln V + \text{constant}$$

$$= mC_P \ln T - \frac{mR}{M} \ln (T_V) + \text{constant} \quad [PV = \frac{mRT}{M}]$$

$$= mC_P \ln T - \frac{mP}{M} \ln (\frac{PM}{mR}) + \text{constant} \quad T_V = \frac{PM}{mR}$$

$$ms = mC_P \ln T - \frac{mP}{M} \ln P + \text{constant}.$$

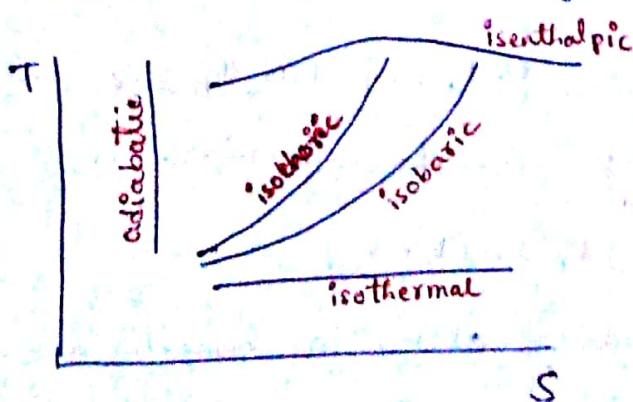
Isothermal system for isothermal change of state of gas  $dU = 0$

$$\therefore ds = \frac{pdv}{T} \text{ and using } PV = NRT$$

$$= \frac{N R dv}{V} \quad \therefore S = N R \ln \left( \frac{V_2}{V_1} \right)$$

Adiabatic system for adiabatic change  $\delta Q = 0$  & so  $ds = 0$ . No change in entropy of the system (isentropic process).

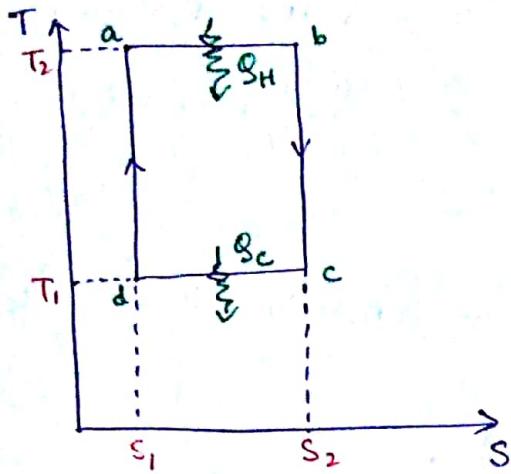
In free expansion of a perfect gas into an empty vessel in a thermally insulated environment, gain in entropy is  $\Delta S = \int \frac{pdv}{T} = R \ln \frac{V_2}{V_1}$ .



$$\text{In a reversible procen } Q_R = \int_i^f T ds$$

So the heat is the area under a curve in  $T-S$  plane.

## Carnot's cycle in TS diagram



The Carnot cycle in TS diagram is a parallelogram.

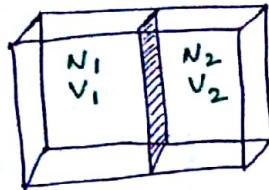
$$Q_H = T_2 (S_2 - S_1)$$

$$Q_C = T_1 (S_2 - S_1) \text{ and } dS = 0 \text{ for bc and da lines.}$$

$$\therefore \text{Efficiency } \eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$

$$= \frac{(S_2 - S_1)(T_2 - T_1)}{T_2 (S_2 - S_1)} = 1 - \frac{T_1}{T_2}$$

## Gibbs' Paradox



Consider an ideal gas of  $N$  particles in a container with volume  $V$ . A partition divides  $N_1$  &  $N_2$  particles & volume  $V_1$  &  $V_2$  such that

$$N = N_1 + N_2, \quad V = V_1 + V_2 \quad \text{and} \quad n = \frac{N_1}{V_1} = \frac{N_2}{V_2} \quad (\text{equal number density})$$

$$\begin{aligned} \text{Using } S &= C_V \ln T + R \ln V + \text{constant} \\ &= \frac{3}{2} R \ln T + R \ln V + \text{constant} \\ &= \frac{3}{2} N_1 k_B \ln T + N_1 k_B \ln V + \text{constant} \end{aligned}$$

firstly,  $T \rightarrow 0, S \rightarrow -\infty !!$  violating 2<sup>nd</sup> law of thermodynamics

Secondly,  $S \propto N$  for a given  $V !!$  This expression from classical framework is not right. This also leads to gives paradox  $\Rightarrow$

$$\text{In the partitioned state } S_1 = \frac{3}{2} N_1 k_B \ln T + N_1 k_B \ln V_1 + \text{cont.}$$

$$S_2 = \frac{3}{2} N_2 k_B \ln T + N_2 k_B \ln V_2 + \text{cont.}$$

The partition is now removed & gas comes to well-mixed state.

$$S = \frac{3}{2} (N_1 + N_2) k_B \ln T + (N_1 + N_2) k_B \ln (V_1 + V_2)$$

Now its monoatomic gas of identical atoms, so removing the partition shouldn't increase entropy as particles are indistinguishable.

$\Delta S = S - (S_1 + S_2) = 0$  But here we find

$$\begin{aligned}\Delta S &= (N_1 + N_2) k_B \ln(V_1 + V_2) + \frac{3}{2} (N_1 + N_2) k_B \ln T - \\&\quad N_1 k_B \ln V_1 - \frac{3}{2} N_1 k_B \ln T - N_2 k_B \ln V_2 - \frac{3}{2} N_2 k_B \ln T \\&= N_1 k_B [\ln(V_1 + V_2) - \ln V_1] + N_2 k_B [\ln(V_1 + V_2) - \ln V_2] \\&= N_1 k_B \ln \frac{V_1 + V_2}{V_1} + N_2 k_B \ln \frac{V_1 + V_2}{V_2} \neq 0.\end{aligned}$$

This paradox cannot be resolved in classical MB statistics & need statistical physics, namely quantum stat mech where atoms are indistinguishable (leads to Sackur-Tetrode formula of entropy in ideal gas) taking Stirling's approximation ( $\ln N! = N \ln N - N$ ). Now, if we correct  $S$  accordingly,

$$S = N k_B \ln \left( \frac{V}{N} \right) + \frac{3}{2} N k_B \ln T + \text{constant}$$

$$\begin{aligned}\text{Then } S - (S_1 + S_2) &= (N_1 + N_2) k_B \ln \left( \frac{V_1 + V_2}{N_1 + N_2} \right) - N_1 k_B \ln \frac{V_1}{N_1} - N_2 k_B \ln \frac{V_2}{N_2} \\&= N_1 k_B \ln \frac{V}{N} - N_1 k_B \ln \frac{V_1}{N_1} + N_2 k_B \ln \frac{V}{N} - N_2 k_B \ln \frac{V_2}{N_2} \\&= N_1 k_B \ln \left( \frac{N N_1}{N V_1} \right) + N_2 k_B \ln \left( \frac{N N_2}{N V_2} \right)\end{aligned}$$

$$\text{But } n = \frac{N}{V} = \frac{N_1}{V_1} = \frac{N_2}{V_2} \quad (\text{no. density is constant})$$

$$\therefore \ln \left( \frac{N N_1}{N V_1} \right) = \ln \left( \frac{n}{n} \right) = \ln(1) = 0$$

$$\ln \left( \frac{N N_2}{N V_2} \right) = 0. \quad \therefore \underline{\Delta S = 0}$$

Gibb's paradox thus gets resolved.

### Entropy increase in Irreversible process

Consider an irreversible process in which temperature of a body at  $T_1$  is increased to  $T_2$  by coupling to a reservoir at  $T_2$ . The initial & final state of the body is same & its irreversible as heat flow from reservoir to body cannot be reversed. But change in entropy of the body is same for both reversible or irreversible process as its not path dependent.

Suppose pressure remains constant, then change in entropy of the body

$$\therefore \Delta S_{\text{body}} = \int_{T_1}^{T_2} C_p \frac{dT}{T} = C_p \ln\left(\frac{T_2}{T_1}\right) > 0 \text{ as } T_2 > T_1.$$

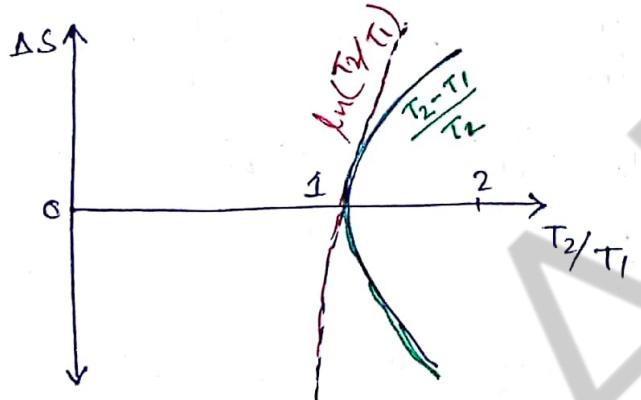
The reservoir temperature  $T_2$  remains constant, so change in entropy is same for reversible isothermal process (heat flowing into reservoir) & irreversible isothermal process (heat only flowing out)

Heat flow into the body  $\therefore \delta Q = C_p(T_2 - T_1)$  & this is the heat came out from reservoir, so decrease in entropy of reservoir

$$\therefore \Delta S_{\text{reservoir}} = -\frac{\delta Q}{T_2} = -\frac{C_p(T_2 - T_1)}{T_2}$$

Total change of entropy of the composite system

$$\Delta S = \Delta S_{\text{body}} + \Delta S_{\text{reservoir}} = C_p \left[ \ln\left(\frac{T_2}{T_1}\right) - \frac{T_2 - T_1}{T_2} \right]$$



$$\text{for } T_2 > T_1, \ln\left(\frac{T_2}{T_1}\right) > \frac{T_2 - T_1}{T_2}$$

$\therefore$  Increase in entropy of the body is always greater than decrease of entropy of reservoir &  $\therefore$  entropy of universe always increases in irreversible process.

Even when the body is at higher temperature than reservoir the situation is reversed but entropy of universe increases. So whenever heat flows across finite temperature difference (~~reversible~~ ~~irreversible~~), entropy of universe increases. For reversible process entropy remains constant.

$$S_f = S_i \text{ for reversible}$$

$$S_f > S_i \text{ for irreversible}$$

This principle of increase in entropy can be termed as 2<sup>nd</sup> law of thermodynamics. Clausius restated that 1<sup>st</sup> law is energy of the universe remains constant & 2<sup>nd</sup> law is entropy of universe tends to be the maximum.

## Entropy flow & entropy production

Consider heat conduction along a copper wire that are held between two reservoirs at  $T_1$  &  $T_2$  ( $T_1 > T_2$ ). If heat current or rate of flow of heat is  $I_Q$  then in unit time, hot source decreases its entropy by  $I_Q/T_1$ , sink increases entropy by  $I_Q/T_2$  & copper wire at steady state suffers no change in entropy. So  $\Delta S_{\text{universe}} = \frac{I_Q}{T_2} - \frac{I_Q}{T_1} > 0$ .

We can see it from the perspective of wire that the hot source lost entropy to the wire & there is a flow of entropy into the wire of  $I_Q/T_1$  per unit time. The sink gained entropy so there was a flow of entropy out of the wire.  $I_Q/T_2$ .

$$\text{Entropy production in wire } \frac{dS}{dt} = \frac{I_Q}{T_2} - \frac{I_Q}{T_1} = I_Q \frac{T_1 - T_2}{T_1 T_2}$$

if  $T_1 = T + \Delta T$ ,  $T_2 = T$ ,  $T_1 T_2 \approx T^2$

$$\therefore \frac{dS}{dt} = I_Q \frac{\Delta T}{T^2} = I_Q \frac{\Delta T}{T} = I_S \frac{\Delta T}{T}$$

↓  
entropy  
production

- Ques. 1. A reversible engine in Carnot cycle between  $100^\circ\text{C}$  &  $0^\circ\text{C}$  does work  $1200 \text{ kg-centre}/\text{cycle}$ . Find the amount of heat drawn from source.  $J = 4.18 \times 10^7 \text{ ergs/cal}$ .

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_1 - Q_2}{T_1 - T_2} = \frac{W}{T_1 - T_2} \quad W = mgh$$

$$\therefore Q_1 = \frac{WT_1}{T_1 - T_2} = \frac{1200 \times 10^3 \text{ m} \times 980 \times 373}{100 \times 4.18 \times 10^7} = 10494 \text{ cal.}$$

2. A body of constant heat capacity  $C_p$  at temperature  $T_i$  is put in contact with reservoir at  $T_f$ . At constant pressure, body comes to equilibrium. Show that entropy change of universe is  $C_p[x - \ln(1+x)]$  where  $x = -\frac{T_f - T_i}{T_f}$ .

$$\text{Gain in entropy of the body } \Delta S_{\text{body}} = \int_{T_i}^{T_f} \frac{C_p dT}{T} = C_p \ln\left(\frac{T_f}{T_i}\right)$$

$$\text{Loss of entropy of reservoir } \Delta S_{\text{reservoir}} = -\frac{\delta Q}{T_f} = -\frac{C_p(T_f - T_i)}{T_f}$$

$$\therefore \text{Total change in entropy of the universe } \Delta S = C_p \ln \frac{T_f}{T_i} - C_p \frac{T_f - T_i}{T_f}$$

$$= (C_p \ln(1+x) + C_p x) = C_p(x - \ln(1+x))$$

3. According to Debye's law, the molar heat capacity at constant volume of Diamond varies with temperature as

$C_V = 3R \frac{4\pi^4}{5} \left(\frac{T}{H}\right)^3$ . What is the entropy change in units of R of a diamond of 1.2 gm when it's heated at constant volume from 10 to 350K. Atomic weight of carbon is 12 gm &  $H = 2230 \text{ K}$ .

$$\Delta S = \frac{1.2}{12} \int_{10}^{350} \frac{C_V dT}{T} = \frac{1.2}{12} 3R \frac{4\pi^4}{5} \frac{1}{H^3} \int_{10}^{350} T^2 dT$$

$$= 0.03 R.$$

4. m gms of water at  $T_1$  is isobarically & adiabatically mixed with an equal mass of water at  $T_2$ , so that they attain a common final temperature  $T_c$ . Show that entropy change of the universe is  $2mC_V \ln \frac{(T_1+T_2)}{\sqrt{T_1 T_2}}$ . What would be the loss of available energy?

$T_c$  will attend when  $mC_V(T_1 - T_c) = mC_V(T_c - T_2)$

$$\text{or } T_c = \frac{T_1 + T_2}{2}. \quad \Delta S_1 = mC_V \int_{T_1}^{T_c} \frac{dT}{T} = mC_V \ln \frac{T_c}{T_1}$$

$$\Delta S_2 = mC_V \int_{T_2}^{T_c} \frac{dT}{T} = mC_V \ln \frac{T_c}{T_2}$$

$$\Delta S_{\text{universe}} = \Delta S_1 + \Delta S_2 = mC_V \ln \frac{T_c^2}{T_1 T_2} = mC_V \ln \left(\frac{T_c}{\sqrt{T_1 T_2}}\right)^2$$

$$= 2mC_V \ln \frac{T_1 + T_2}{2\sqrt{T_1 T_2}}$$

If  $T_0$  is the lowest attainable temperature, then unavailable amount of energy is  $S_{\text{unattain}} = T_0 \Delta S_{\text{universe}} = 2mC_V T_0 \ln \frac{T_1 + T_2}{2\sqrt{T_1 T_2}}$ .

- HW
- The equation of state of a new matter is  $pV = AT^3$ ,  $A = \text{constant}$ . Internal energy of this matter is  $U = BT^n \ln(V/V_0) + f(T)$ . Using first law of thermodynamics, find  $B$  and  $n$ .
  - Suppose an engine works between two reservoirs at  $T_1$  &  $T_2$  ( $T_2 > T_1$ ) until both reservoirs attain final temperature  $T_c$ . Show that  $T_c > \sqrt{T_1 T_2}$ . What is the maximum amount of work obtainable from this engine?

### Entropy & Unavailable energy

Suppose that  $Q$  amount of heat is extracted from a reservoir at temperature  $T_1$  & it is desired to convert this heat into work as much as possible. If  $T_0$  is the temperature of sink, then using a reversible engine,  $W_{\max}^r = Q(1 - \frac{T_0}{T_1})$ .

Consider an irreversible conduction of heat  $Q$  along a metal bar under finite temperature gradient from a region at temperature  $T_1$  to a region at temperature  $T_2$ . After conduction has taken place,  $Q$  amount of heat is available at lower temperature  $T_2$  or the maximum amount of available work is  $W_{\max}^{irr} = Q(1 - \frac{T_0}{T_2})$ . As  $T_1 > T_2$ , so maximum work obtained in  $W_{\max}^{irr}$  is less than  $W_{\max}^r$ .

$\therefore$  The amount of energy that is unavailable for work is,

$$E = Q(1 - \frac{T_0}{T_1}) - Q(1 - \frac{T_0}{T_2}) = T_0 Q (\frac{1}{T_2} - \frac{1}{T_1}) = T_0 \Delta S$$

where  $\Delta S$  is the entropy change of the universe due to the irreversible process. Since irreversible process is continually happening in nature, so energy is continually becoming unavailable for work. This is known as "Principle of degradation of energy".

Thus according to this principle, we are always losing available energy & then a day will come when we will have no available energy for work. This is called "heat death" of the universe.

### Disorder & entropy

Whenever work is dissipated within the system because of friction, viscosity, inelasticity, electric resistance or magnetoo hysteresis, the molecules are more disordered. We learned that irreversible process is associated with an increase in entropy of the universe. Thus, entropy must be related with the disorder.

Disorder of a system depends on the number of microstates accessible to the system. This is called "Thermodynamic probability" ( $\Omega$ ) & we can write  $S = f(\Omega)$ . To obtain the functional form, consider two systems having thermodynamic probability  $\Omega_1$  and  $\Omega_2$  with entropies  $S_1 = f(\Omega_1)$  and  $S_2 = f(\Omega_2)$  respectively.

If these systems are mixed then the total entropy is  $S = S_1 + S_2$  and the total number of microstates of the system will be

$$\Omega = \Omega_1 \Omega_2 \quad \therefore S_1 + S_2 = f(\Omega_1 \Omega_2)$$

$$\therefore f(\Omega_1) + f(\Omega_2) = f(\Omega_1 \Omega_2)$$

$$\begin{aligned} \therefore \frac{\partial f(\Omega_1)}{\partial \Omega_1} + 0 &= \frac{\partial f(\Omega_1 \Omega_2)}{\partial \Omega_1} = \frac{\partial f(\Omega_1 \Omega_2)}{\partial (\Omega_1 \Omega_2)} \frac{\partial (\Omega_1 \Omega_2)}{\partial \Omega_1} \\ &= \Omega_2 \frac{\partial f(\Omega_1 \Omega_2)}{\partial (\Omega_1 \Omega_2)} \end{aligned}$$

$$\text{Multiplying with } \Omega_1, \quad \Omega_1 \frac{\partial f(\Omega_1)}{\partial \Omega_1} = \Omega_1 \Omega_2 \frac{\partial f(\Omega_1 \Omega_2)}{\partial (\Omega_1 \Omega_2)}$$

$$\text{Similarly, } 0 + \frac{\partial f(\Omega_2)}{\partial \Omega_2} = \frac{\partial f(\Omega_1 \Omega_2)}{\partial \Omega_2} \Rightarrow \Omega_2 \frac{\partial f(\Omega_2)}{\partial \Omega_2} = \Omega_1 \Omega_2 \frac{\partial f(\Omega_1 \Omega_2)}{\partial (\Omega_1 \Omega_2)}$$

$$\therefore \Omega_1 \frac{df(\Omega_1)}{d\Omega_1} = \Omega_2 \frac{df(\Omega_2)}{d\Omega_2} \quad \therefore \Omega \frac{df(\Omega)}{d\Omega} = \text{constant (K say)}$$

$$\therefore df(\Omega) = K \frac{d\Omega}{\Omega} \quad \therefore f(\Omega) = K \ln \Omega + C$$

But if  $\Omega = 1$ ,  $f(\Omega) = 0$  as the system is in perfect ordered state.

$$\therefore C = 0. \quad S = K \ln \Omega$$

### Entropy and Information

Since the disorder of a system is related to the available information, therefore the entropy of a system should also have a relation with information.

Suppose we are called upon to guess a person's first name. The number of choices of names of men & women is huge. So there is a great disorder without any information. But given an information that the person is a man, the number of choices of names is reduced. Information is reduced further that man is a physicist and this reduces the disorder. The disorder in choosing names is further reduced if given an information that the physicist is a Nobel laureate.  $\therefore$  Fewer the number of ways a particular state of a system is achieved, the greater is the information.

A measure of the information when the number of choices is reduced from  $\Omega_0$  to  $\Omega_1$  is  $I = K \ln \frac{\Omega_0}{\Omega_1} = S_0 - S_1$ . The bigger the reduction, the bigger the information. Also,  $S_1 = S_0 - I$ .

$\therefore$  Entropy measures the lack of information about the exact state of a system.

### Entropy & 2<sup>nd</sup> law of Thermodynamics

The 2<sup>nd</sup> law provides proper direction to all natural processes while the Kelvin-Planck statement gives a direction for the conversion between

heat and work, Clausius statement gives a direction for heat flow between two bodies at different temperature. Combining the 2<sup>nd</sup> law can be defined in terms of entropy as

"A natural irreversible process will always proceed in a direction in which the entropy of universe increases. In a reversible process, entropy does not change."

This means in approaching equilibrium, the entropy of the universe must increase.  $S_f - S_i = \int_i^f \frac{dq}{T}$ . The principle of unavailable energy is a replacement of Kelvin-Planck's statement of 2<sup>nd</sup> law since both suggest a definite rejection of heat energy if some work is to be obtained from heat. The concept of entropy with reference to disorder shows that the direction of all natural processes are governed by probability laws. This 2<sup>nd</sup> law is a statistical law which is defined as the probability of a process to occur is more if the direction of the process gives an increment in entropy of the universe.

### Practical Engines

We learned, engine is a device that converts heat into work. Practical engines are of two types. (a) Internal-combustion engine (Gasoline & Diesel engine)

(b) External-combustion engine.

(Steam & Stirling engine)

In internal combustion engine, burning of fuel & oxygen with air take place in confined combustion chamber to rise P, & T of the system. In external combustion engine, high temperature surroundings transfer heat to the combustion chamber.