Date
07/09/2021

Thermodyamics

1. Heat & Thermodynamics →
Zeemansky + Dittman

2. Heat & Thermodynamics →
A. B. Gupta + H. P. Roy

3. A Treatise on Heat → M. N. Saha + Srivastava

What is Thermodynamics?

Thermodynamics is an empirical science based upon axioms whose validity has been established experimentally. In thermody. we infer the existence of certain fundamental laws from experimental evidence and then draw our conclusions from these experimental laws. Thermody is mainly concerned with the transformation of heat into mechanical work or vice versa.

Some technical terms to study the subject

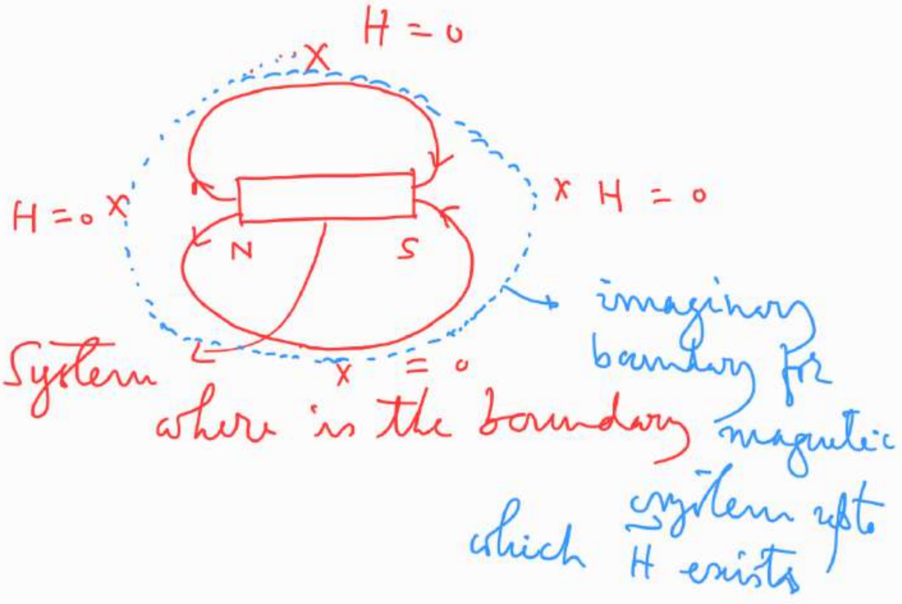
1. System & Surrounding:

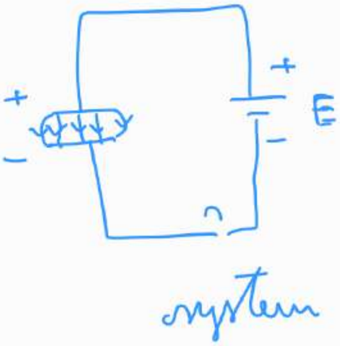
System: A definite quantity of matter or radiation in equilibrium bounded by some closed surface (boundary may be actual or at least imaginary) is known as thermodynamic system. The existence of boundary is essential to visualize the system from the rest of the universe.

Everything outside the system that can influence its (system) behaviour is called the surrounding

$$\boxed{\text{System} + \text{Surrounding} \equiv \text{Universe}}$$

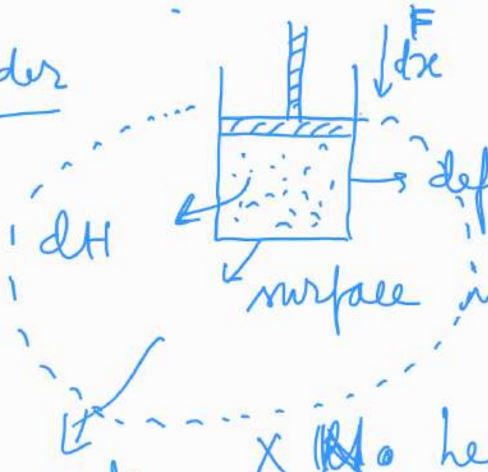
Magnetic system:





Gas cylinder

$dw = F\,dx \Rightarrow dH = \frac{dw}{T}$



definite boundary

surface is conducting

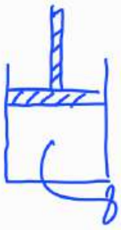
X No heat

surroundings need not to have definite boundary.

To study system thermodynamically, the presence of surroundings is must to respond the behaviour of system.

Microscopic & Macroscopic description & Thermody. variables

1. ideal gas filled with piston



gas system → Microscopic description
gas system → Macroscopic description

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Macroscopic description $(N, V, E) \equiv (N, V, T)$

$\Downarrow$ (P, V, T)

Measurable & large-scale property.

When a system (eq$^{\underline{m}}$ state) is described by some large-scale measurable macroscopic parameters that do not involve time then those are called macroscopic coordinates, e.g. V, T, etc.

When a system is described by some instantaneous variables say position - momenta of individual particles which involves time and mathematical probabilistic theory is to be applied to have some average value of a macroscopic quantity then that type of description is known as microscopic.

Equation of state: A mathematical relation connecting the appropriate thermodynamic variables of a system in equilibrium is called eq$^{\underline{n}}$ of state determined by expt.

$$\left.\begin{array}{l} PV = RT \quad \text{for ideal gas} \\ \left(P+\frac{a}{V^2}\right)(V-b) = RT \end{array}\right\} \text{one gm mole}$$

Classification of systems
→ Open system
→ closed system
→ Isolated system

Open system: can exchange matter & energy with surrounding boundary wall must be conducting & permeable

Closed system : can exchange energy with surrounding
boundary wall (diathermal) conducting but impermeable

Isolated system : can not exchange matter or energy
boundary wall non-conducting & impermeable.
‖ (adiabatic wall)

Thermodynamic eq$^{\underline{m}}$:

Three different eq$^{\underline{m}}$ conditions when simultaneously satisfied by a system then it is called thermodynamic eq$^{\underline{m}}$.

1. Mechanical eq$^{\underline{m}}$ 2. Chemical eq$^{\underline{m}}$ 3. Thermal eq$^{\underline{m}}$

1. ⇒ when no unbalanced force between system & surrounding or within system

2. ⇒ when constituents/construction of the system remain same for all Time

3. ⇒ Temp. of the system remains same.

Intensive & Extensive variables

Intesive : does not depend on mass/ no of particles etc.

Extensive : depend on those

Say, y is a macroscopic variable for a system
y_1, y_2 are the variables of the system after division of the system

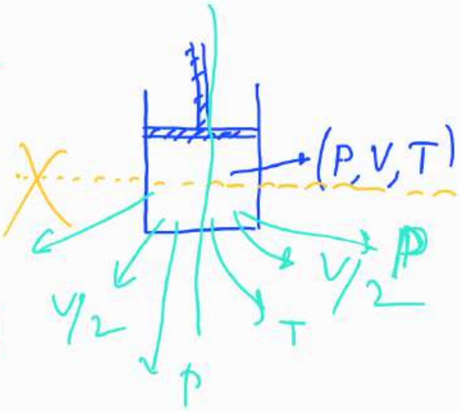
Then, $\boxed{\text{if } y = y_1 = y_2 \to y \text{ is intensive} \quad = y_1 + y_2 \to \text{,, extensive}}$

$y \equiv P \qquad P = P_1 = P_2 \to$ intensive

$\equiv T \qquad T = T_1 = T_2 \to$,,

$\equiv V \qquad V = V/2 + V/2$

$= V_1 + V_2 \to$ extensive



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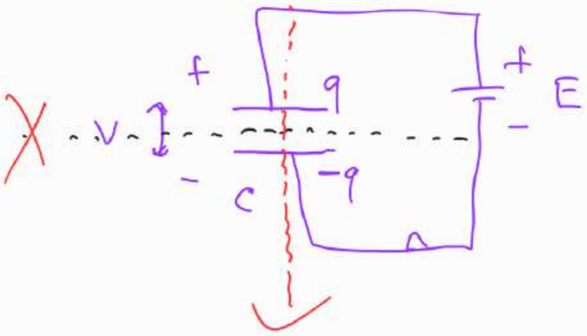


$q = CV$

$\boxed{q = CV} \to$ eq^n of state

q, V, → Thermody variable

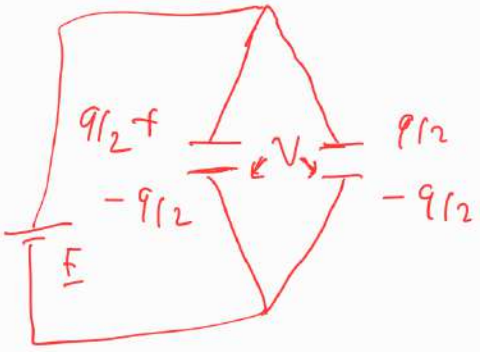
$Q_1 = q/2 \qquad Q = q/2 + q/2 = q$

$Q_2 = q/2 \qquad$ ↳ extensive

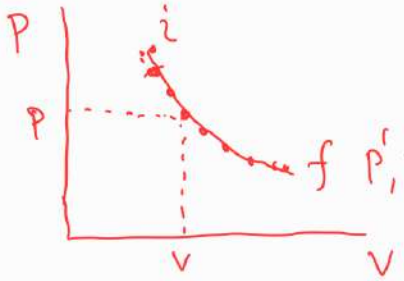
$V' = V_1 = V_2 = V$

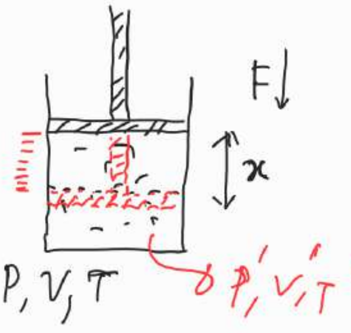
⇓

Intensive



Reversible - Irreversible - Quasistatic process





When a thermodynamic passes from one eq^{m} state to another very slowly so that each intermediate states remain in eq^{m} condition then that process is known as Quasi-static.

If a process becomes quasistatic and no cause of energy dissipation is present then it is called reversible otherwise irreversible.

1. All natural processes are irreversible.

⇓ All natural processes are spontaneous.

Any spontaneous process is irreversible means not quasistatic

There is no example of ideal reversible process.

Carnot's engine cycle process are example of ideal reversible processes

Transfer of heat from high temp to low temp → irreversible

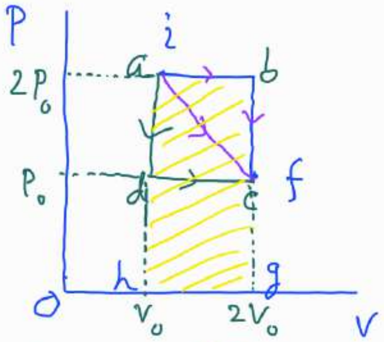
Hydrostatic system: Any isotropic system of constant mass and constant composition that exerts on the surrounding a uniform hydrostatic pressure in absence of gravitational, electric & magnetic effects, then such system is called hydrostatic system.

Thermodynamic variables for such system are P, V, T

eqn of state $f(P, V, T) = 0$

Heat & Work :

When a system changes from an initial state (P_1, V_1, T_1) to (P_2, V_2, T_2) the amount of heat transfer & work done depend on not only those two endpoints but path of transformation also. That's why heat/work are called path function means not state function & hence can be expressed by inexact differential only.



Exact differential ⇒ dX $\quad$ $X \rightarrow$ thermod. variable

Inexact " ⇒ $đX$ or δX

$H \Rightarrow$ heat $\Rightarrow$ small amount of heat $\Rightarrow đH / \delta H$

$W \Rightarrow$ work $\Rightarrow$ - - - .. $\Rightarrow đW / \delta W$

Work done along $abf \Rightarrow$ area of the region under the line ib & volume axis $= 2P_0V_0$

Work done along af = area$(afgha) = \Delta afd + \square dhgf$

$$= \frac{1}{2}V_0 \times P_0 + P_0V_0 = \frac{3}{2}P_0V_0$$

So work path dependent function.

Similarly heat also path dependent ⇒ inexact differential

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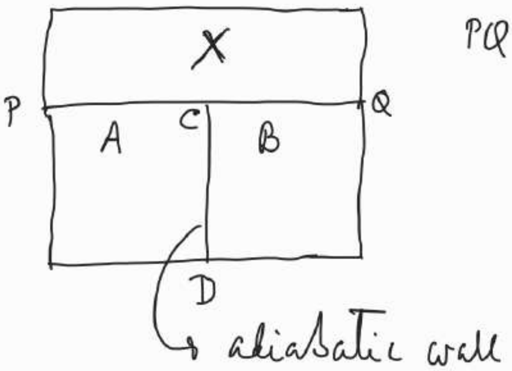
Zeroth law of Thermodynamics : (Fowler 1931)



PQ wall → diathermal

(X & A) (X, B) can exchange energy as separated by diathermal wall

But A, B can not exchange energy due to adiabatic wall

After eq^{m} established between (X, A), (X, B) → no energy exchange.

Now if adiabatic wall → by diathermal wall ⇒ no further energy exchange.

⇒ (A, B) also reach in eq^{m}.

Conclusion : If two systems are in eq^{m} with a 3rd system separately then they are in eq^{m} to each other.

→ Statement of Zeroth law of thermodynamics

Essence of Zeroth law : It defines $\boxed{\text{temperature}}$.

Temperature is the property of a system that determines whether or not the system is in thermal eq^{m} with the neighbouring system.

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Mathematical relations :

If $z = f(x,y)$ i.e. $f(x,y,z) = 0$ is an eqn of state for a system having thermodynamic variables (x, y, z)

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

$$\left[\begin{array}{l} pV = RT \\ p = \frac{RT}{V} \\ V = \frac{RT}{p} \end{array}\right.$$

$$\because \; f(x,y,z) = 0 \Rightarrow x = f(y,z)$$

$$y = f(x,z)$$

$$\Rightarrow \quad dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$dy = \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial y}{\partial z}\right)_x dz$$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x dz + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$= \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z dx + \left[\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y\right] dz$$

Now $dz = 0$ & $dx \neq 0$

$$1 = \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial x}\right)_z \qquad [\because dx \neq 0]$$

$$\Rightarrow \left(\frac{\partial x}{\partial y}\right)_z = \frac{1}{\left(\frac{\partial y}{\partial x}\right)_z} \rightarrow ①$$

If $dx = 0$, $dz \neq 0 \Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x + \left(\frac{\partial x}{\partial z}\right)_y = 0$

$$\Rightarrow \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Isothermal Bulk modulus : $B_T = \left[-\left(\frac{\partial p}{\partial V}\right)_T V\right]$

Adiabatic - - -

$$B_S = -V\left(\frac{\partial p}{\partial V}\right)_S$$

Isothermal compressibility $K_T = \frac{1}{B_T} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

Coefficient of volume expansion $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

$$V_t = V_0(1+\alpha t) \Rightarrow \alpha = \frac{V_t - V_0}{V_0 t} = \frac{\Delta V}{V_0 \Delta T}$$

Isochoric pressure coefficient of expansion $\beta_V = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V$

Isobaric volume - - - - $\beta_p = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

Thermodynamic processes :

① Isothermal $\Rightarrow \Delta T = 0$, T const

② Adiabatic $\Rightarrow \Delta Q = 0 \Rightarrow \Delta S = 0$, $S =$ const, no heat change

③ Isochoric $\Rightarrow \Delta V = 0 \Rightarrow V =$ const

④ Isobaric $\Rightarrow \Delta P = 0 \Rightarrow P =$ const.

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Some examples of Thermodynamic systems

Systems	Thermod. Coordinates	Eqn of state	Int / exten	Work $\delta W =$
1. Hydrostatic	P, V, T	$f(P,V,T)=0$	P, T / V	$P dV$
2. Stretched wire.	τ, L, T tension	$f(\tau, L, T) = 0$	T, τ / L	τdL
3. Surface film	γ, A, T surface tension	$\gamma = \gamma_0 \left(1 - \frac{T}{T_c}\right)^n$, $1 < n < 2$	γ, T / A	γdA
4. Electric cell	V, Q, T emf charge	$f(V, Q, T) = 0$	V, T / Q	$V dQ$
5. Dielectric slab	E, P, T e. field polarisation	$\frac{P}{V} = \left(a + \frac{b}{T}\right)E$ a, b, const.	E, T / P	$E dP$
6. Paramagnetic rod	H, M, T	$M = \frac{\chi H}{T}$	H, T / M	$\mu_0 H dM$

Work done may be +ve/−ve

1st law of Thermodynamics

When a closed system whose surrounding is at different temp and on which diathermal work may be done, undergoes a process then the energy transferred by non-mechanical means (called heat), equal to the difference between the change of internal energy and the diathermal work, mathematically,

$$\boxed{\delta Q = dU + \delta W}$$

Essence of 1st law : i) There exists an internal energy function

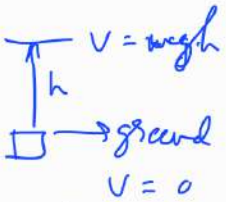
ii) Principle of conservation of energy

iii) The defn of heat as energy transfer due to temp difference.

Internal energy: Energy possessed by a system due to its relative position or, molecular construction or relative orientation which is apparently not shown by the system but is capable to do some useful work, is called internal energy.

$V = \frac{1}{2}kx^2$
$\Downarrow$
Internal energy

Int. energy molecules constrn
$\Uparrow$
Battery emf



Int. energy

$E = mc^2$
$\Downarrow$
X internal energy

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Application of 1st Law

$\boxed{C_p - C_v = nR} \longrightarrow$ Mayer's relation

$n \rightarrow$ no. of mole

$$\delta Q = dU + p\,dV \Rightarrow C_p = \underset{\overset{\|}{1}}{m}\left(\frac{\delta Q}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p \longrightarrow dU \cancel{=} C_p\,dT \rightarrow ①$$

$$C_v = \left(\frac{\delta Q}{\partial T}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v + 0 \Rightarrow \boxed{dU = C_v\,dT}$$

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

$$\Rightarrow \left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore C_p = C_v + \Big[P + \underbrace{\left(\frac{\partial U}{\partial V}\right)_T}_{0}\Big]\left(\frac{\partial V}{\partial T}\right)_P \rightarrow \left[\text{Using ①}\right]$$

$$= C_v + nR$$

$$\Rightarrow \boxed{C_p - C_v = nR}$$

$$PV = nRT \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial U}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -P/V$$

$$(PdV + VdP = nRdT)$$

$$= 0$$

$$\left(\frac{\partial U}{\partial P}\right)_T = 0 \text{ for ideal gas}$$

<u>Alternative</u> $\delta Q = C_v dT + pdV$

$$PV = nRT \Rightarrow pdV + VdP = nRdT$$

$$\delta Q = (C_v + nR)dT - VdP \Rightarrow C_p = \left(\frac{\delta Q}{\partial T}\right)_P = C_v + nR$$

$$= C_p dT - VdP$$

<u>Adiabatic eq^n of ideal gas:</u> $PV^\gamma = \text{cst}$ $\gamma = C_p/C_v$

$$\delta Q = C_v dT + pdV = C_p dT - VdP = 0 \text{ for adiabatic}$$

$$\Rightarrow \frac{dP}{P} = -\gamma \frac{dV}{V} \Rightarrow PV^\gamma = \text{cst} \; [\text{integrating}]$$

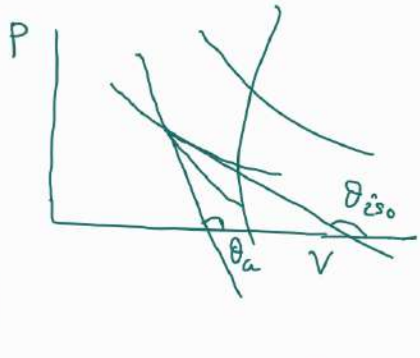
<u>Adiabatic is steeper than isothermal:</u>

For isothermal $PV = \text{cst} \Rightarrow pdV + VdP = 0$

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(-\frac{P}{V}\right) = m$$

For adiabatic $PV^\gamma = \text{cst} \Rightarrow \left(\frac{\partial P}{\partial V}\right)_S = \gamma\left(-\frac{P}{V}\right)$

$$\underbrace{\left(\frac{\partial P}{\partial V}\right)_S}_{\text{slope of adiabatic}} > \left(\frac{\partial P}{\partial V}\right)_T \quad [\because \gamma > 1]$$



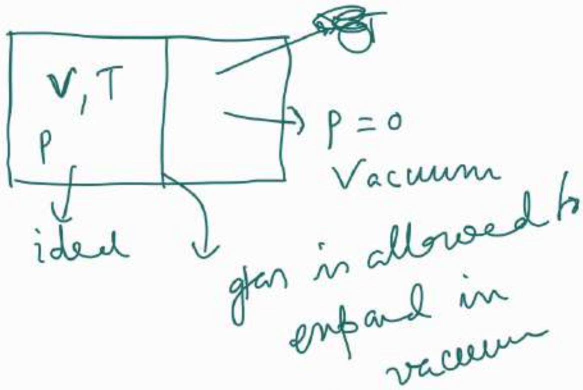
$$\tan\theta_{iso} < \tan\theta_a$$

Free expansion : Joule's expt.

$\Downarrow$

Internal energy of the ideal gas

$$\Longrightarrow f(T) \Rightarrow U = U(T) \text{ only}$$



$\delta W = p\,dv = 0$ no work done

$$U = f(V,T) = f(P,T)$$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V \underset{0}{\underset{\|}{dT}}$$

$$dU = C_V\,dT = 0$$

$$\left(\frac{\partial U}{\partial V}\right)_T = 0 \Rightarrow U \neq f(V)$$

After expt $T_f = T$ $\quad dT = 0$ $\downarrow$ no temp change

$$U = U(P,T) \Rightarrow \underset{0}{\underset{\downarrow}{dU}} = \underset{\left(\frac{\partial U}{\partial P}\right)_T = 0}{\underset{\Downarrow}{\left(\frac{\partial U}{\partial P}\right)_T}} dP + \left(\frac{\partial U}{\partial T}\right)_P \underset{0}{\underset{\downarrow}{dT}} \qquad \Rightarrow U \neq U(P)$$

$$\Rightarrow U = U(T) \text{ only}$$

Heat absorbed in different processes:

23/9/24 Consider a general process characterised by

$PV^n = \text{const.} = A$ (say), $\quad n = 0 \rightarrow$ isobaric process

$= 1 \rightarrow$ isothermal "

$= \gamma \rightarrow$ adiabatic

$= \infty \rightarrow$ isochoric

$$p\,n\,V^{n-1}\Delta V + V^n \Delta P = 0$$

$$\Rightarrow pn\Delta V + \Delta P V = 0 \Rightarrow \lim_{n\to\infty}\left(\frac{\Delta V}{\Delta P}\right) = -\left[\left(\frac{V}{P}\right)\frac{1}{n}\right]_{n\to\infty} \longrightarrow 0 \rightarrow \Delta V \rightarrow 0 \Rightarrow V \rightarrow \text{const.}$$

$$\delta Q = dU + p\,dv = C_v\,dT + p\,dv$$

$$\Rightarrow [Q] = \int_i^f C_v\,dT + \int_i^f \frac{A}{v^n}\,dv = C_v(T_f - T_i) + \frac{P_i V_i - P_f V_f}{n-1}, \quad n \neq 1$$

$$= C_v(T_f - T_i) + \frac{R(T_i - T_f)}{n-1}, \quad n \neq 1$$

$$\frac{A v_i}{v_i^n} - \frac{A v_f}{v_f^n} = \frac{P_i V_i^n v_i}{V_i^n} - \frac{P_f V_f^n v_f}{V_f^n}$$

$$[Q]_T = \underbrace{C_v(T_f - T_i)}_{=0} + \underbrace{RT}_{A} \ln \frac{v_f}{v_i} \quad \text{for } n = 1$$

$$\hookrightarrow W_T = Q_T$$

$A \rightarrow$ for one gm mole gas (nRT for n-gm)

$$[Q]_p = (n=0) = C_v(T_f - T_i) + R\frac{T_i - T_f}{-1} = C_p(T_f - T_i)$$

$$[Q]_V = (n=\infty) = C_v(T_f - T_i) + \frac{(C_p - C_v)(T_i - T_f)}{\infty} = C_v(T_f - T_i)$$

$$[Q]_S = (n=\gamma) = C_v(T_f - T_i) + \frac{(C_p - C_v)(T_i - T_f)}{\frac{C_p}{C_v} - 1} = 0$$

Adiabatic work: $\delta W = p\,dv \Rightarrow W = \frac{R}{\gamma - 1}(T_i - T_f)$

$$= C_v(T_i - T_f)$$

Adiabatic Lapse Rate:

The change in temp. with height is called adiabatic lapse rate which arises due to convection air current in the troposphere (lowest dense region of atmosphere). When air from sea level rises to the upper region of lower pressure it expands and very little heat is exchanged by the air as it is poor conducting one & hence the process is adiabatic.

$$p V^{\gamma} = \text{cst (adiabatic)} \Rightarrow p\left(\frac{RT}{p}\right)^{\gamma} = \text{cst} \qquad [pV = RT]$$

$$\Rightarrow p^{1-\gamma} T^{\gamma} = \text{cst} \Rightarrow \gamma \ln T + (1-\gamma)\ln p = \text{cst}$$

$$\Rightarrow \frac{\Delta T}{T} + \frac{1-\gamma}{\gamma}\frac{\Delta p}{p} = 0 \Rightarrow \frac{dp}{p} = \frac{\gamma}{\gamma-1}\frac{dT}{T} \rightarrow ①$$

$dp = -g\rho(dh)$ → −ve sign to imply falling of pressure with height

$$= -g\frac{PM}{RT}dh$$

$$\Rightarrow \frac{dp}{p} = -\frac{gM}{RT}dh \rightarrow ②$$

$PV = \frac{g}{M}RT \leftarrow nRT$

$g \rightarrow$ mass of air

$M \rightarrow$ mol. wt. of air ↘ ㉙

$\rho = \frac{g}{V} = \frac{PM}{RT}$

$$① \ \& \ ② \Rightarrow -\frac{gM}{RT}dh = \frac{\gamma}{\gamma-1}\frac{dT}{T}$$

$$\Rightarrow \frac{dT}{dh} = -\frac{\gamma-1}{\gamma}\left(\frac{Mg}{R}\right)$$

$$= -9.78\times10^{-3}\ \text{K/m}$$

$$= -9.78\ \text{K/km}.$$

$\gamma = 1.4 \quad g = 9.8$

$R = 8.31\ \text{J mol}^{-1}\text{K}^{-1}$

$M = 0.029\ \text{kg mol}^{-1}$

Another form of 1st law: Perpetual motion machine of 1st kind is impossible.

Perpetual → never ending → ever running

1st Kind → A machine capable of running itself without any fuel.

$$\boxed{\delta Q = dU + \delta W} \Rightarrow \delta Q = 0 \ (\text{no fuel supplied})$$

$$\delta W = -dU \quad (dU = 0)$$

$$= 0$$

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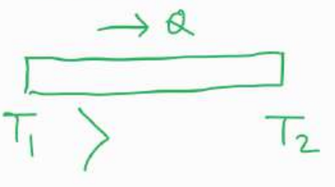
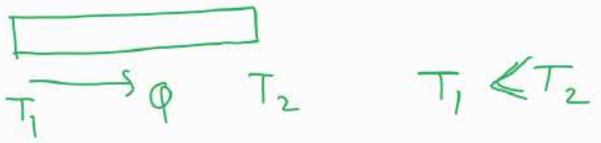
Why and how 2nd law of thermodynamics?

$$\delta Q = dU + \delta W$$

$$\Downarrow \; = \delta W \qquad \text{when } dU = 0$$





$\boxed{S=1}$ $\delta W = \delta Q$

⇓ +ve

<u>Deficiency of 1st Law</u>: The 1st law denies the possibility of creating or destroying energy. It just says the conversion of heat & work but never gives the direction of occurrence of a process. To remove this limitation 2nd law is formulated which denies the possibility of utilizing energy in a particular way.

"Perpetual motion machine of (2nd kind) is impossible"

⇓

<u>2nd kind machine</u>: A machine capable of running by drawing internal energy from one heat reservoir.

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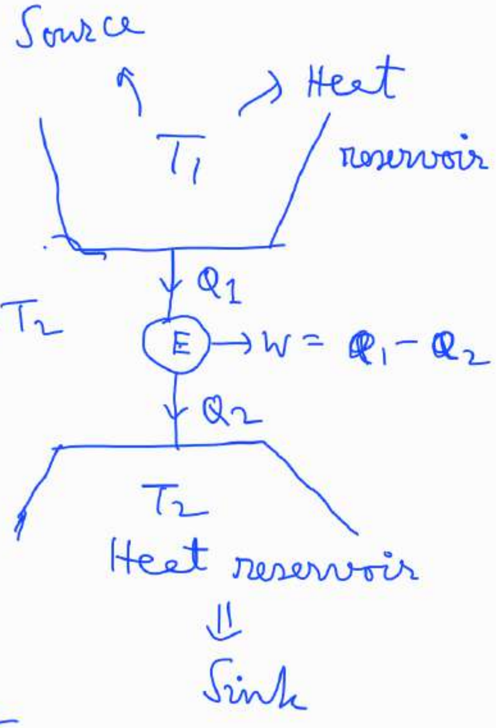
Heat Engine



$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = \left(1 - \frac{Q_2}{Q_1}\right)$$

$T_1 > T_2$

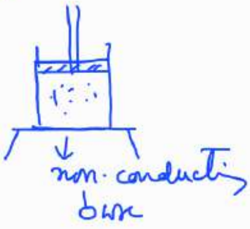
For $\eta_{max} = 1$, $\left.\begin{matrix} Q_2 = 0 \\ Q_1 = \infty \end{matrix}\right\} \frac{Q_2}{Q_1} = 0$

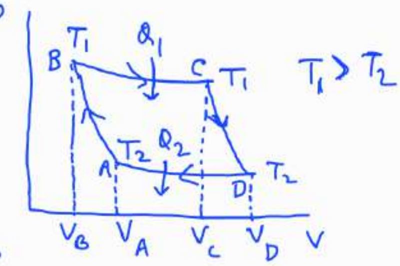
$W_{max} = Q_1 - Q_2 = Q_1 \quad (Q_2 = 0)$

$\eta_{min} < 1$ can not be unity

Carnot Engine: (Ideal Reversible Engine) (1824)

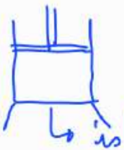
A carnot engine consists of an ideal gas (enclosed by a cylinder) which acts as a working subs, undergoes four successive reversible processes and comes to initial state, performing some work.





1. Reversible adiabatic compression (A → B) –
   Due to compression generated heat raise the temp of the gas from $T_2 \rightarrow T_1$

2. Reversible isothermal expansion (B → C)



   Cylinder is kept on source so that Q_1 heat is drawn by the gas to keep temp const. T_1
   ↳ is kept on source at temp T_1

3. Reversible adiabatic expansion (C → D)
   Due to adiabatic expansion temp falls from $T_1 \rightarrow T_2$

4. Reversible isothermal compression (D → A)
   Due to compression generated heat Q_2 is rejected to sink keeping temp T_2 const.

Work done / Efficiency

$$W_{AB} = \frac{R}{\gamma-1}(T_1 - T_2) \qquad W_{BC} = RT_1 \ln\frac{V_C}{V_B}, \quad W_{CD} = \frac{R}{\gamma-1}(T_2 - T_1)$$

$$W_{DA} = RT_2 \ln\frac{V_A}{V_D}$$

$$W = \sum W = R\left(T_1 \ln\frac{V_C}{V_B} + T_2 \ln\frac{V_A}{V_D}\right) = R\left(T_1 \ln\frac{V_C}{V_B} - T_2 \ln\frac{V_D}{V_A}\right) \rightarrow ①$$

$$PV^{\gamma} = \text{cnt} \Rightarrow \frac{RT}{V}V^{\gamma} = \text{cnt} \Rightarrow TV^{\gamma-1} = \text{cnt}$$

$\because$ A, B connected by adiabatic $\quad T_2 V_A^{\gamma-1} = T_1 V_B^{\gamma-1} \Rightarrow \frac{T_1}{T_2} = \left(\frac{V_A}{V_B}\right)^{\gamma-1}$

C, D - - - - $\quad T_1 V_C^{\gamma-1} = T_2 V_D^{\gamma-1} \Rightarrow \frac{T_1}{T_2} = \left(\frac{V_D}{V_C}\right)^{\gamma-1}$

$$\Rightarrow \frac{V_A}{V_B} = \frac{V_D}{V_C} \Rightarrow \frac{V_C}{V_B} = \frac{V_D}{V_A}$$

① $\Rightarrow W = R(T_1 - T_2)\ln\frac{V_C}{V_B} > 1 \quad \left(\frac{V_C}{V_B} > 1\right)$

$$Q_1 = W_{BC} = RT_1 \ln\frac{V_C}{V_B}$$

$$\eta = \frac{W}{Q_1} = \frac{T_1 - T_2}{T_1} = \left(1 - \frac{T_2}{T_1}\right) = \frac{Q_1 - Q_2}{Q_1} = \left(1 - \frac{Q_2}{Q_1}\right)$$

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

$\eta = \left(1 - \frac{T_2}{T_1}\right)$, $\quad T_2 = 0$, $T_1 = \infty \rightarrow$ X

$= 1$, if $T_2 = 0 \quad Q_2 = 0 \rightarrow$ X not possible

⇓

never possible

⇒ absolute zero can not be attained

−272.3 °C

T = 0K = −273 °C

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Kelvin statement of 2nd law

It is impossible by means of inanimate material agency to derive mechanical effort from any portion of matter by cooling it below the temp. of the coldest of the surrounding objects.

Planck statement:

It is impossible to construct an engine which working in complete cycle will produce no effect other than the raising of a weight and cooling of a heat reservoir.

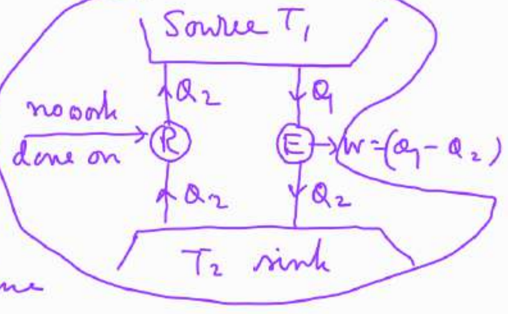
K-P joint statement:

It is impossible to construct an engine that operating in a cycle will produce no effect other than the extraction of heat from a reservoir and the performance of an equivalent amount of work.

Clausius's statement: It is impossible to construct a refrigerator that operating in cycle will produce no effect other than the transfer of heat from a lower temp reservoir to a higher temp. reservoir.

Equivalence between K-P & Clausius statement

Two statements are said to be equivalent when the truth of one implies the truth of the other and vice-versa or the falsity of one statement implies the falsity of the other and vice-versa.



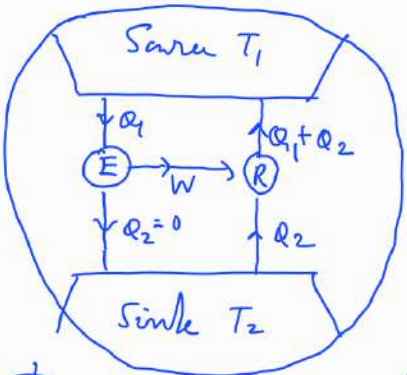
Consider a refrigerator that requires no work to transfer heat Q_2 from sink to a source & hence violating Clausius statement.
Another engine E also operates between the same two heat reservoirs in such a way that the same heat Q_2 is delivered

to sink which does not violate any law.

But the (R+E) constitute a self-acting device that takes $(Q_1 - Q_2)$ heat from source and converts all into work without producing any change in the sink which violates K-P statement.

21/10/21 Suppose an engine E that rejects no heat to the sink and thus violates K-P statement and converts heat fully to work W.

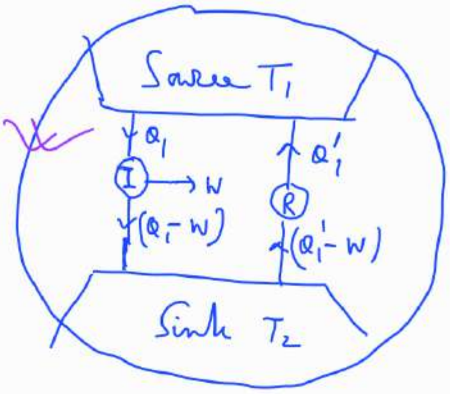
Now, a refrigerator operates between the same heat reservoirs and uses up all the work performed by E & thus violates no law. But the engine (E+R) jointly acts as self-acting device that transfers heat Q_2 from sink to Source without producing any changes elsewhere which violates Clausius's statement.



So two statements are completely equivalent.

Carnot's theorem:

1. Operating between two given reservoirs at two definite temp, no engine is more efficient than a Carnot engine.
2. All reversible engines have same efficiency working between the two given temperatures whatever may be the working substance.



Proof: Let us consider a reversible engine R and irreversible engine I, where I draws Q_1 heat from source, performs W work and rejects $(Q_1 - W)$ heat to sink.

$$\therefore \eta_I = \frac{W}{Q_1}$$

Similarly, R draws Q_1' heat from source, does same same W rejects $(Q_1'-W)$ heat to sink, $\eta_R = \frac{W}{Q_1'}$

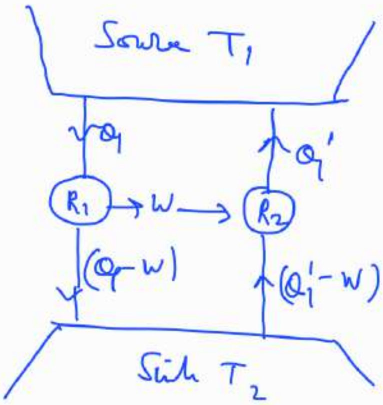
Suppose $\eta_I > \eta_R \Rightarrow \frac{W}{Q_1} > \frac{W}{Q_1'} \Rightarrow Q_1 < Q_1' \Rightarrow (Q_1' - Q_1) > 0 \rightarrow$ ①

Now, let I drives R backwardly i.e. R is now acts as refrigerator driven by I, ⇒ (R+I) form a self-acting device, extracts heat $(Q_1'-W)$ from sink, requires work W to be done on it by I, rejects Q_1' heat to source. Thus (R+I) together draws ~~Q~~ net heat from sink $(Q_1'-W)-(Q_1-W) = (Q_1'-Q_1)$ +ve & rejects $(Q_1'-Q_1)$ to the source without work done by external agency which is a violation of Clausius statement.

$\eta_I > \eta_R$ is false

$$\Rightarrow \boxed{\eta_I \le \eta_R}$$

2nd part:



Now consider two reversible engines R_1 & R_2 operating between same two reservoirs. If we imagine R_1 driving R_2 backward then by the above Theorem

$$\eta_{R_1} \le \eta_{R_2} \rightarrow ②$$

If R_2 drives R_1 backwardly then $\eta_{R_2} \le \eta_{R_1} \rightarrow$ ③

① & ② ⇒ $\eta_{R_1} = \eta_{R_2}$

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$\eta_I \ne \eta_R$; $\eta_R > \eta_I$ to be established

Engine-I & R together acting as self-acting device operating in a complete cycle results no change in the reservoirs if $\eta_I = \eta_R \Rightarrow Q_1' = Q_1$ and no external work is got implying the changes due to irreversible engine I get compensated due to reversible engine R run backwardly which is against the definition of irreversibility, so

$$\eta_I \ne \eta_R$$

$$\Rightarrow \eta_I < \eta_R$$

Clausius inequality theorem :

Statement: If a system performs a cyclic process consisting of a sequence of states and interacts with a series of heat reservoirs at temperatures $T_1, T_2, T_3, \dots T_i \dots T_n$ exchanging heats $Q_1, Q_2, Q_3 \dots Q_i \dots Q_n$ with them then,

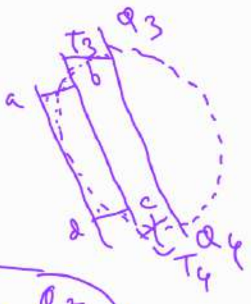
$$\sum_i \frac{Q_i}{T_i} \le 0 \quad \text{or} \quad \oint \frac{\delta Q}{T} \le 0$$ where $\oint \rightarrow$ sum over cycle

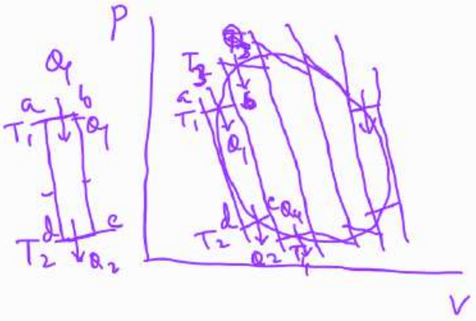
δQ - heat absorbed by system at T. $Q \rightarrow$ +ve, system absorbs heat
-ve " rejects "

$<\rightarrow$ irreversible cycle, '=' $\rightarrow$ reversible cycle

Proof :

For abcd carnot engine





$$\frac{Q_1}{T_1} = -\frac{Q_2}{T_2}$$

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

$$\Rightarrow \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

$$\frac{Q_3}{T_3} + \frac{Q_4}{T_4} = 0$$

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} + \frac{Q_3}{T_3} + \cdots = 0$$

$$\Rightarrow \sum_i \frac{Q_i}{T_i} = 0$$

$$\Rightarrow \oint_R \frac{\delta Q}{T} = 0 \quad - \text{①}$$

Now consider an irreversible cyclic engine working between temp T_1 & T_2. If a reversible engine were operating between the same temp limit then from Carnot theorem

$$\eta_I < \eta_R$$

$$\Rightarrow \frac{Q_1^I - Q_2^I}{Q_1^I} < \frac{Q_1^R - Q_2^R}{Q_1^R} \Rightarrow \frac{Q_2^I}{Q_1^I} > \frac{Q_2^R}{Q_1^R} = \frac{T_2}{T_1}$$

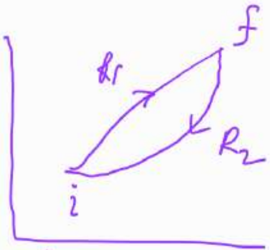
$$\Rightarrow \frac{Q_2^I}{T_2} > \frac{Q_1^I}{T_1} \Rightarrow \oint_I \frac{\delta Q}{T} = \frac{Q_1^I}{T_1} - \frac{Q_2^I}{T_2} < 0$$

$$\Rightarrow \oint_I \frac{\delta Q}{T} < 0 \quad - \text{②}$$

① & ② $\Rightarrow$ $\oint \frac{\delta Q}{T} \leq 0$ $\quad$ < → irreversible

= → reversible

Entropy :



Let a system undergoing a reversible process from i to f

Clausius theorem → $\oint_{R_1R_2} \frac{\delta Q}{T} = 0 \Rightarrow \int_{R_1\, i}^{f} \frac{\delta Q}{T} + \int_{R\, f}^{i} \frac{\delta Q}{T} = 0$

$$\Rightarrow \int_{R_1\, i}^{f} \frac{\delta Q}{T} = - \int_{R_2\, f}^{i} \frac{\delta Q}{T} = \int_{R_2\, i}^{f} \frac{\delta Q}{T}$$

$\Rightarrow \int_{R\, i}^{f} \frac{\delta Q}{T}$ is independent of path → State function

$$\Rightarrow S_f - S_i = \int_{R\, i}^{f} \frac{\delta Q}{T} \Rightarrow \boxed{dS = \frac{\delta Q_R}{T}}$$

Change in entropy (extensive variable)

$$\delta Q = T\,dS = C_v\,dT + p\,dV$$

$$\Rightarrow dS = C_v \frac{dT}{T} + p\frac{dV}{T} \Rightarrow S = C_v \int \frac{dT}{T} + nR\ln V + S_0$$

T-S

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$\delta Q_R = T\,dS \Rightarrow Q = \int_i^f T\,dS$ → total amount of heat transferred in a reversible process.

$dS = \frac{\delta Q}{T} = 0$ for adiabatic

$\Rightarrow S =$ cat. → for adiabatic

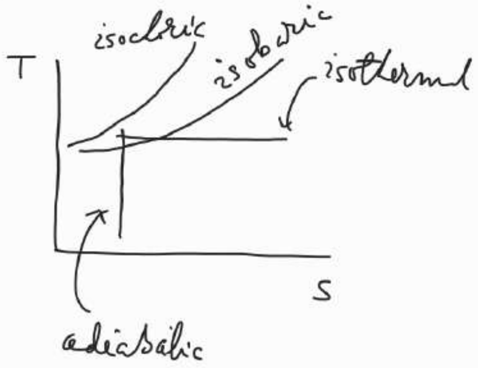
$$\delta Q = C_v\,dT + p\,dV = T\,dS = (C_p - nR)\,dT + nR\,dT - V\,dp$$

$$= C_p\,dT - V\,dp$$

$$\Rightarrow dS = C_p\frac{dT}{T} - \frac{V}{T}dp = C_p\frac{dT}{T} - nR\frac{dp}{p}$$

$$\left(\frac{\partial T}{\partial S}\right)_p = \frac{T}{C_p} \qquad \left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_v} \quad \Big/ \quad \left(\frac{\partial T}{\partial S}\right)_p < \left(\frac{\partial T}{\partial S}\right)_V$$

$\left(\frac{\partial T}{\partial S}\right)_V > \gamma\left(\frac{\partial T}{\partial S}\right)_P \Rightarrow$ Slope of isochoric > slope of isobaric



= Entropy change in case of Reversible process

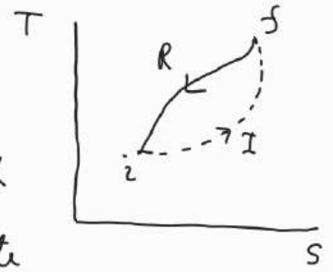
If δQ is the heat exchange between system & heat reservoir the entropy change of the system $dS_1 = \pm \frac{\delta Q}{T}$

+ heat is absorbed by system
− " " rejected " "

For reservoir $dS_2 = \mp \frac{\delta Q}{T}$

Total entropy change of the universe $\Delta S = dS_1 + dS_2 = 0$
$\Rightarrow S = \text{const.}$

= Entropy change in case of irreversible process.



Let us consider a cycle in which a system starts from initial state i, passing through irreversible path I to find state 'f' & returns back to initial state via reversible path R.

Since entropy is a state function, $\oint dS = 0 \Rightarrow \int_{I\,i}^{f} dS + \int_{R\,f}^{i} dS = 0 \rightarrow$ ①

Again for irreversible cycle from C. inequality

$$\oint_I \frac{\delta Q}{T} < 0 \Rightarrow \oint_I \frac{\delta Q}{T} = \int_{I\,i}^{f}\frac{\delta Q}{T} + \int_{R\,i}^{f}\frac{\delta Q}{T} < 0 \rightarrow ②$$

But $\int_{R\,i}^{f}\frac{\delta Q}{T} = \int_{R\,i}^{f} dS \Rightarrow \int_{I\,i}^{f}\frac{\delta Q}{T} - \int_{R\,i}^{f} dS < 0 \rightarrow$ ③

$$① - ③ \Rightarrow \int_{I\,i}^{f} dS + \int_{R\,f}^{i} dS - \int_{I\,i}^{f}\frac{\delta Q}{T} + \int_{R\,i}^{f} dS > 0$$

$$\Rightarrow \int_{I\,i}^{f} dS - \int_{I\,i}^{f}\frac{\delta Q}{T} > 0 \Rightarrow \int_{I\,i}^{f} dS > \int_{I\,i}^{f}\frac{\delta Q}{T} \Rightarrow dS \geqslant \frac{\delta Q}{T}$$

= for reversible

$$\Rightarrow \quad S_2 - S_1 \geq \int_1^2 \frac{\delta Q}{T}$$ ⇒ In all natural process entropy increases.

Principle of increase of entropy :

We consider a irreversible process in which a quantity of heat δQ flows from surrounding at temp T_2 to the system at temp T_1. Let δW be the work done by the system

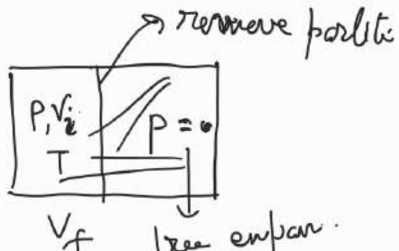
$$\therefore \Delta S_{system} \geq \frac{\delta Q}{T_1} \qquad \delta S_{surr} = -\frac{\delta Q}{T_2}$$

$$\Delta S_{univ} = \delta Q\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \geq 0 \qquad (T_2 > T_1)$$

If $T_1 > T_2$ then heat transfer is from system to surround $\delta Q\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ would be −ve yields the same result $\Delta S_U \geq 0$

$> \rightarrow$ irreversible
$= \rightarrow$ reversible

Entropy change in case of free expansion:



In case of free expansion of ideal gas no heat transfer takes place ⇒ $\delta Q = 0$

$$p = 0, \ \delta W = 0$$
$$dU = 0$$

Yet enctropy changes

$$ds = \frac{\delta Q}{T} \neq 0 \quad \text{though } \delta Q = 0$$

To calculate entropy change the free expansion is to be replaced by a reversible process

$$S_f - S_i = \int_{R\,V_i}^{V_f} \frac{\delta Q_R}{T} \qquad \delta Q_R = p\,dV = nR\frac{dV}{V}$$

$$= nR \ln \frac{V_f}{V_i} \quad +ve \qquad V_f > V_i$$

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Irreversibility & Unavailable energy

Let us consider heat conduction along a bar having Temp. of two ends T_1 & T_2 ($T_1 > T_2$). Suppose Q amount of heat is conducted from T_1 to T_2 and T_0 is the lowest temp. available to us in the surrounding. If an engine is operated between T_1 & T_0 the max^m work would be

$$W_1 = Q\left(1 - \frac{T_0}{T_1}\right)$$

After conduction this heat is available at lower temp T_2. If we now operate the engine between T_0 & T_2, the max^m work would be

$$W_2 = Q\left(1 - \frac{T_0}{T_2}\right)$$

$$\therefore \quad W_2 < W_1 \quad (\because T_2 < T_1)$$

$\therefore$ The energy lost $\Delta E = W_1 - W_2 = Q T_0 \left(\frac{1}{T_2} - \frac{1}{T_1}\right) = T_0 \Delta S$

where ΔS = entropy increase of the universe

i.e. energy is unavailable for useful work during an irreversible process which is equal to T_0 (increase in entropy of the universe)

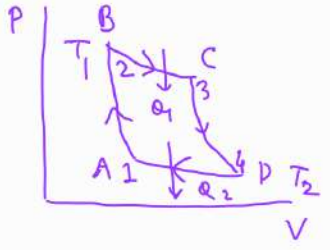
When it will correspond to a state of max^m entropy and all the temp differences between various bodies of the universe will vanish due to convection etc. no heat engine can run. This is known as degradation of energy & universe is marching towards a stagnant state to suffer what is called 'Thermal Death' of the Universe.

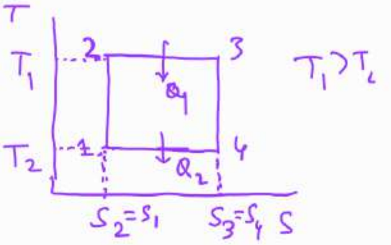
Carnot engine in T-S diagram

$Q_1 = T_1 (S_3 - S_2) \qquad S_3 = S_4, \; S_2 = S_1$

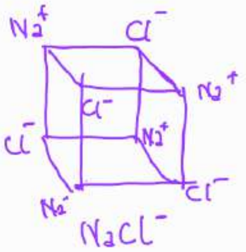
$Q_2 = T_2 (S_4 - S_1) = T_2 (S_3 - S_2)$

$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

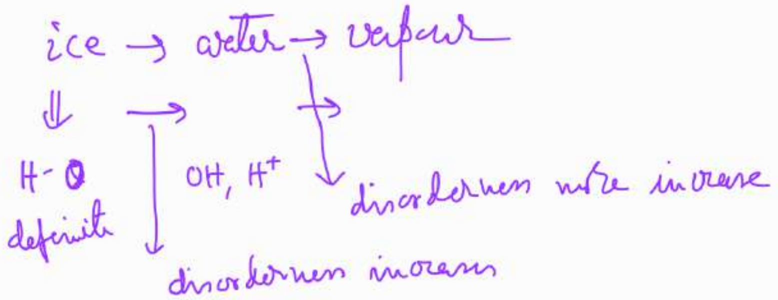




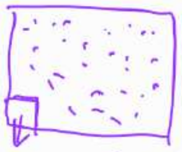
Entropy & Disorderness



$$NaCl \rightleftharpoons Na^+ + Cl^-$$



Books settled in definite order in a Almirah is minimum entropy state w.r.t. scattered state on the floor.



gas molecules in corner more ordered state w.r.t. occupying whole volume

minimum entropy state

disordered state maxm entropy

An increase in entropy of a system can be described as an increase in the disorderness of the system. A piece of salt represents an orderly arrangement of molecules w.r.t. salt solution which is more molecules disorder state & ~~and~~ more entropy state. Thus there is a tendency of nature to proceed towards a state of greater molecular disorderness which implies increase in entropy. A hight temp phase of a system corresponds to greater disorder system meaning to a greater entropy state.