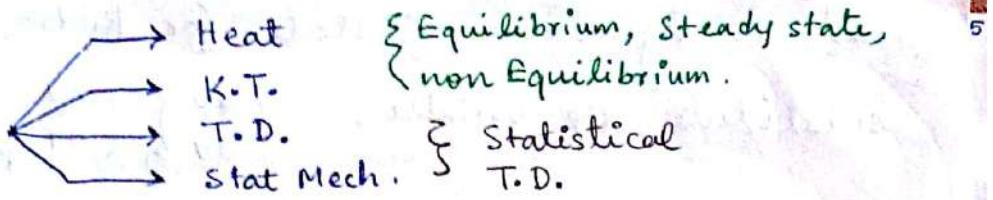


Thermodynamics

Thermal Physics



Useful Mathematical Tools

(a) Partial differentiation : $\frac{\partial f}{\partial a_i}(a_1, a_2, \dots, a_n)$ a_1, \dots, a_n = independent variables.

Let $z = f(x, y)$ is an explicit function (surface plot in XYZ plane)
Motion of a coordinate point on the surface \rightarrow 3 choices (i) $x = \text{constant}$
 y varies (ii) x varies $y = \text{constant}$, (iii) both x, y varies.

$x \rightarrow x + dx$, $y = \text{constant}$, $z = f(x+dx, y)$ from $f(x, y)$.

$$\left(\frac{\partial f}{\partial x}\right)_y = \lim_{dx \rightarrow 0} \frac{f(x+dx) - f(x)}{dx} = f_x$$

$$\text{Similarly } f_y = \left(\frac{\partial f}{\partial y}\right)_x = \lim_{dy \rightarrow 0} \frac{f(x, y+dy) - f(x, y)}{dy}$$

& Higher order derivatives, $f_{xx} = \frac{\partial^2 f}{\partial x^2}$, $f_{xy} = f_{yx} = \frac{\partial^2 f}{\partial x \partial y}$ etc.

(b) Total differentials :

Let $z = f(x, y)$ an explicit function where, x, y are independent.
means $dz \rightarrow 0$ implies $dx \rightarrow 0$ & $dy \rightarrow 0$ independently. Then
 dz is the total differential $dz = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy$.

If an implicit function, say $f(x, y, z) = 0$ then

$$df = 0 = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz = f_x dx + f_y dy + f_z dz$$

If $dx = 0$, $\left(\frac{\partial y}{\partial z}\right)_x = -\frac{f_z}{f_y}$, If $dy = 0$, $\left(\frac{\partial z}{\partial x}\right)_y = -\frac{f_x}{f_z}$ &

If $dz = 0$, $\left(\frac{\partial x}{\partial y}\right)_z = -\frac{f_y}{f_x}$. $\therefore \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$.

Also $dz = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = M dx + N dy$ is perfect differential

$$\text{if } \left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y \Rightarrow \frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y}$$

Example Equation of state for hydrostatic system $f(P, V, T) = 0$
 substitute the variables, $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \quad (\text{volume expansivity})$$

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T \quad (\text{isothermal compressibility})$$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = - \left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = + \frac{1}{\kappa V} PV = \frac{\beta}{\kappa}$$

Get back the ~~same~~ expression $P = P(V, T)$

$$\Rightarrow dP = \left(\frac{\partial P}{\partial V}\right)_T dV + \left(\frac{\partial P}{\partial T}\right)_V dT = -\frac{1}{\kappa V} dV + \frac{\beta}{\kappa} dT$$

(c) Line integral & exact differential :

$dz = M dx + N dy \rightarrow$ required $z(x, y)$ at (x_1, y_1) & (x_2, y_2)

means $\int_{x_1}^{x_2} M(x, y) dx$, $\int_{y_1}^{y_2} N(x, y) dy$ be evaluated, provided

$y = f(x)$ dependency is given, meaning path in XY plane is given.
 path dependent integration !! Each $f(x)$ gives different result.

However if dz is total differential, then

$$M = \frac{\partial z}{\partial x}, \quad N = \frac{\partial z}{\partial y} \Rightarrow \frac{\partial M}{\partial y} = \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial N}{\partial x}$$

from this we can evaluate z by $\iint_{x,y}$ without using $y = f(x)$
 path independent integration !!

It only depends on (x_1, y_1) & (x_2, y_2) ; z is called "point function".

If contour integral over complete cycle $\oint dz = 0$ if dz
 is exact or total differential.

Change of state of a system may be of different types:

Isothermal: If the change of state is such that the temperature (diathermic) of the system remains constant, then that state is called isothermal ($T = \text{constant}$).

Isobaric: If the process is such that the pressure remains constant then it is called isobaric ($P = \text{constant}$).

Isochoric: If during the change of state, the volume of the system does not change, then it is called isochoric ($V = \text{constant}$)

Adiabatic: If the change is such that there is no exchange of heat then it is called adiabatic ($Q = \text{constant}$)

Isentropic: If during the change, the entropy of the system remains constant, then it is called isentropic ($S = \text{constant}$)

Isenthalpic: If during the change of state, the total heat content remains constant, then it is called isenthalpic process
($H = U + PV = \text{constant}$)

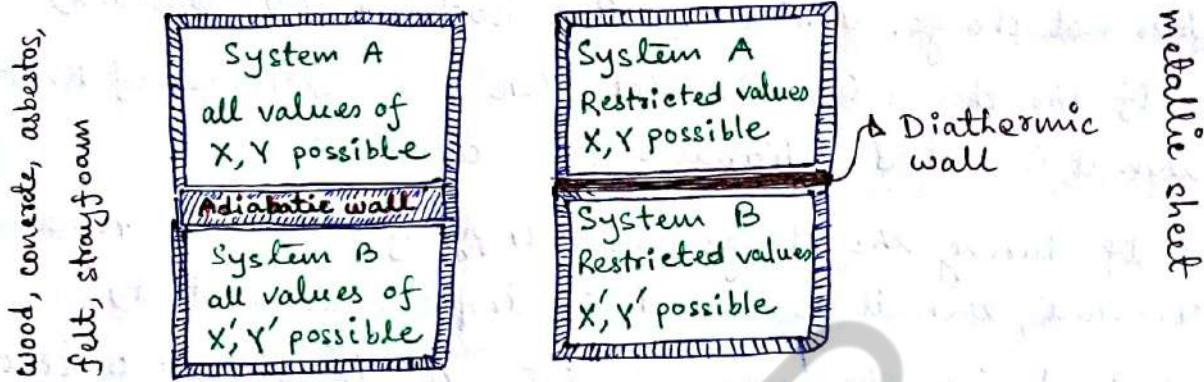
Thermodynamic System "System" refers to a certain portion of the universe within some closed surface (boundary). Boundary may enclose a solid, liquid, gas, collection of magnetic dipoles, portion of liquid surface, batch of radiant energy & so forth. Boundary is not necessarily fixed in shape or size & can be real or imaginary. Like inner surface \leftarrow of tank containing a compressed gas or surface \leftarrow enclosing certain mass of fluid.
imaginary \rightarrow

Many problems involve interchange of energy between a given system & others. Such other systems that can interchange energy with the system are called "surroundings". System & surrounding together constitute the universe.

When conditions are such that no energy interchange with the surroundings can take place, then the system is said to be "isolated". If no matter can cross the boundary, then its a "closed" system. But if interchange of matter between system & surrounding, then its an "open" system.

Thermal Equilibrium

Consider a system having two independent coordinates X, Y (say pressure, volume or temperature). A state of the system in which X & Y have definite values that remain constant as long the external conditions are not changed is called an equilibrium state. Such equilibrium state in a system depends on the proximity of other systems & also on the nature of the separating wall.

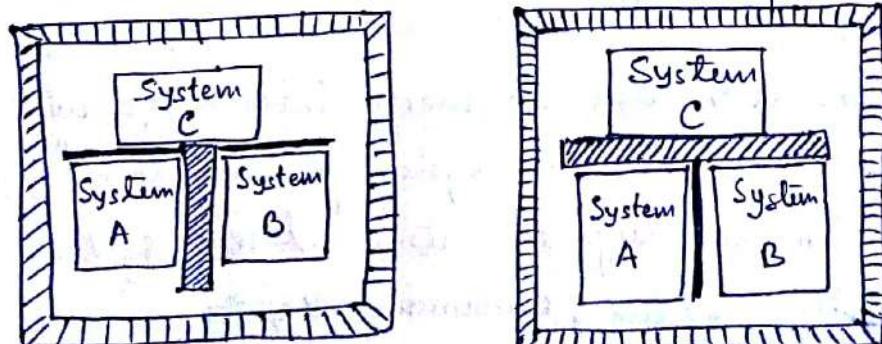


For adiabatic wall, state X, Y for system A may coexist with state X', Y' of system B as equilibrium state. But for diathermic wall, (X, Y) & (X', Y') will change spontaneously until an equilibrium state of the combined system is attained.

Zeroth law of Thermodynamics (Fowler, 1908)

If two system A & B separated by an adiabatic wall but each of them are in contact with a third system C through diathermic wall, then A & B will come to equilibrium with C & no further change will occur if the adiabatic wall between A & B is replaced by diathermic wall.

0th law of T.D. : 2 systems in thermal equilibrium with third are in thermal equilibrium with each other.



Thermodynamic equilibrium

A system is said to be in a state of thermodynamic equilibrium if (a) mechanical equilibrium, (b) chemical equilibrium & (c) thermal equilibrium is satisfied.

When there is no unbalanced force in the interior of a system & also no net force between a system & its surrounding (also net torque is zero), then the system is in a state of mechanical equilibrium.

When a system in mechanical equilibrium does not undergo a spontaneous change in its internal structure (e.g. chemical reaction) mass transfer due to diffusion) then the system is in a state of chemical equilibrium.

Thermal equilibrium exists when there is no spontaneous change in the (thermodynamic) coordinates (e.g. P, V, T) of a system in mechanical & chemical equilibrium when separated from surroundings by diathermic wall.

Non equilibrium states cannot be described in terms of T.D. coordinates as $P = P(x, y, z)$ that varies in space & time.

In the absence of surface, gravitational, electric, magnetic effects a constant mass system that exerts uniform hydrostatic pressure to surroundings is a "hydrostatic system". Categorically 3 systems:

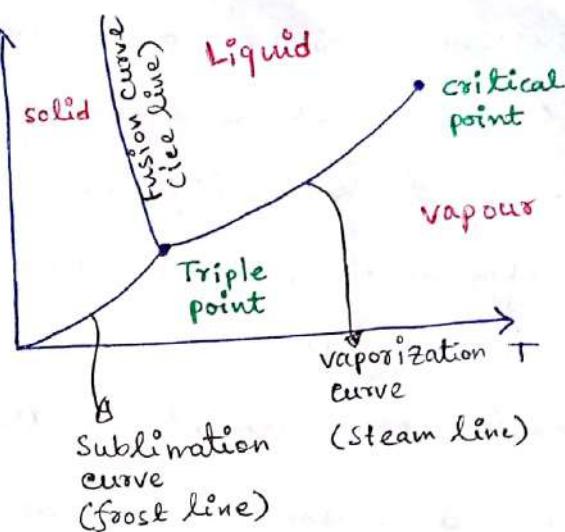
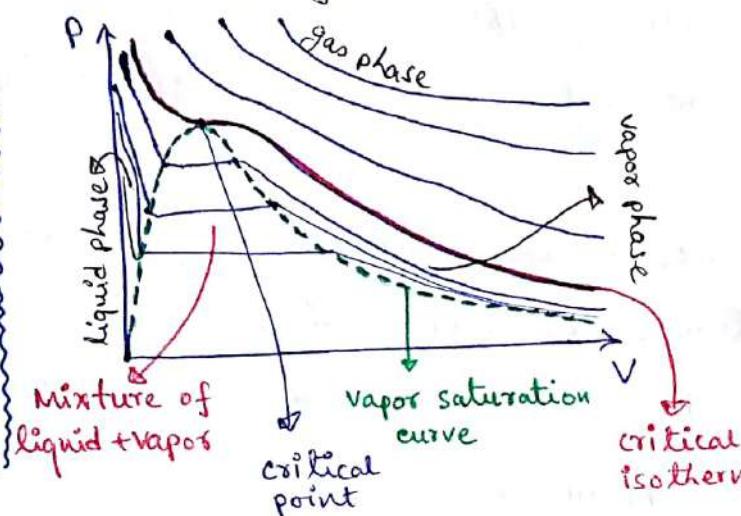
1. A pure substance : 1 chemical constituent (solid, liquid, gas) mixture (s-l, l-g, s-g) or three of them (s-l-g).

2. Homogeneous mixture : mixture of inert gases, mixture of liquids of different constituents (solution)

3. Heterogeneous mixture : mixture of different gases in contact with a mixture of different liquids.

PV & PT diagram for pure substance

INDICATOR DIAGRAM



Thermodynamic description of system other than $f(P, V, T) = 0$

Thermodynamics of a gaseous system is described by three thermodynamic coordinates P, V, T , but for other systems require different types of coordinates.

Stretched Wire $P, V \approx$ unchanged. Thermodynamically equivalent coordinates (a) Tension in the wire (\mathcal{F}), (b) Length of the wire (L) (c) Ideal gas temperature (T). In S.I. units, \mathcal{F} is Newton, L is metre, T in $^{\circ}\text{K}$.

Equivalent of equation of state $f(P, V, T) = 0$ is the Hooke's law at constant temperature within elastic limit.

$$\mathcal{F} = K(L - L_0), \quad L_0 = \text{length at no tension}$$

$$\text{So, } L = L(\mathcal{F}, T) \quad \& \text{ for infinitesimal change}$$

$$\therefore dL = \left(\frac{\partial L}{\partial \mathcal{F}} \right)_T d\mathcal{F} + \left(\frac{\partial L}{\partial T} \right)_{\mathcal{F}} dT$$

$$\text{Linear expansivity } \alpha = \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_{\mathcal{F}}$$

$$\text{Isothermal Young's modulus } Y = \left(\frac{\partial \mathcal{F}/A}{\partial L/L} \right)_T = \frac{L}{A} \left(\frac{\partial \mathcal{F}}{\partial L} \right)_T$$

$$\therefore dL = \frac{L}{AY} d\mathcal{F} + \alpha L dT.$$

In isothermal condition, all resultants of Young's modulus $dL = 0$,

9

for isothermal condition $dT \approx 0$ & $dL = \frac{L}{AY} dT \approx 0$

therefore work done in expanding a wire is

$$W = \int g dL = \int g \frac{L}{AY} dT = \frac{L}{2AY} g^2.$$

Surface film physical chemistry / chemical engineering / other areas.

- Examples (a) Liquid-vapour interface in equilibrium,
(b) soap bubble/film \rightarrow two surface films with in between liquid.
(c) thin oil film on the surface of water.

Three coordinates (a) surface tension γ (Newton/metre), (b) area of film (A) metre², (c) ideal-gas temperature T . To describe a stretched membrane.

Equation of state $\gamma = \gamma_0 (1 - \frac{T}{T_c})^n$ for surface tension
 γ_0 = surface tension at 0°C, $T' \approx$ near T_c & $n \approx 1.22$.

As $T >$, $\gamma < \gamma_0$ at $T = T'$.

Dielectric slab

Thermodynamic behaviour of a dielectric slab (whether molecules are polar or nonpolar) is described by three coordinates, (a) electric field intensity E (V/m), (b) electric polarisation (P) in Coulomb/m³ which is the amount of dipole moment per unit volume along the direction of the electric field.

The equation of state of the dielectric

$P = (A + \frac{B}{T})E$ where A, B are constants & depends upon the nature of the dielectric material.

Paramagnetic Rod

When a paramagnetic rod is placed within a solenoid, where the magnetic intensity is H , the rod develops a magnetic moment M . Magnetic induction B in volume V is

$$B = \mu_0 (H + \frac{M}{V}).$$

Equivalent thermodynamic coordinates are (1) Magnetic field intensity H (Ampere/metre), (2) Magnetization M (Ampere metre²), (3) Ideal gas temperature T . (in °K).

The equation of state of thermodynamic equilibrium is

$$M = C \frac{H}{T} \quad (\text{Curie's law})$$

Intensive & Extensive Parameters

If a system in equilibrium is divided into two parts, each with equal mass, then those properties of each half of the system that remain same are called intensive & those which become half are called extensive.

Systems	Intensive coordinates	Extensive coordinates
(a) Hydrostatic system	Pressure (P)	Volume (V)
(b) stretched wire.	Tension (F)	Length (L)
(c) surface film	Surface tension (S)	Area (A)
(d) Dielectric slab	Electric field Intensity (E)	Polarization (P)
(e) Paramagnetic rod	Magnetic field Intensity (H)	Magnetization (M)

Equation of state for adiabatic process

Let us consider an ideal gas system of volume V at pressure P . Then for isothermal change, $PV = nRT = \text{constant}$ (as $T = \text{constant}$)

Now for an adiabatic process without any exchange of heat, using first law of thermodynamics $Q = dU + PdV$.

where dU is the internal energy change & if the change in temperature for one mole of gas is dT , then $dU = C_V dT$ where C_V is the specific heat at constant volume.

$\therefore C_V dT + PdV = 0$ for adiabatic process.

from equation of state $PV = RT \therefore PdV + VdP = RdT$

$$\therefore dT = \frac{PdV + VdP}{R} = \frac{PdV + VdP}{C_p - C_v} \text{ as } C_p - C_v = R \text{ for ideal gas}$$

$$\therefore C_v \left(\frac{PdV + VdP}{C_p - C_v} \right) + PdV = 0$$

$$\therefore \frac{C_v PdV + C_v VdP + C_p PdV - C_v PdV}{C_p - C_v} = 0 \therefore C_v VdP + C_p PdV = 0$$

$$\therefore \frac{dp}{P} + \frac{C_p}{C_v} \frac{dv}{v} = 0, \text{ integrating } \ln P + \gamma \ln v = \text{constant}$$

$$\therefore PV^\gamma = \text{constant}$$

$$\text{Using } PV = RT \therefore v = \frac{RT}{P} \Rightarrow P \left(\frac{RT}{P} \right)^\gamma = \text{constant}$$

$$\therefore P^{1-\gamma} T^\gamma = \text{constant}$$

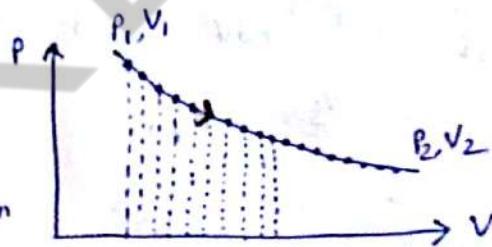
$$\text{Again using } PV = RT, P = \frac{RT}{V} \Rightarrow \frac{RT}{V} v^\gamma = \text{constant}$$

$$\therefore V^{\gamma-1} T = \text{constant}$$

Quasistatic Process

A finite unbalanced force may cause a system to pass through nonequilibrium states. Thus during a process if it is required to describe every state of the system by means of thermodynamic coordinates, the process should not conceive a finite unbalanced force; because a nonequilibrium state cannot be defined by thermodynamic coordinates. Therefore we think of an ideal situation in which external forces vary slightly so as the unbalance force is infinitesimal. A process performed in such ideal way is "quasistatic". [In stat mech course, rethink about "local equilibrium"]

During a quasistatic process the system is infinitesimally near a state of thermodynamic equilibrium, & all states through which the system passes can be described with equation of state with thermodynamic coordinates.



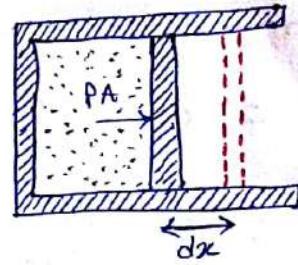
Workdone "on" or "by" a system in a quasistatic process

a) Gaseous hydrostatic System

pressure exerted by the system on piston = P_A

opposing force on the system by external agent

moves piston by dx in opposite direction to P_A



$$\text{Then } dW = -P_A dx = -P dV \quad (dV = Adx)$$

If $dV > 0$ (expansion), $dW < 0$ (negative work)

$dV < 0$ (compression), $dW > 0$ (positive work)

$$\text{for finite quasistatic process } W = - \int_{V_i}^{V_f} P dV$$

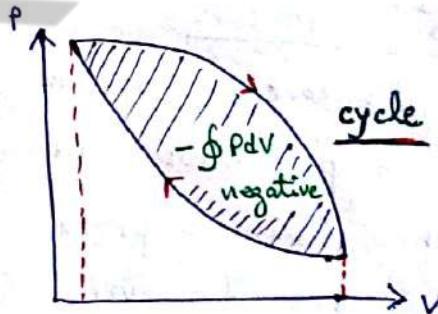
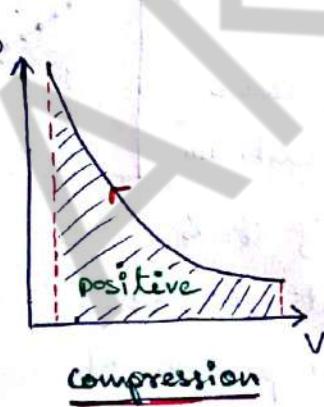
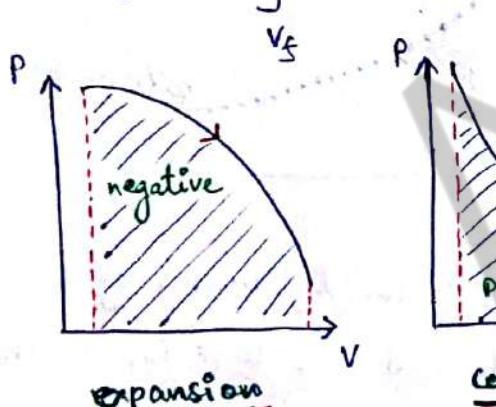
This depends on path because $P = P(T, V) \Rightarrow P = P(V)$ for given T .

∴ Workdone "on" a system from larger volume (V_i) to smaller volume

(V_f) is $W_{if} = - \int_{V_i}^{V_f} P dV$ & for expansion, workdone "by" system

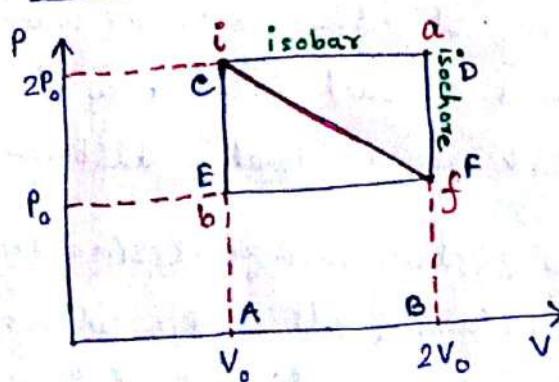
is $W_{fi} = - \int_{V_f}^{V_i} P dV$ and when path is quasistatic, $W_{fi} = -W_{if}$

INDICATOR DIAGRAM



net workdone is negative

Path dependency: Exact & inexact differentials



Many route to go from $i \rightarrow f$.

a) $i \rightarrow a$ (isobaric) $\Rightarrow a \rightarrow f$ (isochoric)

$$\text{W.D.} = - \int P dV = - 2P_0 V_0$$

area ABDC

b) $i \rightarrow b$ (isochoric) $\Rightarrow b \rightarrow f$ (isobaric)

$$\text{W.D.} = - \int P dV = - P_0 V_0$$

area ABFE

$$\textcircled{c} \quad i \rightarrow f, \text{ W.D.} = - \int_{\text{area ABFC}} P dV = - \int_{\text{area ABEF}} P dV - \int_{\text{area EFC}} P dV = - \frac{3}{2} P_0 V_0$$

Infinitesimal amount of work is "inexact differential", means it is not the differential of a function of thermodynamic coordinates. That's represented with dW , & it depends on the path.

Suppose if functional differential $df = 2xy^3 dx + 3x^2y^2 dy$
 $= d(x^2y^3)$.

$\int_{x=y=3}^{x=y=1} df$ depends only on the limit & not on path. df is an "exact differential".

Isothermal quasistatic expansion/compression

$$\text{Using } PV = nRT, \quad W = - \int_{V_i}^{V_f} P dV = - \int_{V_i}^{V_f} \frac{nRT}{V} dV = -nRT \ln \frac{V_f}{V_i}$$

$$n = 2 \text{ kmol}, \quad T = 273K (0^\circ C), \quad R = 8.31 \text{ kJ/kmol}\cdot K, \quad V_i = 4m^3, \quad V_f = 1m^3$$

(compression), $W = 6300 \text{ kJ}$ = positive work (work done "on" gas)

Isothermal quasistatic increase of pressure on solid

$$V = V(P, T) \quad \therefore dV = \left(\frac{\partial V}{\partial P}\right)_T dP + \left(\frac{\partial V}{\partial T}\right)_P dT = \left(\frac{\partial V}{\partial P}\right)_T dP$$

$$\text{isothermal compressibility} = \frac{1}{\text{bulk modulus}} = \frac{1}{dP/(dV/V)} \quad (\text{isothermal})$$

$$\kappa_V = - \frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$\therefore dV = - \kappa_V dP$$

$$\text{so Work done} = \int_{P_i}^{P_f} P \kappa_V dP \approx \frac{\kappa_V}{2} (P_f^2 - P_i^2) = \frac{Km}{2\rho} (P_f^2 - P_i^2)$$

for copper, at $T = 273K$, $\rho = 8930 \text{ kg/m}^3$, $K = 7.16 \times 10^{-12} \text{ Pa}^{-1}$, $m = 100 \text{ kg}$, $P_i = 0$, $P_f = 1000 \text{ atm} = 1.013 \times 10^8 \text{ Pa}$

$W = 0.411 \text{ kJ.}$ = positive work (work done "on" copper)

(b) Isothermal stretching a wire

If tension F changes length of wire from L to $L+dL$ (extension)
then work done on the wire (positive work) is

$$W = \int_{L_i}^{L_f} F dL, \quad \text{remember, } L = L(F, T) \text{ for isothermal}$$

$$dL = \left(\frac{\partial L}{\partial F} \right)_T dF + \left(\frac{\partial L}{\partial T} \right)_F dT = \left(\frac{\partial L}{\partial F} \right)_T dF$$

$$= \int_F^F \frac{L}{AY} F dF \quad \text{using "isothermal Young's modulus"}$$

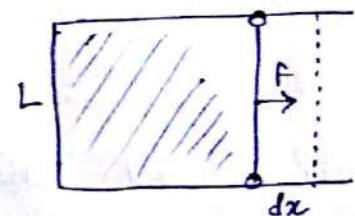
$$= \frac{L}{2AY} F^2.$$

(c) Surface film

If σ is surface tension of a double surface film with liquid in between then force exerted on both film is $2\sigma L$ & for displacement dx , work done "on" the film (positive)

$$dW = 2\sigma L dx = \sigma dA \quad (\text{as } dA = 2L dx)$$

$$\therefore W = \int_{A_i}^{A_f} \sigma dA \quad [\text{For soap bubble } A = 2 \times 4\pi R^2, W = 8\pi \sigma R^2]$$



(d) Polarization of a dielectric solid

Consider a slab of isotropic dielectric material between conducting plates of a parallel-plate capacitor, with area A & separation l connected to a battery to yield potential difference E .

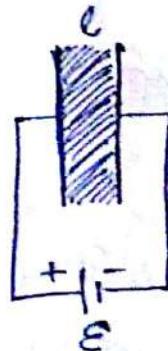
$$\text{Uniform field intensity } E = \frac{V}{l}.$$

Work done against the electric field to move dz amount of charge

$$\therefore dW = Edz = Edz = E l A dd = EV dd \quad [\text{as } dz = dA = \text{total charge} \\ \text{ & } d = \text{electric displacement}]$$

$$\text{Now } D = \epsilon E = \epsilon_0 E + \frac{\rho}{V}$$

$$[\text{as } V = EA]$$



$$\therefore dD = (\epsilon_0 dE + \frac{dP}{V}) \quad \text{& then}$$

$$dW = EV(\epsilon_0 dE + \frac{dP}{V}) = V\epsilon_0 E dE + EdP$$

[vacuum] [material]

\therefore Net work on dielectric is $dW = EdP$, $W = \int_{P_i}^{P_f} EdP$

e) Magnetization of a magnetic solid

magnetic ring cross sectional area A,
circumference L. Insulated wire is wind
on that (Toroidal winding)

Current in the winding initiate magnetic
field with induction B (uniform). Using
Rheostat if current is changed in time dt then

$$E = -NA \frac{dB}{dt} \quad (\text{Faraday's principle of EM induction})$$

$$N = \text{number of turns} \quad H = ni = \frac{Ni}{L} = \frac{(NAi)}{V} \quad (V=AL)$$

If dZ charge is transferred in circuit, work done "by" system
to maintain current is $dW = -E dZ = NA \frac{dB}{dt} dZ$

$$= NA \frac{dZ}{dt} dB = \frac{(NAi)}{V} dB$$

$$= VH dB.$$

If M = total magnetic moment, then

$$B = \mu H = \mu_0 H + \mu_0 \frac{M}{V} \Rightarrow dB = \mu_0 dH + \mu_0 \frac{dM}{V}$$

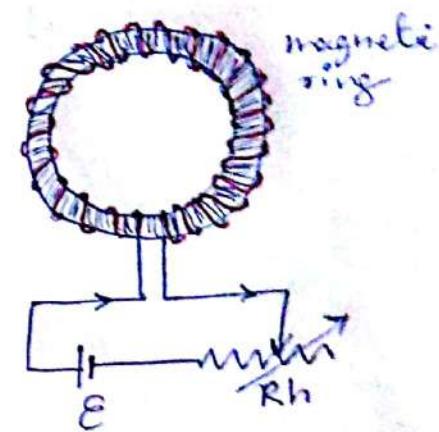
$$\therefore dW = V\mu_0 H dH + \mu_0 H dM$$

[vacuum] [material]

Work done to change the magnetization is $dW = \mu_0 H dM$

$$\therefore W = \mu_0 \int_{M_i}^{M_f} H dM.$$

$$\boxed{\text{Work (extensive)} = \text{Intensive quantity} \times \text{Extensive quantity}}$$

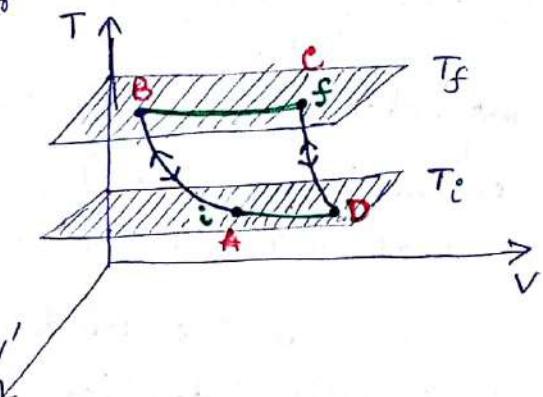
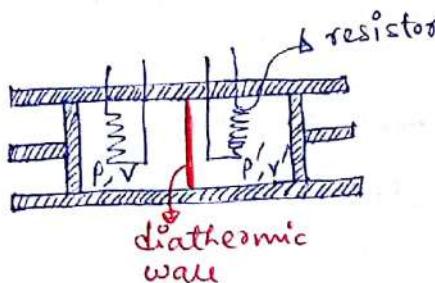


Using Curie's law $M = C \frac{H}{T}$

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

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

Adiabatic Work



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

- ⑥ 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 of 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 $U = U(V, T)$, $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

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

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

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

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

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

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

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.

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

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

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

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

$$C_P = C_V + nR$$

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

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

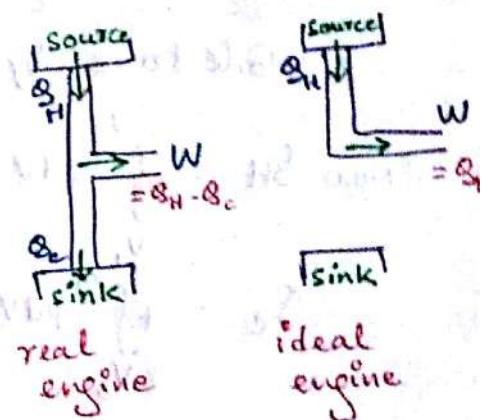
In previous examples, we saw how heat can be generated indefinitely at the expense of work. To study the converse process, there may be 1 or more than 1 (series of) processes.

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

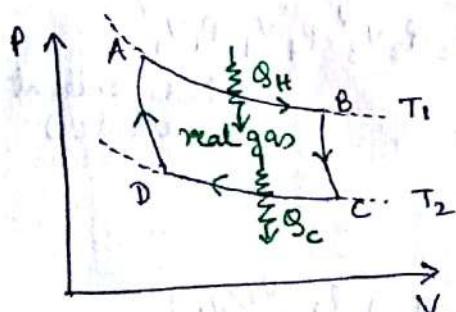
$$\eta = \frac{\text{Work output}}{\text{Heat input}} = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$

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



Carnot cycle

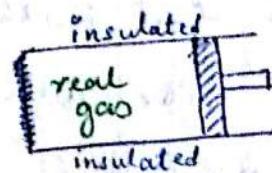
It's maximum efficient engine (nearly ideal)



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 $+W_3$ (positive 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 $+W_1$ (plus because workdone "on" the gas).

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

$$\text{or } \oint_C dQ - \oint_C dW = 0 \text{ or } Q_H + 0 - Q_C + 0 = -W_1 + W_2 + W_3 + W_4$$

∴ Work done by engine = difference of heat absorbed & rejected.

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

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

But for isothermal processes $P_1V_1 = P_2V_2, P_3V_3 = P_4V_4$

for adiabatic processes $P_2V_2^{\gamma} = P_3V_3^{\gamma}, P_4V_4^{\gamma} = P_1V_1^{\gamma}$

$$\text{Multiplying, } P_1V_1 P_2V_2^{\gamma} P_3V_3^{\gamma} P_4V_4^{\gamma} = P_2V_2 P_3V_3^{\gamma} P_4V_4^{\gamma} P_1V_1^{\gamma} \quad (\text{independent events})$$

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

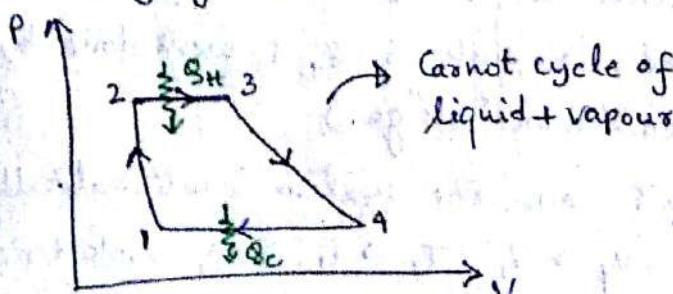
$$\text{or } V_2/V_1 = V_3/V_4$$

$$\therefore \text{Efficiency } \eta = \frac{Q_H - Q_C}{Q_H} = \frac{-R(T_1 - T_2) \ln(V_2/V_1)}{-RT_1 \ln(V_3/V_4)}$$
$$= \frac{T_1 - T_2}{T_1} \neq 100\%$$

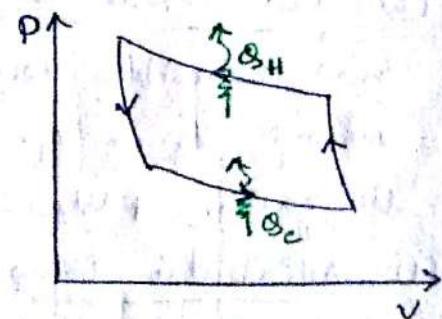
$$\therefore \boxed{\frac{Q_H}{T_1} = \frac{Q_C}{T_2}}$$

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

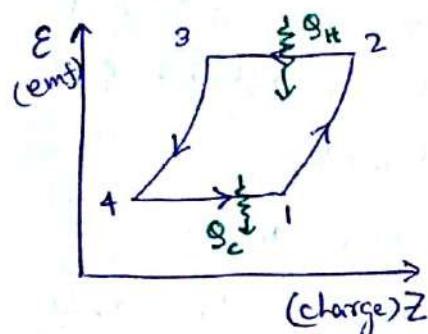
In that case Q_C heat is removed from sink & Q_H is delivered to source & work must be done to the system. The system then works as a refrigerator.



Carnot cycle of
liquid+vapour



- $1 \rightarrow 2$ 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

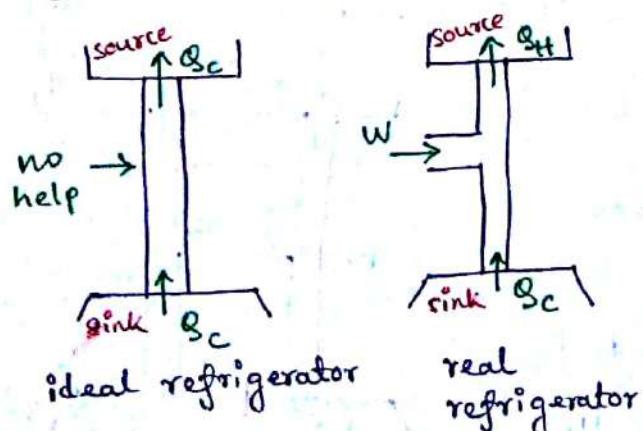
Second law of Thermodynamics

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.

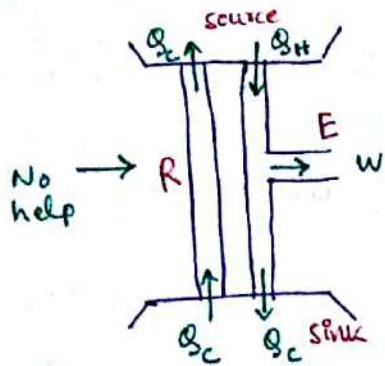
Plank's Statement It is impossible to fabricate an engine working in a complete cycle to produce no effect other than raising a weight & cooling of a hot reservoir.

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.



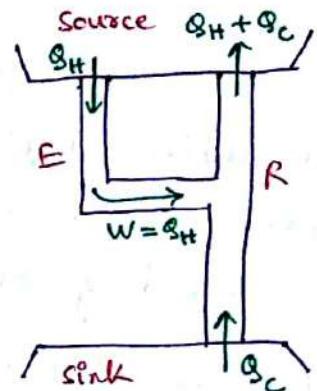
Equivalence of Kelvin-Plank & Clausius statement



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.



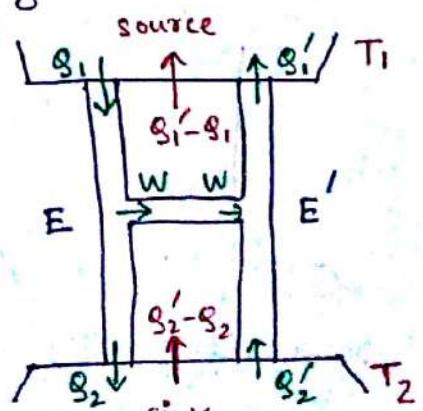
1st law of Thermodynamics = conservation of energy

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. η 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 η (efficiency) of E $>$ η' 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.

$$\therefore \eta > \eta'$$

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

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

for irreversible engine we can show by the same procedure that $\eta_{irr} > \eta_{rev}$ but due to irreversibility we "cannot" show $\eta_{rev} > \eta_{irr}$
 $\therefore \eta_{irr}$ is either equal to or less than η_{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 2nd law. ∴ $T=0$ is the lowest attainable temperature when one gets an ideal engine.