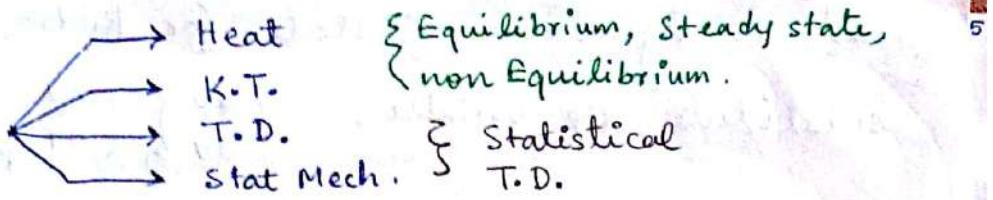


Thermodynamics

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 :

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

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
($H = U + PV = \text{constant}$)

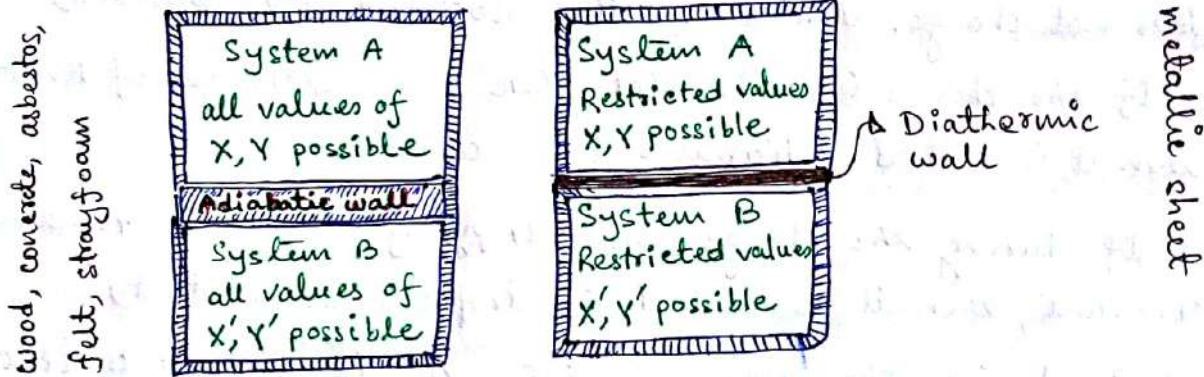
Thermodynamic System "System" refers to a certain portion of the universe within some closed surface (boundary). Boundary may enclose a solid, liquid, gas, collection of magnetic dipoles, portion of liquid surface, batch of radiant energy & so forth. Boundary is not necessarily fixed in shape or size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

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.

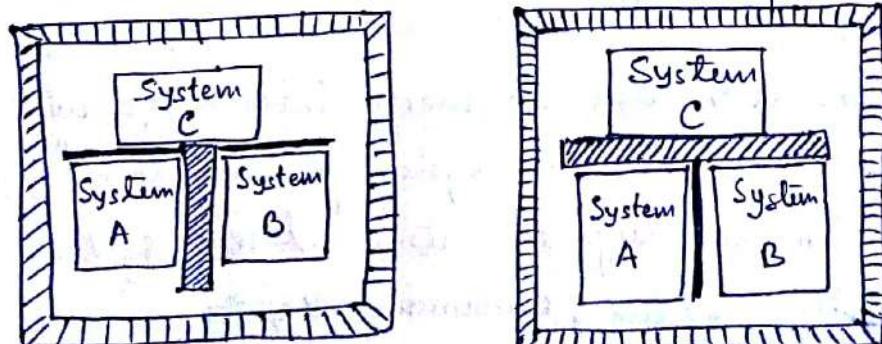


For adiabatic wall, state X, Y for system A may coexist with state X', Y' of system B as equilibrium state. But for diathermic wall, (X, Y) & (X', Y') will change spontaneously until an equilibrium state of the combined system is attained.

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:

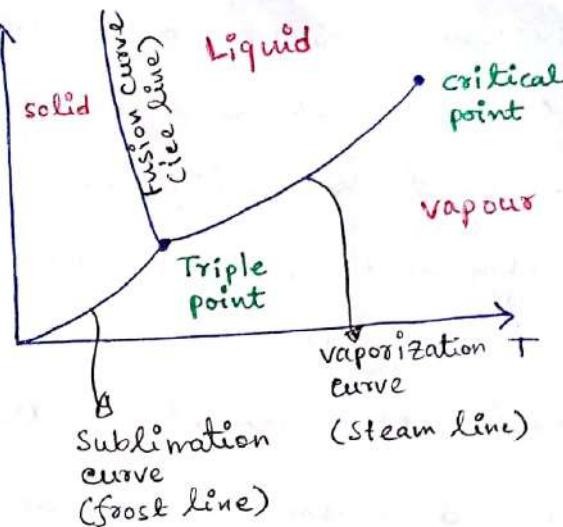
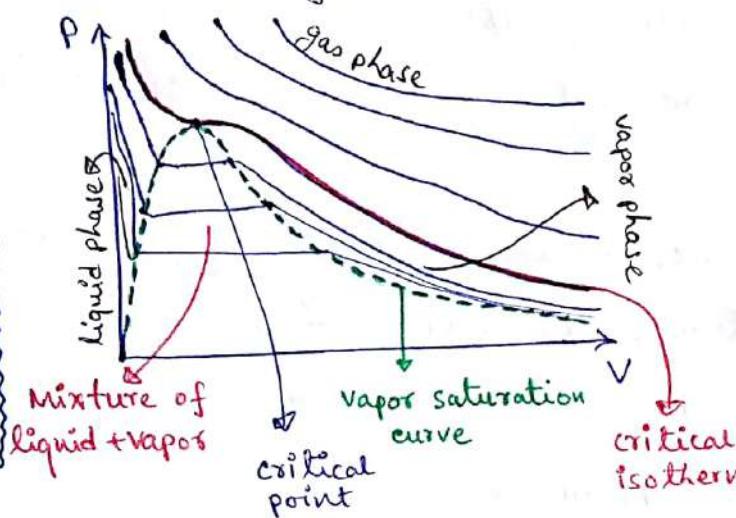
1. A pure substance : 1 chemical constituent (solid, liquid, gas) mixture (s-l, l-g, s-g) or three of them (s-l-g).

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 $dL = 0$,

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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 $T \gg$, $\gamma < \gamma_0$ 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.

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

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

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

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

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

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

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

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

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

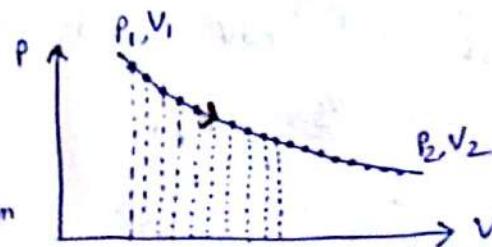
$$\text{Again using } PV = RT, P = \frac{RT}{V} \Rightarrow \frac{RT}{V} v^\gamma = \text{constant}$$

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

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.



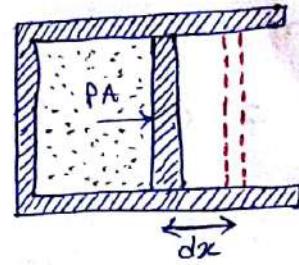
Workdone "on" or "by" a system in a quasistatic process

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)

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

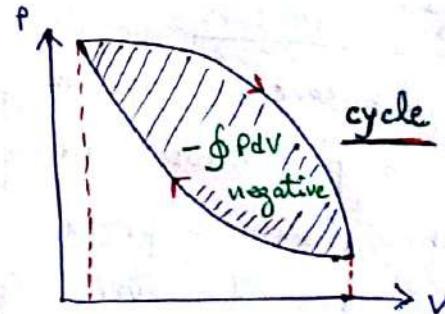
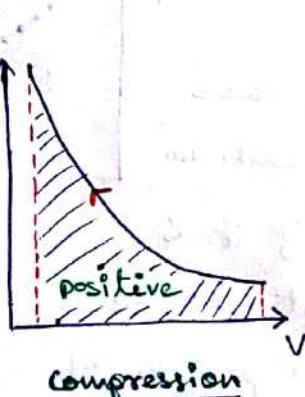
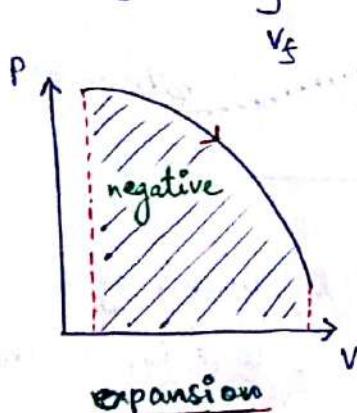
This depends on path because $P = P(T, V) \Rightarrow P = P(V)$ for given T .

∴ 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

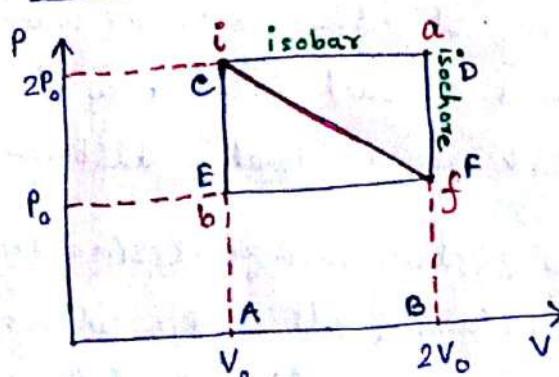
is $W_{fi} = - \int_{V_f}^{V_i} P dV$ and when path is quasistatic, $W_{fi} = -W_{if}$

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) $\Rightarrow b \rightarrow f$ (isobar)

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

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

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

$n = 2 \text{ kmol}$, $T = 273K (0^\circ\text{C})$, $R = 8.31 \text{ kJ/kmol}\cdot\text{K}$, $V_i = 4m^3$, $V_f = 1m^3$
 (compression), $W = 6300 \text{ kJ}$ = positive work (work done "on" gas)

Isothermal quasistatic increase of pressure on solid

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

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

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

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

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

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

$W = 0.411 \text{ kJ}$. = 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

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

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

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

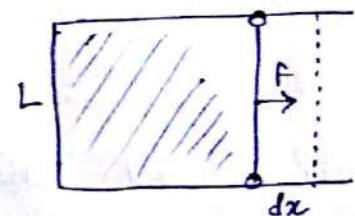
$$= \frac{L}{2AY} F^2.$$

(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 .

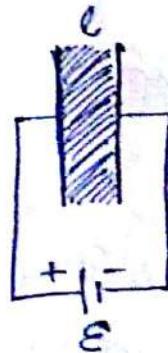
$$\text{Uniform field intensity } E = \frac{V}{l}.$$

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

$$\therefore dW = Edz = Edz = E l A dz = EV dD \quad [\text{as } dz = dA = \text{total charge}]$$

$$= EV dD \quad [dD = \text{electric displacement}]$$

$$\text{Now } D = \epsilon E = \epsilon_0 E + \frac{\rho}{V} \quad [\text{as } V = EA]$$



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

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

[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 $dW = \mu_0 H dM$

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

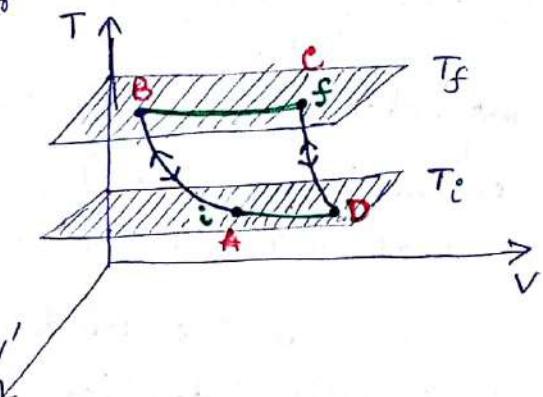
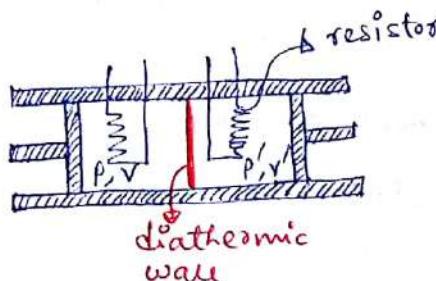
$$\boxed{\text{Work (extensive)} = \text{Intensive quantity} \times \text{Extensive quantity}}$$

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

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

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

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

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

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

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

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

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

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

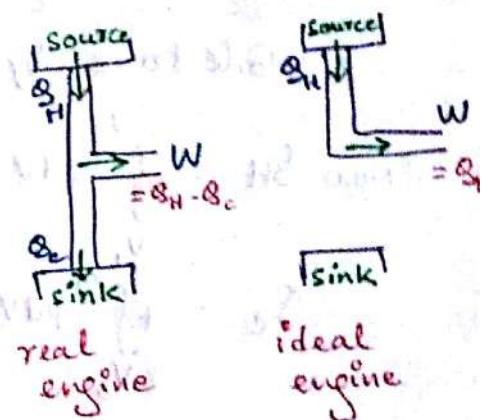
In previous examples, we saw how heat can be generated indefinitely at the expense of work. To study the converse process, there may be 1 or more than 1 (series of) processes.

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

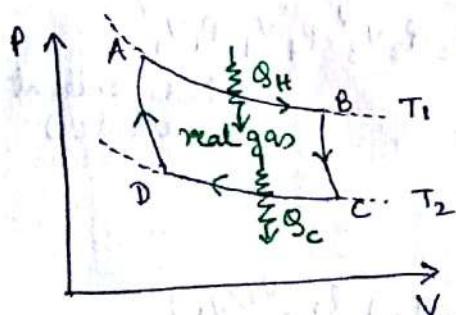
$$\eta = \frac{\text{work output}}{\text{Heat input}} = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$

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 $\oint_C dU = 0$

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

∴ 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 $P_1 V_1 = P_2 V_2, P_3 V_3 = P_4 V_4$

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

$$\text{Multiplying, } P_1 V_1 P_2 V_2^\gamma P_3 V_3^\gamma P_4 V_4^\gamma = P_2 V_2 P_3 V_3^\gamma P_4 V_4^\gamma P_1 V_1^\gamma$$

(independent events)

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

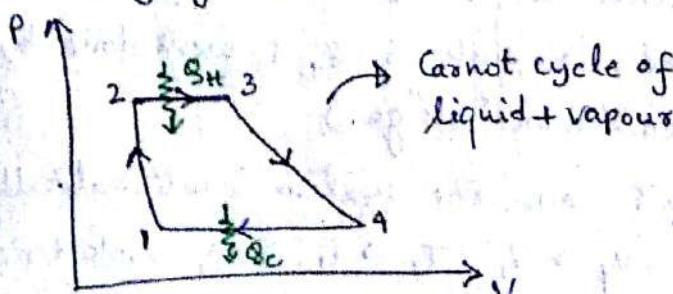
$$\Leftrightarrow V_2/V_1 = V_3/V_4$$

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

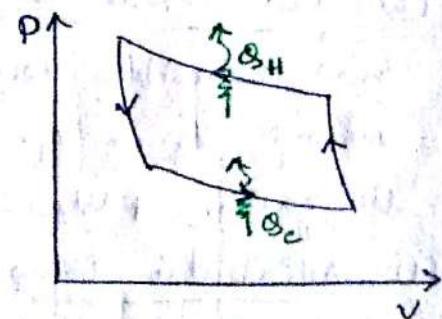
$$\therefore \boxed{\frac{Q_H}{T_1} = \frac{Q_C}{T_2}}$$

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

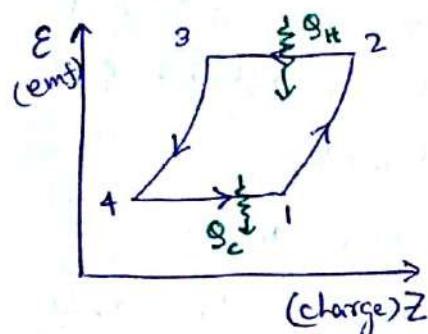
In that case Q_C heat is removed from sink & Q_H is delivered to source & work must be done to the system. The system then works as a refrigerator.



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

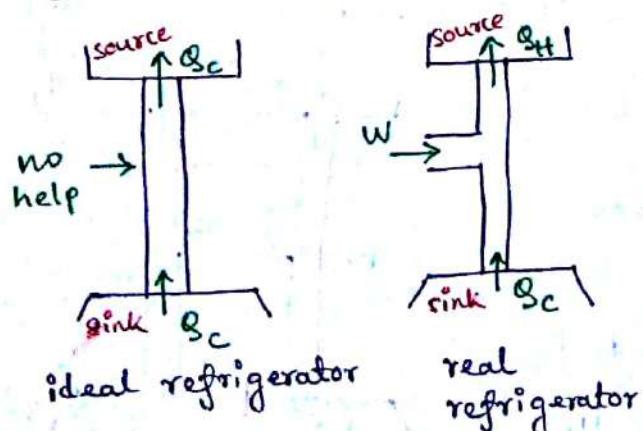
Second law of Thermodynamics

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.

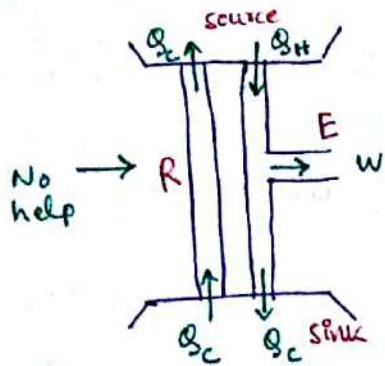
Plank's Statement It is impossible to fabricate an engine working in a complete cycle to produce no effect other than raising a weight or cooling of a hot reservoir.

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.



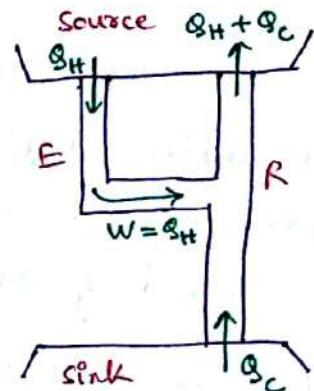
Equivalence of Kelvin-Plank & Clausius statement



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.



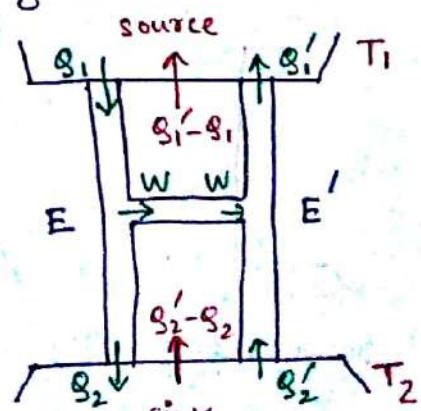
1st law of Thermodynamics = conservation of energy

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 this 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.

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.

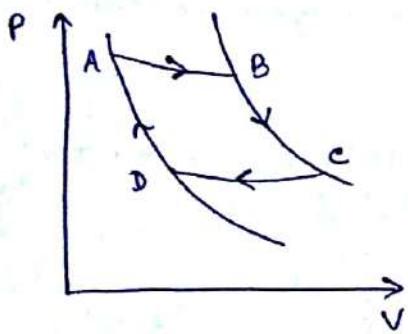
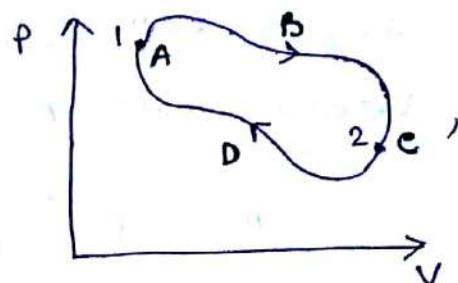
For AD & BC, $dQ = 0 \therefore dS = 0$. & hence

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

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 .

Then 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 =	Inexact differential \times Integrating factor	
(ds)	(ds)	(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 $\underbrace{xy}_{I.F.} df = d\phi = 3x^2y^2dx + 2x^3ydy = d(x^3y^2)$ = exact.

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 δQ , 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 $C_P - C_V = \beta_M$.

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

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

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

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

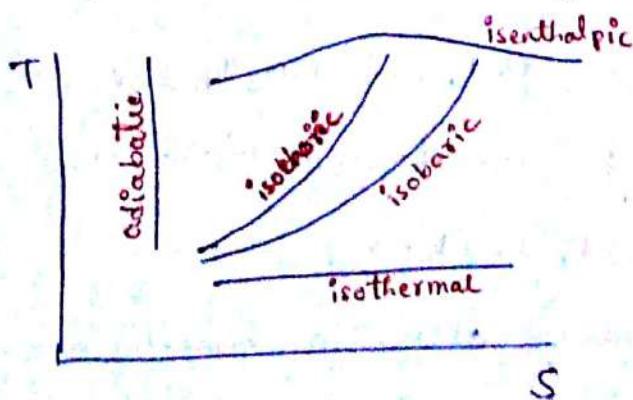
Isothermal system for isothermal change of state of gas $dU = 0$

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

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

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

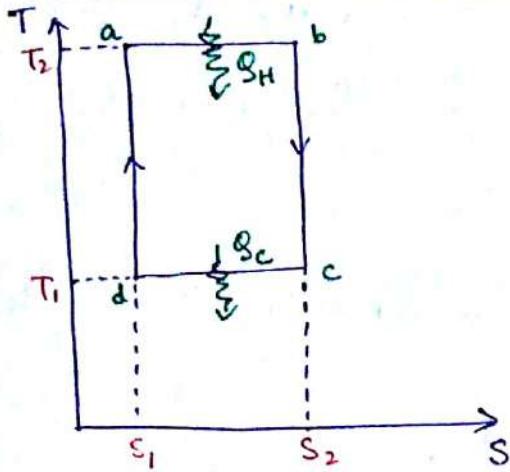
In free expansion of a perfect gas into an empty vessel in a thermally insulated environment, gain in entropy is $\Delta S = \int \frac{pdv}{T} = R \ln \frac{V_2}{V_1}$.



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.

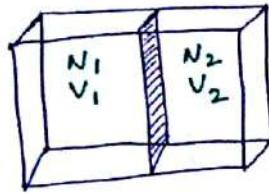
$$Q_H = T_2 (S_2 - S_1)$$

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

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

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

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 2nd 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.

So $\Delta S = S - (S_1 + S_2) = 0$ 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,

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

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

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

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

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

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

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

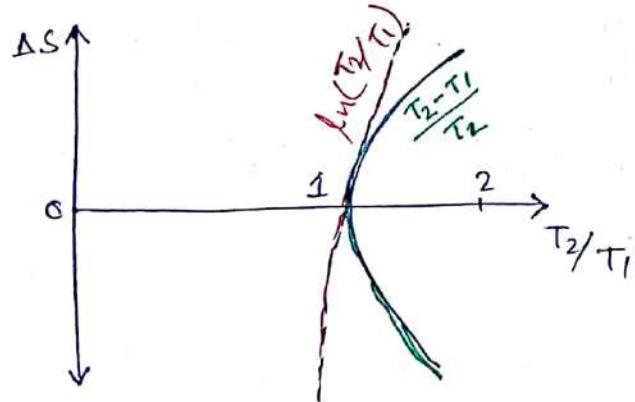
The reservoir temperature T_2 remains constant, so change in entropy is same for reversible isothermal process (heat flowing into reservoir) & irreversible isothermal process (heat only flowing out)

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

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



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

∴ Increase in entropy of the body is always greater than decrease of entropy of reservoir & ∴ 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 2nd law of thermodynamics. Clausius restated that 1st law is energy of the universe remains constant & 2nd 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 $T_1 = T + \Delta T$, $T_2 = T$, $T_1 T_2 \approx T^2$

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

\downarrow
entropy
production

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

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

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

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 $x = -\frac{T_f - T_i}{T_f}$.

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

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

∴ Total change in entropy of the universe $\Delta S = C_p \ln \frac{T_f}{T_i} - C_p \frac{T_f - T_i}{T_f}$
 $= (C_p R \ln(1+x)^{-1} + C_p x) = C_p(x - \ln(1+x))$

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 & $H = 2230 \text{ K}$.

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

$$= 0.03 R.$$

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 ΔS 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" (Ω) & we can write $S = f(\Omega)$. To obtain the functional form, consider two systems having thermodynamic probability Ω_1 and Ω_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 Ω_0 to Ω_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 & 2nd law of Thermodynamics

The 2nd 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 2nd 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 2nd 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 2nd 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.

Otto Cycle & Gasoline Engine

The cycle involves performance of 6 processes, 4 of which require "stroke" (vertical motion) of the piston

1. Intake stroke:

A mixture of gasoline vapour and air

is drawn into the combustion chamber at constant pressure by the succession of the piston, represented by $5 \rightarrow 1$, & according to equation

$$P_0 V = n R T_1, \quad P_0 = \text{atmospheric pressure}, \quad V = \text{vol. of chamber},$$

T_1 = temperature of air outside & n moles of atom.

2. Compression stroke: The mixture is compressed in quasi-static adiabatic stroke until its pressure & temperature rise considerably.

No friction & no loss of heat at the cylinder wall. $1 \rightarrow 2$ process

is represented as. $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

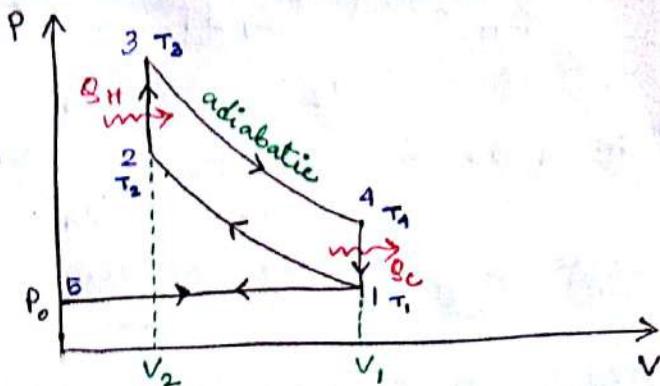
3. Ignition or combustion: Process $2 \rightarrow 3$ represents quasi-static isochoric increase of temperature from T_2 to T_3 where combustion takes place very rapidly by an electric spark.

4. Power stroke: The hot combustion product expands and push the piston out. $3 \rightarrow 1$ represents quasi-static adiabatic process so that temperature falls down to T_4 with equation $T_3 V_2^{\gamma-1} = T_4 V_1^{\gamma-1}$

5. Valve Exhaust: The combusted product at the end of power stroke are still at a higher pressure and temperature than outside. An exhaust valve allows the gas mixture to escape, that is $1 \rightarrow 5$.

6. Exhaust Stroke: The piston pushes all the remaining combustion product out of the chamber by exerting a sufficiently large pressure $1 \rightarrow 5$ represents this isobaric exhaust.

If the specific heat C_V of the gas mixture is constant then heat absorbed in process $2 \rightarrow 3$ is



$Q_H = \int_{T_2}^{T_3} C_V dT = C_V(T_3 - T_2)$. and the heat rejected in $1 \rightarrow 1$ is $Q_C = - \int_{T_1}^{T_4} C_V dT = C_V(T_4 - T_1)$. Thus the thermal efficiency of the gasoline engine is $\eta = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_4 - T_1}{T_3 - T_2}$

Also for the two adiabatic process we know

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}, \quad T_4 V_1^{\gamma-1} = T_3 V_2^{\gamma-1}$$

$$\therefore (T_4 - T_1) V_1^{\gamma-1} = (T_3 - T_2) V_2^{\gamma-1} \Rightarrow \frac{T_4 - T_1}{T_3 - T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$$

$$\therefore \eta = 1 - \left(\frac{1}{r}\right)^{\gamma-1} \quad \text{where } r = \frac{V_1}{V_2} \text{ is the compression ratio.}$$

In actual gasoline engine $r \leq 10$. If r is large then temperature of the gasoline-air mixture upon compression is huge enough to cause combustion before the advent of spark. This is called "Preignition". Taking $r=9$, $\gamma=1.4$, we obtain

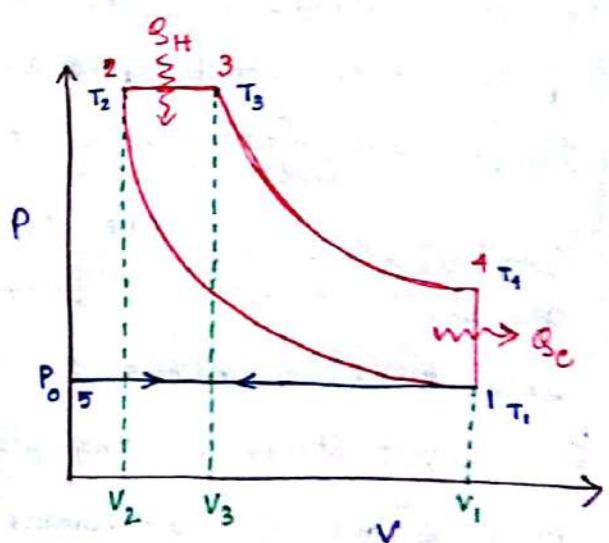
$\eta = \underline{\underline{67\%}}$. In actual engine however due to turbulence, heat conduction etc, the efficiency is less than 67%.

Diesel Engine

Rudolf Diesel in 1897 designed this air-standard Diesel cycle where only air is admitted on intake stroke. The air is compressed adiabatically until temperature reaches high to ignite oil after compression stroke. Combustion stroke happens isobarically & piston moves out. Process 4,5,6

happen like the Otto cycle. Only change is $2 \rightarrow 3$ is horizontal.

$$\text{Quasistatic isobaric heat absorption } (2 \rightarrow 3) \quad Q_H = \int_{T_2}^{T_3} C_p dT = C_p(T_3 - T_2)$$



and valve exhaust releases (4→1) Q_c heat as in Otto engine,

$Q_c = - \int_{T_4}^{T_1} C_V dT = C_V (T_1 - T_4)$. Thus the thermal efficiency of an idealized diesel engine is $\eta = 1 - \frac{Q_c}{Q_H} = 1 - \frac{T_1 - T_4}{\gamma(T_2 - T_1)}$.

We want to calculate the ratio in terms of adiabatic expansion ratio $\rho = \frac{V_1}{V_2}$ and combustion expansion ratio $e = \frac{V_3}{V_2}$. So we've to evaluate $\frac{T_1 - T_4}{T_3 - T_2}$ in that.

for path 1→2, adiabatic

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\Rightarrow T_1 = T_2 \left(\frac{V_2}{V_1} \right)^{\gamma-1} = T_2 \frac{1}{\rho^{\gamma-1}}$$

for path 2→3 isobaric

$$\frac{T_3}{V_3} = \frac{T_2}{V_2}$$

$$\Rightarrow T_3 = T_2 \frac{V_3}{V_2} = T_2 e$$

for path 3→4, adiabatic

$$T_3 V_3^{\gamma-1} = T_4 V_4^{\gamma-1}, \text{ as } V_1 = V_4$$

$$\Rightarrow T_4 = T_3 \left(\frac{V_3}{V_4} \right)^{\gamma-1} = T_3 \left(\frac{V_3}{V_2} \right)^{\gamma-1} \left(\frac{V_2}{V_1} \right)^{\gamma-1}$$

$$= T_3 e^{\frac{\gamma-1}{\rho^{\gamma-1}}} = T_2 e^{\frac{\gamma-1}{\rho^{\gamma-1}}}$$

$$\therefore \eta = 1 - \frac{1}{\gamma} \left[\frac{T_2 e^{\frac{\gamma-1}{\rho^{\gamma-1}}} - T_2 \frac{1}{\rho^{\gamma-1}}}{T_2 e - T_2} \right] = 1 - \frac{1}{\gamma} \frac{1}{\rho^{\gamma-1}} \left[\frac{e^{\frac{\gamma-1}{\rho^{\gamma-1}}} - 1}{e - 1} \right]$$

$$\text{if } e = 5, \gamma = 1.4, T_1 = 300K, T_2 = 990K, \eta = 59\% \quad \underline{\underline{=}}$$

Efficiency of Diesel engine < Efficiency of Otto engine

Q1 1. find the efficiency of a Carnot's engine working between the steam point and the ice point.

$$T_1 = 100^\circ C = 373K, T_2 = 0^\circ C = 273K$$

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{273}{373} = \frac{100}{373} \quad \therefore \% \text{ efficiency} = \frac{100}{373} \times 100 \\ = 26.81\%$$

2. find the efficiency of a Carnot's engine working between $127^\circ C$ and $27^\circ C$. It absorbs 80 cals of heat. How much heat is rejected?

$$T = 400\text{K}, T_2 = 300\text{K}, \eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{400} = 0.25$$

$$\therefore \eta = 25\%, W = \eta Q_1 = 0.25 \times 80 = 20 \text{ cals.}$$

$$\text{Heat rejected } Q_2 = Q_1 - W = 80 - 20 = 60 \text{ cals.}$$

HW 1. A Carnot engine has an efficiency of 30% when the sink temperature is 27°C . What must be the change in temperature of the source to make its efficiency 50%?

2. An inventor claims to have developed an engine working between 600K and 300K to deliver an efficiency of 52%. Is this claim valid? [Hint: use Carnot's theorem].

3. Two Carnot engines X & Y are operating in series. X receives heat at 1200K & rejects to a reservoir at temperature $T\text{K}$. The 2nd engine Y receives the heat rejected by X & in turn rejects to a heat reservoir at 300K . Calculate the temperature T for the situation when, reservoir at 300K . Calculate the temperature T for the situation when,

(i) The work outputs of two engines are equal.

(ii) The efficiency of two engines are equal.

4. A Carnot's refrigerator takes heat from water at 0°C and discards it to a room temperature at 27°C . 1kg of water at 0°C is to be changed into ice at 0°C . How many calories of heat are discarded to the room? What is the work done by the refrigerator in this process? What is the coefficient of performance ($P = \frac{Q_2}{Q_1 - Q_2}$) of the machine? [1 Cal = 4.2 Joule].

Third law of Thermodynamics : Nernst's Heat Theorem

In 1906, Nernst proposed a general principle on atomic heat of solids at low temperature. The third law of thermodynamics states that the heat capacities of all solids tend to zero as the absolute zero of temperature is approached & the internal energies and entropies of all substances become equal there, approaching their common value

Asymptotically tending to zero. In terms of entropy, at absolute zero temperature, the entropy tends to zero & the molecules of a substance are in perfect order.

We cannot have less than zero K temperature because if $T_2 < 0\text{K}$ then efficiency $\eta = 1 - \frac{T_2}{T_1} = 1 + \frac{T_2}{T_1} > 1$. So we cannot make more than 100% efficient engine.

Maxwell's Thermodynamical Relationship

from the 1st law of thermodynamics, Maxwell derived 6 fundamental thermodynamic relations using P, V, T, S with any two pair as dependent & other as independent variable.

from 1st law, $dQ = dU + PdV$ & from 2nd law, $dS = Tds$

$$\therefore dU = dQ - PdV = Tds - PdV \quad \text{--- (1)}$$

Here dU, dS, dV are all exact differentials. Considering U, S, V as function of two independent variables x & y where $\{x, y\}$ = combination of P, V, T, S any two. Then,

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy, \quad dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy$$

$$dV = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy$$

$$\text{Substituting in (1), } \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T \left[\left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy \right] - P \left[\left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy \right]$$

$$= \left[T \left(\frac{\partial S}{\partial x}\right)_y - P \left(\frac{\partial V}{\partial x}\right)_y \right] dx + \left[T \left(\frac{\partial S}{\partial y}\right)_x - P \left(\frac{\partial V}{\partial y}\right)_x \right] dy$$

Comparing the coefficients of dx & dy , we get

$$\left(\frac{\partial U}{\partial x}\right)_y = T \left(\frac{\partial S}{\partial x}\right)_y - P \left(\frac{\partial V}{\partial x}\right)_y, \quad \left(\frac{\partial U}{\partial y}\right)_x = T \left(\frac{\partial S}{\partial y}\right)_x - P \left(\frac{\partial V}{\partial y}\right)_x$$

Since dU is a perfect differential, $\frac{\partial^2 U}{\partial x \partial y} = \frac{\partial^2 U}{\partial y \partial x}$, so

$$\left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x + T \cancel{\frac{\partial^2 S}{\partial x \partial y}} - P \cancel{\frac{\partial^2 V}{\partial x \partial y}} =$$

$$\left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y + T \cancel{\frac{\partial^2 S}{\partial x \partial y}} - P \cancel{\frac{\partial^2 V}{\partial x \partial y}}$$

$$\therefore \left(\frac{\partial T}{\partial x}\right)_y \left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial T}{\partial y}\right)_x \left(\frac{\partial S}{\partial x}\right)_y = \left(\frac{\partial P}{\partial x}\right)_y \left(\frac{\partial V}{\partial y}\right)_x - \left(\frac{\partial P}{\partial y}\right)_x \left(\frac{\partial V}{\partial x}\right)_y$$

This is the general expression for Maxwell's T.D. relation, which can be written in determinant form

$$\begin{vmatrix} \left(\frac{\partial T}{\partial x}\right)_y & \left(\frac{\partial T}{\partial y}\right)_x \\ \left(\frac{\partial S}{\partial x}\right)_y & \left(\frac{\partial S}{\partial y}\right)_x \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial P}{\partial x}\right)_y & \left(\frac{\partial P}{\partial y}\right)_x \\ \left(\frac{\partial V}{\partial x}\right)_y & \left(\frac{\partial V}{\partial y}\right)_x \end{vmatrix}$$

$$\text{or, } \boxed{\frac{\partial(T, S)}{\partial(x, y)} = \frac{\partial(P, V)}{\partial(x, y)}}$$

There are $4C_2 = 6$ combinations (S, V) , (T, V) , (S, P) , (T, P) , (P, V) , (T, S) .

1st Relation: Let $x = T$, $y = V$, then we have

$$\begin{vmatrix} 1 & 0 \\ \left(\frac{\partial S}{\partial T}\right)_V & \left(\frac{\partial S}{\partial V}\right)_T \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial P}{\partial T}\right)_V & \left(\frac{\partial P}{\partial V}\right)_T \\ 0 & 1 \end{vmatrix} \quad \text{or} \quad \boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}$$

So the first relation says, increase of entropy per unit increase of volume at constant temperature is equal to the increase of pressure per unit increase of temperature when the volume is kept constant.

2nd Relation: Let $x = T$, $y = P$, then we have

$$\begin{vmatrix} 1 & 0 \\ \left(\frac{\partial S}{\partial T}\right)_P & \left(\frac{\partial S}{\partial P}\right)_T \end{vmatrix} = \begin{vmatrix} 0 & 1 \\ \left(\frac{\partial V}{\partial T}\right)_P & \left(\frac{\partial V}{\partial P}\right)_T \end{vmatrix} \quad \text{or} \quad \boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P}$$

This means decrease of entropy per unit increase of pressure during an isothermal transformation is equal to the increase in volume per unit increase in temperature when the pressure remains constant.

3rd Relation: Let $x=S$, $y=V$, $\begin{vmatrix} \left(\frac{\partial T}{\partial S}\right)_V & \left(\frac{\partial T}{\partial V}\right)_S \\ 1 & 0 \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial P}{\partial S}\right)_V & \left(\frac{\partial P}{\partial V}\right)_S \\ 0 & 1 \end{vmatrix}$

$$\therefore \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

4th Relation: Let $x=S$, $y=P$, $\begin{vmatrix} \left(\frac{\partial T}{\partial S}\right)_P & \left(\frac{\partial T}{\partial P}\right)_S \\ 1 & 0 \end{vmatrix} = \begin{vmatrix} 0 & 1 \\ \left(\frac{\partial V}{\partial S}\right)_P & \left(\frac{\partial V}{\partial P}\right)_S \end{vmatrix}$

$$\therefore \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

5th Relation: Let $x=P$, $y=V$, $\begin{vmatrix} \left(\frac{\partial T}{\partial P}\right)_V & \left(\frac{\partial T}{\partial V}\right)_P \\ \left(\frac{\partial S}{\partial P}\right)_V & \left(\frac{\partial S}{\partial V}\right)_P \end{vmatrix} = \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix}$

$$\therefore \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial S}{\partial V}\right)_P - \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial S}{\partial P}\right)_V = 1$$

6th Relation Let $x=T$, $y=S$, $\begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial P}{\partial T}\right)_S & \left(\frac{\partial P}{\partial S}\right)_T \\ \left(\frac{\partial V}{\partial T}\right)_S & \left(\frac{\partial V}{\partial S}\right)_T \end{vmatrix}$

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

Applications of Maxwell's Thermodynamic Relations

from the relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ after multiplying by T we

obtain $T \left(\frac{\partial S}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V \quad \text{&} \quad \left(\frac{\partial Q}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V$

$\left(\frac{\partial Q}{\partial V}\right)_T$ represents heat absorbed or liberated per unit change in volume at constant temperature. This heat represents latent heat when substance changes from solid to liquid (melting) or liquid to vapour (boiling) state at constant temperature. If L is the heat required to change unit mass of substance, V_2 & V_1 be specific volume (volume per unit mass) then $\left(\frac{\partial Q}{\partial V}\right)_T = \frac{L}{V_2 - V_1}$

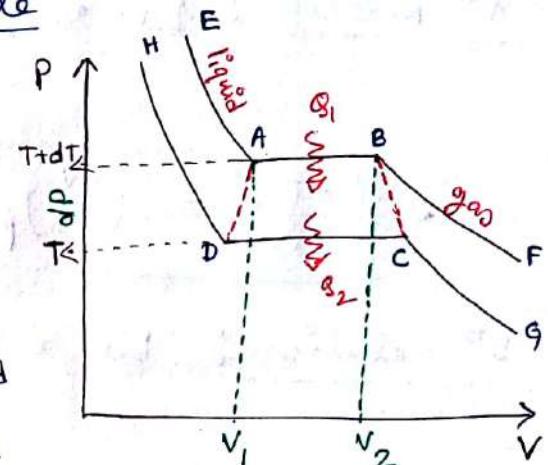
$$\therefore \frac{L}{V_2 - V_1} = T \left(\frac{\partial P}{\partial T} \right)_V$$

$$\therefore \frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

Clausius-Clapeyron's latent heat equation.

Latent heat equation using Carnot's cycle

Consider two isothermals FBAE and GCDH with a cycle ABCD where Carnot's theorem can be applied. At point A, volume is V_1 & temperature $T+dT$ & pressure is just below its saturation pressure & liquid begins to evaporate till point B at volume V_2 where it's in the vapour state. If mass of liquid at B is 1 gm, the amount of heat absorbed is $Q_1 = L + dL$ is latent heat at $T+dT$.



At B, pressure decreases by dP & vapour expands & temperature falls to point C at temperature T. Here the gas starts to condense & changes to liquid state at point D. The amount of heat rejected for $C \rightarrow D$ is $L = Q_2$. Increasing the pressure, reversibly A point is restored.

$$\text{from Carnot's theorem, } \frac{Q_1}{T_1} = \frac{Q_2}{T_2} \Rightarrow \frac{Q_1 - Q_2}{Q_2} = \frac{T_1 - T_2}{T_2}$$

$$\text{Here } Q_1 - Q_2 = dL, \quad T_1 - T_2 = dT, \quad Q_2 = L, \quad T_2 = T.$$

$$\therefore \frac{dL}{L} = \frac{dT}{T}. \quad \text{Now } dL = Q_1 - Q_2 = dP(V_2 - V_1) = \text{area of } ABCD$$

$$\therefore \frac{dP(V_2 - V_1)}{L} = \frac{dT}{T} \quad \Rightarrow \quad \boxed{\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}}$$

Using this, let's calculate the change in freezing point of a substance by pressure. Consider the melting of ice to water at 0°C , where $T = 273.16\text{K}$ & $L = 99.6 \times 4.2 \times 10^9 \text{ Ergs}$, V_2 = volume of unit mass of water = 1.0001 cc & V_1 = volume of unit mass of ice = 1.0908 cc

$$\therefore \left(\frac{dp}{dT} \right)_{\text{Saturation}} = \frac{99.6 \times 4.2 \times 10^7}{273.16 \times (1.0001 - 1.0908)} . \text{ If } dp = 1 \text{ atm} \\ = 1.01 \times 10^6 \text{ dynes/cm}^2$$

then we obtain $dT = -0.0075^\circ\text{C}$. \therefore To reduce 1°C temperature of the melting point of ice, one has to apply $\Delta P = \frac{1}{0.0075} \approx 133 \text{ atm}$ of pressure.

Consider the other extreme i.e. boiling point of water at 100°C where $L = 537.6 \times 1.2 \times 10^7 \text{ ergs}$, $V_1 = 1.0001 \text{ cc}$ & $V_2 = 1674 \text{ cc}$.

In this case, $\frac{dp}{dT} > 0$ meaning there will be an increase in boiling point if the pressure on the water is increased.

\therefore Ice will melt at lower than 0°C at a higher pressure than 76 cm of Hg. Also water will boil at a lower temperature under reduced pressure or boiling point increases with increase in pressure.

Adiabatic Stretching of wire using Maxwell's relations

from 1st & 2nd law, using $d\vartheta = dU + PdV$, we have

$$TdS = dU + PdV . \text{ In case of stretching a wire, } dW = +\vec{F} \cdot d\vec{l}$$

$$\therefore dU = TdS + Fdl$$

$$\boxed{P \leftrightarrow -F \quad V \leftrightarrow l} \quad \text{replacement.}$$

$$\text{we get from } \left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V , \quad \left(\frac{\partial T}{\partial l} \right)_S = \left(\frac{\partial F}{\partial S} \right)_V = T \left(\frac{\partial F}{\partial T} \right)_V \\ = T \left(\frac{\partial F}{\partial \vartheta} \right)_V$$

$$\therefore \left(\frac{\partial T}{\partial l} \right)_S = T \left(\frac{\partial F}{\partial T} \right)_F \left(\frac{\partial T}{\partial \vartheta} \right)_F . \quad \text{--- (1)}$$

$$\text{Now } l = l(F, T) \quad \therefore dl = \left(\frac{\partial l}{\partial F} \right)_T dF + \left(\frac{\partial l}{\partial T} \right)_F dT$$

$$\text{Under no elongation } dl = 0, \quad 0 = \left(\frac{\partial l}{\partial F} \right)_T dF + \left(\frac{\partial l}{\partial T} \right)_F dT$$

$$\therefore \left(\frac{\partial F}{\partial T} \right)_F = - \frac{\left(\frac{\partial l}{\partial T} \right)_F}{\left(\frac{\partial l}{\partial F} \right)_T}$$

$$\text{Substituting this in equation (1), we get } \left(\frac{\partial T}{\partial l} \right)_S = -T \left(\frac{\partial l}{\partial F} \right)_T \left(\frac{\partial T}{\partial \vartheta} \right)_F$$

Coefficient of linear expansion $\beta = \frac{1}{l} \left(\frac{\partial l}{\partial T} \right)_F$

Isothermal Young's modulus $Y_T = \frac{l}{A} \left(\frac{\partial F}{\partial l} \right)_T$

Specific heat at constant length $c_e = \left(\frac{\partial S}{\partial T} \right)_e$

$$\therefore \left(\frac{\partial T}{\partial l} \right)_S = - T \frac{\beta l}{\left(\frac{l}{Y_T A} \right)} \frac{1}{c_e} = - \frac{T \beta Y_T A}{mc}, \quad m = \text{mass/unit length}$$

$c = \text{sp. heat of wire}$

Using $Y_s = \frac{l}{A} \left(\frac{\partial F}{\partial l} \right)_S$, we have $\left(\frac{\partial T}{\partial F} \right)_S = \left(\frac{\partial T}{\partial l} \right)_S \left(\frac{\partial l}{\partial F} \right)_S$

$$= - \frac{T \beta Y_T A}{mc} \frac{1}{Y_s A} \approx - \frac{T \beta}{mc}$$

$$\therefore dT = - \frac{T \beta}{mc} dF \quad (Y_T \approx Y_s)$$

for solids

If $\beta > 0$, then increase in tension should cool the wire. for an adiabatic stretching.

Adiabatic stretching of a liquid film using Maxwell's relations

$$dQ = dU + dW \quad (1^{\text{st}} \text{ law}) \quad \text{yields} \quad dU = dQ - dW$$
$$= dQ + 2\gamma dA$$

where $-2\gamma dA$ is the work done by the surface film with surface tension γ . Comparing with PdV , $P \leftrightarrow -2\gamma$
 $V \leftrightarrow A$

From $\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad \therefore T \left(\frac{\partial S}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V$

$$\therefore \left(\frac{\partial S}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V \quad \text{Substituting, } \left(\frac{\partial S}{\partial A} \right)_T = -2T \left(\frac{\partial \gamma}{\partial T} \right)_A$$

\therefore for a finite change of area dA we have

$$dQ = -2T \left(\frac{\partial \gamma}{\partial T} \right)_A dA. \quad \text{for a liquid, surface tension decreases}$$

with temperature so $\left(\frac{\partial \gamma}{\partial T} \right)_A < 0$, or $dQ > 0$. \therefore To keep temperature constant of the film, dQ amount of heat is to be supplied when stretch

In adiabatic stretching, the fall in temperature is

$$\Delta T = \frac{c}{C} \left(\frac{\partial S}{\partial T} \right)_A dA \quad \text{where } C \text{ is the heat capacity for the liquid film}$$

Clausius latent heat equation

for a change of state from liquid to vapour, $S_v - S_l = \frac{L}{T}$. Differentiating with respect to T , we have

$$\frac{dS_v}{dT} - \frac{dS_l}{dT} = -\frac{L}{T^2} + \frac{L}{T} \frac{dL}{dT}$$

$$\therefore T \left(\frac{dS_v}{dT} \right) - T \left(\frac{dS_l}{dT} \right) = -\frac{L}{T} + \frac{dL}{dT}$$

$$\therefore C_v - C_l = \frac{dL}{dT} - \frac{L}{T} \quad *(\text{see page 10})$$

More applications of Maxwell's relations

Using $\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P$, we have $T \left(\frac{\partial S}{\partial P} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_P$

$\therefore \left(\frac{\partial S}{\partial P} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_P$. But the coefficient of volume expansion $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad \therefore \left(\frac{\partial V}{\partial T} \right)_P = V\alpha$.

$\therefore \left(\frac{\partial S}{\partial P} \right)_T = -TV\alpha$. If $\alpha > 0$ or if the substance expands on heating then $\left(\frac{\partial S}{\partial P} \right)_T < 0$, meaning heat must be withdrawn from the substance to keep temperature constant when the pressure is increased. On other hand if $\alpha < 0$, the substance contracts on heating, $\left(\frac{\partial S}{\partial P} \right)_T > 0$ meaning heat must be added to keep its temperature constant, when the pressure is increased.

|| Increase in pressure heats a body that expands on rise of temperature. Cooling is produced when a substance, which contracts on heating, is suddenly compressed.

Energy Equations of Pure Substances

from first law of T.D. $dU = TdS - PdV$ — ①

• $(\frac{\partial U}{\partial V})_T = T(\frac{\partial S}{\partial V})_T - P$. Using Maxwell's relation

$$(\frac{\partial S}{\partial V})_T = (\frac{\partial P}{\partial T})_V,$$

$$(\frac{\partial U}{\partial V})_T = T(\frac{\partial P}{\partial T})_V - P$$

1st Energy equation

for Ideal Gas

$$PV = uRT \quad \therefore (\frac{\partial P}{\partial T})_V = \frac{uR}{V}$$

∴ from energy equation, $(\frac{\partial U}{\partial V})_T = T \frac{uR}{V} - P = 0$. So U is a function T only and does not depend on V .

for Van der Waals Gas

$$(P + \frac{a}{v^2})(v-b) = RT$$

$$\therefore P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\therefore (\frac{\partial P}{\partial T})_V = \frac{R}{v-b} \quad \therefore \text{Using 1st Energy equation}$$

$$(\frac{\partial U}{\partial V})_T = \frac{RT}{v-b} - P = \frac{RT}{v-b} - \frac{RT}{v-b} + \frac{a}{v^2} = \frac{a}{v^2}$$

$$\therefore du = C_V dT + \frac{a}{v^2} dv \quad \therefore u = \int C_V dT - \frac{a}{v} + \text{const.}$$

So the internal energy increases with increasing volume at constant temperature.

Again, using ①, $(\frac{\partial U}{\partial P})_T = T(\frac{\partial S}{\partial P})_T - P(\frac{\partial V}{\partial P})_T$

using Maxwell's relation, $(\frac{\partial S}{\partial P})_T = -(\frac{\partial V}{\partial T})_P$ we obtain

$$(\frac{\partial U}{\partial P})_T = -T(\frac{\partial V}{\partial T})_P - P(\frac{\partial V}{\partial P})_T$$

2nd Energy equation

Using equation of state $f(p, v, T) = 0$, $df = 0$

$$\Rightarrow \left(\frac{\partial f}{\partial p}\right) dp + \left(\frac{\partial f}{\partial v}\right) dv + \left(\frac{\partial f}{\partial T}\right) dT = 0.$$

For isobaric process, $\left(\frac{\partial f}{\partial v}\right) dv = -\left(\frac{\partial f}{\partial T}\right) dT$ $\Rightarrow \left(\frac{\partial v}{\partial T}\right)_p = -\frac{\left(\frac{\partial f}{\partial T}\right)}{\left(\frac{\partial f}{\partial v}\right)}$

For isochoric process, $\left(\frac{\partial f}{\partial p}\right) dp = -\left(\frac{\partial f}{\partial T}\right) dT$ $\Rightarrow \left(\frac{\partial p}{\partial T}\right)_v = -\frac{\left(\frac{\partial f}{\partial T}\right)}{\left(\frac{\partial f}{\partial p}\right)}$

For isothermal process, $\left(\frac{\partial f}{\partial p}\right) dp = -\left(\frac{\partial f}{\partial v}\right) dv$, $\Rightarrow \left(\frac{\partial p}{\partial v}\right)_T = -\frac{\left(\frac{\partial f}{\partial v}\right)}{\left(\frac{\partial f}{\partial p}\right)}$

$$\therefore \left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p \left(\frac{\partial T}{\partial p}\right)_v = -1.$$

Using this, we can recompute 1st Energy equation as

$$\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial p}{\partial v}\right)_T \left(\frac{\partial v}{\partial T}\right)_p = \left[-v \left(\frac{\partial p}{\partial v}\right)_T\right] \left[\frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p\right] = \frac{\beta}{K}$$

where K_p = isothermal compressibility & β = volume expansivity.

$$\therefore \boxed{\left(\frac{\partial U}{\partial V}\right)_T = \frac{T\beta}{K} - p}$$

$\left(\frac{\partial U}{\partial V}\right)_T$ is known as "internal pressure" that arises due to the intermolecular attraction. Fact that gases condense to form liquid & solids shows that there exist intermolecular attraction that pulls the gas atoms together even without any external pressure. When the temperature is increased, the pressure diminishes till it becomes zero at the perfect gas stage.

T-dS Equations Entropy of a pure substance is

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

$$\therefore TdS = T \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$= \left(\frac{\partial S}{\partial T}\right)_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\therefore \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\therefore \boxed{TdS = C_V dT + T \left(\frac{\partial P}{\partial T}\right)_V dV}$$

1st T-dS Equation

Similarly, $S = S(T, P)$, $dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP$$

$$= \left(\frac{\partial Q}{\partial T}\right)_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

$$\text{or } TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

$$\therefore \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

2nd T-dS Equation

Equating the first & second T-dS equation, we obtain

$$C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\text{or } (C_P - C_V) dT = T\left(\frac{\partial V}{\partial T}\right)_P dP + T\left(\frac{\partial P}{\partial T}\right)_V dV$$

$$\text{or } dT = \frac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_P - C_V} dP + \frac{T\left(\frac{\partial P}{\partial T}\right)_V}{C_P - C_V} dV$$

$$\text{Also, } T = T(P, V) \text{ or } dT = \left(\frac{\partial T}{\partial P}\right)_V dP + \left(\frac{\partial T}{\partial V}\right)_P dV$$

$$\therefore \text{Equating the coefficients, we get, } \left(\frac{\partial T}{\partial P}\right)_V = \frac{T\left(\frac{\partial V}{\partial T}\right)_P}{C_P - C_V}$$

$$\text{or } C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V$$

Using $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1$, we have $C_P - C_V = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T$

$$= TV \left[\frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P \right]^2 \left[-V \left(\frac{\partial P}{\partial V}\right)_T \right] = \frac{TV\beta^2}{K_T}$$

$$\text{or } C_P - C_V = -T \left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T = \frac{TV\beta^2}{K_T}$$

This is one of the important equations of Thermodynamics which shows that **(a)** As $\left(\frac{\partial P}{\partial V}\right)_T < 0$ always for most substances, therefore $C_P - C_V > 0$ or $C_P > C_V$. **(b)** As $T \rightarrow 0$, $C_P \rightarrow C_V$ or at absolute zero the two heat capacities are equal. **(c)** When $\left(\frac{\partial V}{\partial T}\right)_P = 0$, we obtain $C_P = C_V$. Water at 4°C have maximum density & minimum volume so that heat capacities become equal.

If $K_s = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S$ and $K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_T$ then using 1st & 2nd T-ds equation at constant S, we have

$$TdS = 0 = Cp dT_S - T \left(\frac{\partial V}{\partial T} \right)_P dP_S \quad \therefore Cp dT_S = T \left(\frac{\partial V}{\partial T} \right)_P dP_S$$

$$TdS = 0 = C_V dT_S + T \left(\frac{\partial P}{\partial T} \right)_V dV_S \quad \therefore C_V dT_S = -T \left(\frac{\partial P}{\partial T} \right)_V dV_S$$

$$\therefore \frac{C_P}{C_V} = \gamma = - \frac{\left(\frac{\partial V}{\partial T} \right)_P}{\left(\frac{\partial P}{\partial T} \right)_V} \frac{\left(\frac{\partial P}{\partial V} \right)_S}{\left(\frac{\partial V}{\partial P} \right)_T} = + \frac{\left(\frac{\partial P}{\partial V} \right)_S}{\left(\frac{\partial P}{\partial V} \right)_T} = \frac{-\frac{1}{V} \left(\frac{\partial P}{\partial V} \right)_S}{-\frac{1}{V} \left(\frac{\partial P}{\partial V} \right)_T} = \frac{K_S}{K_T}$$

$$(\text{using } \left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_V = -1)$$

$$\boxed{\gamma = \frac{C_P}{C_V} = \frac{K_S}{K_T}} = \frac{\text{adiabatic compressibility}}{\text{isothermal compressibility}}$$

HW ① Consider a metal (say Copper) at 300K with the following values, $V = 7.06 \text{ cm}^3/\text{mol}$, $K_T = 7.78 \times 10^{-12} \text{ N/m}^2$, $\beta = 50.4 \times 10^{-6} \text{ K}^{-1}$, $C_P = 24.5 \text{ J/mol K}$. Determine C_V .

② Prove that ratio of adiabatic ($\alpha_s = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_S$) to isobaric ($\alpha_p = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$) coefficient of expansion is $\frac{1}{1-\gamma}$. Also prove that

adiabatic ($E_s = -V \left(\frac{\partial P}{\partial V} \right)_S$) to isothermal ($E_T = -V \left(\frac{\partial P}{\partial V} \right)_T$) elasticities is equal to ratio of specific heats.

③ Prove that adiabatic ($\beta_s = \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_S$) to isochoric ($\beta_v = \frac{1}{P} \left(\frac{\partial P}{\partial T} \right)_V$) pressure coefficient of expansion is $\frac{\gamma}{\gamma-1}$.

Variation of C_V with V and C_P with P

From 1st T-ds equation, $dS = \frac{C_V dT}{T} + \left(\frac{\partial P}{\partial T} \right)_V dV$

As dS is a perfect differential, $\frac{\partial}{\partial V} \left(\frac{C_V}{T} \right) = \frac{\partial}{\partial T} \left(\frac{\partial P}{\partial T} \right)_V$

$\therefore \frac{\partial C_V}{\partial V} = T \left(\frac{\partial^2 P}{\partial T^2} \right)_V$. If $\left(\frac{\partial P}{\partial T} \right)_V = 0$ then C_V is independent of volume (initial).

Similarly from the 2nd Tds equation $ds = \frac{C_p dT}{T} - \left(\frac{\partial V}{\partial T}\right)_p dP$
 & ds being exact differential, $\frac{\partial}{\partial P} \left(\frac{C_p}{T} \right) = - \frac{\partial}{\partial T} \left(\frac{\partial V}{\partial T} \right)_p$
 $\therefore \frac{\partial C_p}{\partial P} = - T \left(\frac{\partial^2 V}{\partial T^2} \right)_p$

Negative specific heat of steam *

Clausius latent heat equation between two arbitrary states 1 & 2 :
 $c_2 - c_1 = \frac{dL}{dT} - \frac{L}{T}$ where c is the specific heat of substance
 in states 1 and 2 which is neither at constant volume nor at constant
 pressure. The vapour always remain in equilibrium with the evaporating
 liquid, so vapour is in saturated state called "specific heat of saturated
vapour." From $s = s(T, P)$, $ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP$

$$\therefore \left(\frac{\partial s}{\partial T}\right)_{\text{saturation}} = \left(\frac{\partial s}{\partial T}\right)_P + \left(\frac{\partial s}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_{\text{saturation}}$$

Using Clausius- Clapeyron latent heat equation, $\left(\frac{\partial P}{\partial T}\right)_{\text{saturation}} = \frac{L}{T(V_2 - V_1)}$
 and Maxwell's relation $\left(\frac{\partial s}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P$, we obtain

$$\left(\frac{\partial s}{\partial T}\right)_{\text{saturation}} = \left(\frac{\partial s}{\partial T}\right)_P - \left(\frac{\partial V}{\partial T}\right)_P \frac{L}{T(V_2 - V_1)}$$

$$\therefore c_s = C_p - \left(\frac{\partial V}{\partial T}\right)_P \frac{L}{T(V_2 - V_1)}$$

for evaporation of water at 100°C, $V_1 = 1 \text{ cc}$, $V_2 = 1674 \text{ cc}$, $L = 537.5 \text{ cal}$
 $C_p = 0.47$, $\left(\frac{\partial V}{\partial T}\right)_P = 4.813$ gives $c_s = -1.07 \text{ cal/K}$. Thus the specific
 heat of saturated water vapour at 100°C is negative. Though its a
 paradoxical result but it holds true because specific heat may vary
 from $+\infty$ to $-\infty$ depending on external condition, which is saturation here.
 Saturated water vapour exerts pressure of 760 mm of Hg at 100°C
 787.6 mm of Hg at 101°C. i.e. the specific volume of saturated water
 vapour at 100°C decreases with increasing temperature. When heated,

to 101°C at constant pressure, vapour becomes unsaturated & to satisfy the condition of saturation it is to be compressed till the pressure becomes 787.6 mm. The compression generated heat is large that has to be extracted out to keep the temperature fixed at 101°C . Thus the specific heat of saturated vapour sometimes become negative.

Properties of van der Waals gas

$$\text{VN equation of state } (P + \frac{a}{v^2})(v - b) = RT.$$

Using T-ds equation & exact differentiability of S we know

$$(\frac{\partial C_V}{\partial V})_T = T (\frac{\partial^2 P}{\partial T^2})_V$$

$$\text{Now } P = \frac{RT}{v-b} - \frac{a}{v^2}$$

$$\therefore (\frac{\partial P}{\partial T})_V = \frac{R}{v-b}, \quad (\frac{\partial^2 P}{\partial T^2})_V = 0$$

$$\therefore (\frac{\partial C_V}{\partial V})_T = 0$$

$\therefore C_V$ is independent of volume for VN gas & function of temperature only.

To calculate the variation of entropy of VN gas use T-ds equation

$$dS = \frac{C_V dT}{T} + (\frac{\partial P}{\partial T})_V dv = \frac{C_V}{T} dT + \frac{R}{v-b} dv$$

$$\therefore S = C_V \ln T + R \ln (v-b) + S_0 = \text{constant for adiabatic process}$$

$$\therefore \ln T^{C_V} + \ln (v-b)^R = \text{constant}$$

$$\therefore \ln T^{C_V} (v-b)^{C_P-C_V} = \text{const.} \quad \text{or} \quad T(v-b)^{\frac{C_P-C_V}{C_V}} = \text{constant}$$

$$\boxed{\therefore T(v-b)^{\frac{d-1}{d+1}} = \text{constant}}$$

To calculate the change in internal energy, $U = U(V, T)$

$$dU = (\frac{\partial U}{\partial V})_T dv + (\frac{\partial U}{\partial T})_V dT = \left\{ T (\frac{\partial P}{\partial T})_V - P \right\} dv + C_V dT$$

$$= C_V dT + \left(\frac{RT}{v-b} - P \right) dv$$

$$= C_V dT + \frac{a}{v^2} dv$$

$$P + \alpha_{V^2} = \frac{RT}{v-b}$$

$$\text{or, } \frac{RT}{v-b} - P = \alpha_{V^2}$$

$$\text{or } \boxed{U = \int_{T_1}^{T_2} C_V dT + \int_{V_1}^{V_2} \frac{a}{v^2} dv = C_V (T_2 - T_1) + a \left(\frac{1}{V_1} - \frac{1}{V_2} \right)}$$

So internal energy of a VW gas depends on the VW pressure coefficient "a" and not on volume coefficient "b". This is because "a" is a measure of the force of attraction between the molecules (Potential energy) that changes as the specific volume of the gas changes & the intermolecular separation changes. "b" is proportional to volume occupied by molecules & it affects the entropy because entropy is volume dependent & occupation of molecules of container volume makes the available volume less than the volume of the container.

$$\text{Finally let's calculate } C_p - C_v = TV\beta/k_T = -T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial P}{\partial V} \right)_T$$

$$\text{Now } (P + \frac{a}{V^2})(V-b) = RT \Rightarrow \left(\frac{\partial V}{\partial T} \right)_P (P + \frac{a}{V^2}) + (V-b)(-\frac{2a}{V^3}) \left(\frac{\partial V}{\partial T} \right)_P = R$$

$$\therefore \left(\frac{\partial V}{\partial T} \right)_P \left[P + \frac{a}{V^2} - \frac{2a}{V^3}(V-b) \right] = R$$

$$\therefore \left(\frac{\partial V}{\partial T} \right)_P = \frac{R}{\frac{RT}{V-b} - \frac{2a}{V^3}(V-b)} = \frac{R}{\frac{RT}{V-b} \left[1 - \frac{2a}{RTV^3}(V-b)^2 \right]}$$

$$\text{Now from } P = \frac{RT}{V-b} - \frac{a}{V^2}, \quad \left(\frac{\partial P}{\partial V} \right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

$$= -\frac{RT}{(V-b)^2} \left[1 - \frac{2a(V-b)^2}{RTV^3} \right].$$

$$\therefore C_p - C_v = T \frac{\frac{R^2}{(V-b)^2} \left[1 - \frac{2a}{RTV^3}(V-b)^2 \right]^2 \frac{RT}{(V-b)^2} \left[1 - \frac{2a(V-b)^2}{RTV^3} \right]}{\left(\frac{RT}{V-b} \right)^2 \left[1 - \frac{2a}{RTV^3}(V-b)^2 \right]^2}$$

$$= \frac{R}{1 - \frac{2aV^2}{RTV^3} \left(1 - \frac{b}{V} \right)^2} \underset{[as \frac{b}{V} \ll 1]}{\approx} \frac{R}{1 - \frac{2a}{RTV}}$$

$$= R \left(1 - \frac{2a}{RTV} \right)^{-1} \underset{[as \frac{2a}{RTV} \ll 1]}{\approx} R \left(1 + \frac{2a}{RTV} \right)$$

$$\therefore C_p - C_v = R \left(1 + \frac{2a}{RTV} \right)$$

Finally work done by VW gas, $W = - \int P dV = - \int_{V_1}^{V_2} \frac{RT}{V-b} dV + \int_{V_1}^{V_2} \frac{a}{V^2} dV$

$$W = a \left(\frac{1}{V_1} - \frac{1}{V_2} \right) - RT \ln \left[\frac{V_2-b}{V_1-b} \right].$$

Liquefaction of Gases

Different methods of liquefaction of gases : (a) Method of freezing mixture, (b) Adiabatic expansion of gas, (c) Joule-Thomson expansion, (d) Throttling process & regenerative cooling, (e) Adiabatic demagnetisation of paramagnetic salt. Adding salt to ice is the well known example of method (a) thereby reducing temperature (eutectic temperature) significantly.

Enthalpy It has been found that a term $U + PV$ appeared several times in describing various properties of gas, that is termed as Enthalpy $H = U + PV$. To study its properties, consider change in enthalpy for an infinitesimal process from initial to final equilibrium state,

$$dH = dU + PdV + VdP. \quad \text{But from 1st law of thermodynamics,}$$

$$dQ = dU + dW = dU + PdV. \quad \therefore dH = dQ + VdP.$$

$$\text{At constant pressure, } \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial Q}{\partial T}\right)_P + V \left(\frac{\partial P}{\partial T}\right)_P = C_P$$

Since $dH = dQ + VdP$, the change in enthalpy during an isobaric process is equal to the heat transferred, so the latent heat measured during a phase transition at constant pressure (e.g. melting, boiling, sublimation) is the change in enthalpy.

$$\therefore H_f - H_i = Q = \int_i^f C_P dT.$$

Isobaric processes are more important than isochoric process in science & technology, so enthalpy plays important role.

from $dH = TdS + VdP$, $\left(\frac{\partial H}{\partial S}\right)_P = T$, $\left(\frac{\partial H}{\partial P}\right)_S = V$. So on a three dimensional diagram $H = H(S, P)$, slopes of the tangent to the surface at a point determines (T, V) .

Throttling process

Suppose a cylinder (thermally insulated) with two nonconducting pistons at two sides of a porous wall contains a gas. The wall (horizontal green lines) is a porous plug made of small holes on a narrow constriction. Initially the gas is at (P_i, V_i) with right hand piston against the wall to prevent seeping of gas, retaining equilibrium. If we now move both pistons simultaneously so that constant pressure P_i (left side of wall) and constant lower pressure P_f (right side of wall) then in final equilibrium state, all gas is sipped to the right side of wall. This is called a "throttling process".

Though it's a nonequilibrium process but initial & final equilibrium states can be described, by applying 1st law

$$\delta = U_f - U_i - W.$$

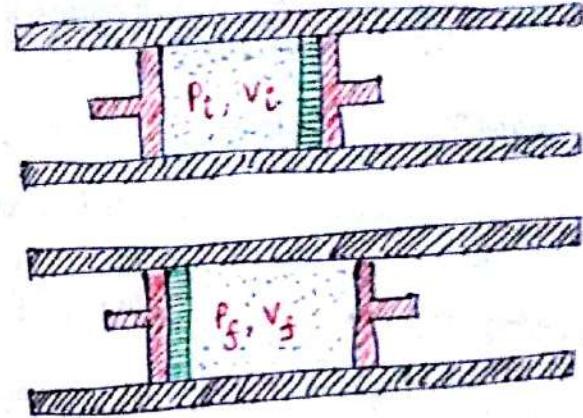
$$\text{No heat transfer happens, so } \delta = 0 \text{ and } W = - \int_0^{V_f} P_f dV - \int_{V_i}^0 P_i dV$$

$$(\text{as pressure remains constant}) = -P_f V_f + P_i V_i$$

$$\therefore 0 = U_f - U_i + P_f V_f - P_i V_i$$

$$\therefore U_i + P_i V_i = U_f + P_f V_f \quad \boxed{H_i = H_f}$$

So in a throttling process, final & initial enthalpies are equal although intermediate nonequilibrium states cannot have any information about enthalpy & thus cannot be plotted in an indicator diagram as continuous lines/surfaces but points.



Comparison of Internal Energy U & Enthalpy H

<u>Internal Energy (U)</u>	<u>Enthalpy (H)</u>
# $dU = \delta Q - PdV$, $\left(\frac{\partial U}{\partial T}\right)_V = C_V$	# $dH = \delta Q + VdP$, $\left(\frac{\partial H}{\partial T}\right)_P = C_P$
# Isochoric process $U_f - U_i = Q = \int_i^f C_V dT$	# Isobaric process, $H_f - H_i = Q = \int_i^f C_P dT$
# Adiabatic process $U_f - U_i = - \int_i^f PdV$	# Adiabatic process, $H_f - H_i = \int_i^f VdP$
# free expansion, $U_i = U_f$	# Throttling process, $H_i = H_f$
# for an ideal gas $U = \int C_V dT + \text{constant}$	# for an ideal gas, $H = \int C_P dT + \text{constant}$
# Nearby equilibrium states $dU = TdS - PdV$, $T = \left(\frac{\partial U}{\partial S}\right)_V$, $P = -\left(\frac{\partial U}{\partial V}\right)_S$	# Nearby equilibrium states $dH = TdS + VdP$, $T = \left(\frac{\partial H}{\partial S}\right)_P$, $V = \left(\frac{\partial H}{\partial P}\right)_S$

Joule - Thomson/Kelvin effect : Adiabatic Throttling of gases

Gay-Lussac & Joule's experiments independently showed that $\left(\frac{\partial U}{\partial V}\right)_T = 0$ for perfect gases but with real gases slight cooling was found, meaning $\left(\frac{\partial U}{\partial V}\right)_T \neq 0$. To find out the relation, Lord Kelvin modified the Gay-Lussac-Joule's experiments, known as "Porous plug experiment". A highly compressed gas is continuously forced at constant pressure through a constricted nozzle to throttle & thus to expand in volume. We already learned that $H_i = H_f$. Now we calculate the change in temperature.

$$\begin{aligned} \text{if } H = U + PV \Rightarrow dH &= dU + PdV + Vdp = \delta Q + Vdp = TdS + Vdp \\ \therefore 0 &= T \left[\left(\frac{\partial S}{\partial P}\right)_T dP + \left(\frac{\partial S}{\partial T}\right)_P dT \right] + Vdp \\ \therefore 0 &= -T \left(\frac{\partial V}{\partial T}\right)_P dP + \left(\frac{\partial S}{\partial T}\right)_P dT + Vdp \quad \left[\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \right] \end{aligned}$$

$$\text{or } C_p dT - \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] dp = 0$$

$$\text{or } \left(\frac{\partial T}{\partial P} \right)_H = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] = \mu, \text{ or } \Delta T = \int_{P_1}^{P_2} \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T} \right)_p - V \right] dp$$

$$\boxed{\mu = \frac{T^2}{C_p} \frac{\partial}{\partial T} \left(\frac{V}{T} \right)}$$

for perfect gas, $T \left(\frac{\partial V}{\partial T} \right)_p - V = T \frac{V}{T} - V = 0$

$$[PV = RT]$$

$$\left(\frac{\partial V}{\partial T} \right)_p = \frac{R}{P} = \frac{V}{T}$$

Hence the J-T effect vanishes for ideal gas.

$$\text{Again, } C_p dT = - \left[T \left(\frac{\partial S}{\partial P} \right)_T + V \right] dp$$

$$\text{or } C_p \left(\frac{\partial T}{\partial P} \right)_H = - \left(\frac{\partial U}{\partial P} \right)_T - \frac{\partial}{\partial P} (PV) \quad \text{as } T ds = dU + PdV$$

J-T effect

Deviation from Joule's law

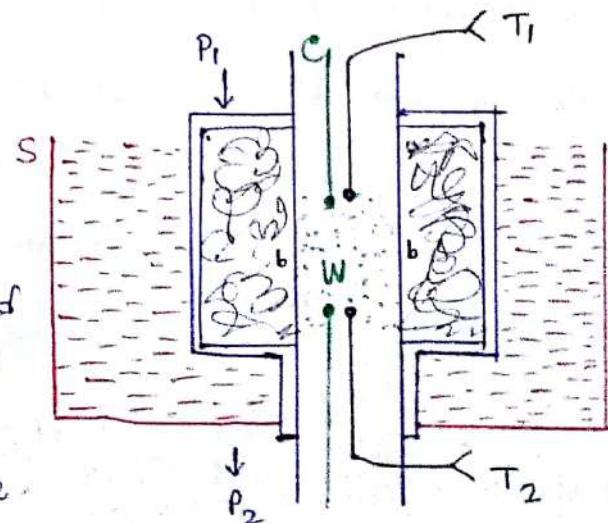
Deviation from Boyle's law

Now $\left(\frac{\partial U}{\partial P} \right)_T < 0$ because internal energy decreases with decreasing volume (or increase of pressure). \therefore Due to deviation from Joule's law, J.T. effect will be a cooling effect $\left(\frac{\partial T}{\partial P} \right)_H > 0$ mean fall of temperature per unit fall in pressure. The effect of deviations from Boyle's law can be a cooling ($\frac{\partial(PV)}{\partial P} < 0$) or heating ($\frac{\partial(PV)}{\partial V} > 0$) effect.

\uparrow
[H₂, He]

The porous plug Experiment

Joule & Thomson employed a cylindrical plug where the compressed gas flows through a copper tube immersed in a thermostat to the porous plug, which consists of silk, cotton wool or other porous materials W between two piece of wire gauge I enclosed in a cylinder of (nonconducting) wood



bb. The plug and part of the tube is surrounded by asbestos contained in a tin cylinder so that no heat reaches from the bath. The temperature drop is measured by the thermocouples. They worked with O_2 , N_2 , CO_2 within $4^\circ C$ & $100^\circ C$ with initial pressure 4.5 atm & final pressure 1 atm.

A small cooling effect on expansion is seen for gases while for H_2 , He (surprisingly) heating on expansion is seen. This paradox was resolved by applying van der Waal's equation of state.

We have $\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T}\right)_P - V \right]$. Using VdV equation of state

$$(P + \frac{a}{V^2})(V-b) = RT \Leftrightarrow P + \frac{a}{V^2} = \frac{RT}{V-b}$$

$$\therefore -\frac{2a}{V^3} \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{V-b} - \frac{RT}{(V-b)^2} \left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \left[-\frac{2a}{V^3} + \frac{RT}{(V-b)^2}\right] \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{V-b}.$$

$$\therefore \mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p} \left[\frac{RT}{V-b} \left\{ \frac{1}{-\frac{2a}{V^3} + \frac{RT}{(V-b)^2}} \right\} - V \right]$$

$$= \frac{1}{C_p} \left[\frac{\frac{RT}{V-b}}{\frac{RT}{(V-b)} \left\{ 1 - \frac{2a(V-b)^2}{RTV^3} \right\}} - V \right] = \frac{1}{C_p} \left[\frac{V-b - V \left\{ 1 - \frac{2a}{RTV^3}(V-b)^2 \right\}}{1 - \frac{2a}{RTV^3}(V-b)^2} \right]$$

$$= \frac{1}{C_p} \left[\frac{\frac{2a}{RT} \left(1 - \frac{b}{V}\right)^2 - b}{1 - \frac{2a}{RTV^3}(V-b)^2} \right] \approx \frac{1}{C_p} \left(\frac{2a}{RT} - b \right)$$

$\therefore \mu > 0$ if $\frac{2a}{RT} > b$ $\Rightarrow T < \frac{2a}{Rb}$ and this gives cooling effect.

At $T > \frac{2a}{Rb}$, the gas is heated on suffering J-T expansion. The temperature $T = \frac{2a}{Rb}$ is called the temperature of inversion. One can

show that $T_i = \frac{2a}{Rb} = \frac{27}{4} T_c$ with T_c = critical temperature of the gas and this relation is approximately true because vander Waal's equation isn't accurate for real gases.

For N_2 , O_2 , CO_2 etc, T_i is greater than the temperature at which J-T expansion was carried out, hence a cooling effect was obtained.

for H_2 , He, $T_i < 300K$, no heating effect was found. It was found later that if H_2 , He are sufficiently precooled then they exhibit cooling on J-T expansion.

If we don't neglect $\frac{b}{v}$ and $\frac{2a}{RTv}$ term in μ , then for very

high pressures,

$$\mu \approx \frac{1}{C_p} \left[\frac{2a}{RT} - b - \frac{6ab}{R^2 T^2} P \right]$$

and for van der Waals gas, $C_p = C_{p_0} + \frac{2a}{RT^2} - \frac{3ab}{R^2 T^3} P^2$

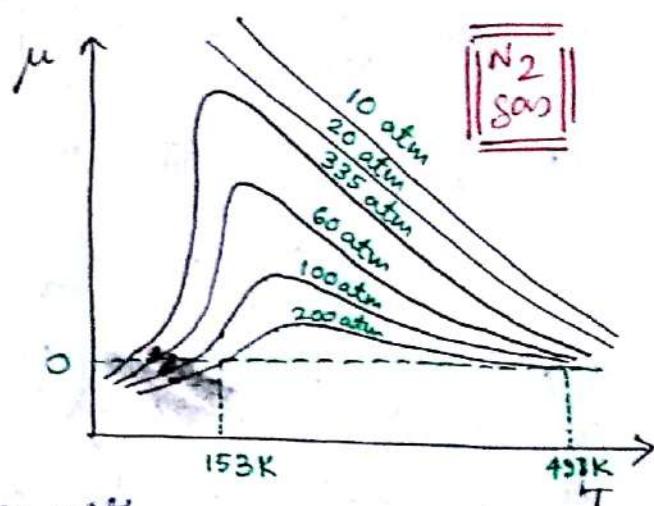
Combination of above gives

$\mu = \mu(P, T)$. The experimental results of J-T effect on N_2 is shown for different initial pressures.

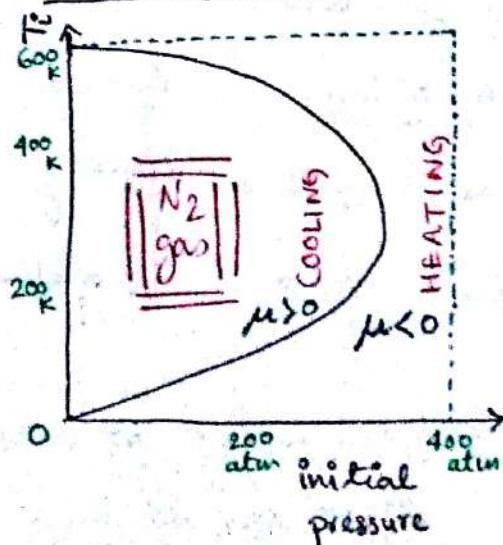
Observations

(a) For equal temperature, μ is greater at lower initial pressures in accordance with

$\mu = \frac{1}{C_p} \left(\frac{2a}{RT} - b - \frac{6ab}{R^2 T^2} P \right)$, (b) for a definite pressure, μ passes through a maximum & decreases to zero on both sides. \therefore There exist two inversion temperatures for J-T effect corresponding to an initial pressure. For example at 200 atm for N_2 $\mu=0$ happens at $-120^\circ C = 153K$ & other at $225^\circ C = 498K$.



Curve of inversion



Temperature of inversion depends on the initial pressure. Inversion curve gives inversion temperature at different initial pressure. Roebuck & Osterberg obtained the experimental graph shown beside.

To have a cooling effect, the J-T expansion should be carried out at points to the left of the inversion curve. This can be explained by considering the reduced equation of state of van der Waals gas.

In term of P^* , V^* , T^* , $\mu = \frac{1}{C_p} \left[T^* \left(\frac{\partial V^*}{\partial T^*} \right)_{P^*} - V^* \right]$ and

$$\frac{8}{3} T^* = \left(P^* + \frac{3}{V^{*2}} \right) \left(V^* - \frac{1}{3} \right), \text{ differentiating,}$$

$$\frac{8}{3} \left(\frac{\partial T^*}{\partial V^*} \right)_{P^*} = P^* + \frac{3}{V^{*2}} - \frac{6}{V^{*3}} \left(V^* - \frac{1}{3} \right)$$

$$\begin{aligned} \therefore \mu &= \frac{1}{C_p} \left[\frac{T^*}{\frac{3}{8} \left(P^* + \frac{3}{V^{*2}} - \frac{6}{V^{*3}} \right)} - V^* \right] = \frac{1}{C_p} \frac{\left[\frac{8}{3} T^* - V^* \left(P^* - \frac{3}{V^{*2}} + \frac{2}{V^{*3}} \right) \right]}{\left(P^* - \frac{3}{V^{*2}} + \frac{2}{V^{*3}} \right)} \\ &= \frac{\left(P^* + \frac{3}{V^{*2}} \right) \left(V^* - \frac{1}{3} \right) - V^* \left(P^* - \frac{3}{V^{*2}} + \frac{2}{V^{*3}} \right)}{C_p \left(P^* - \frac{3}{V^{*2}} + \frac{2}{V^{*3}} \right)} = \frac{\left(-\frac{P^*}{3} + \frac{6}{V^*} - \frac{3}{V^{*2}} \right)}{C_p \left(P^* - \frac{3}{V^{*2}} + \frac{2}{V^{*3}} \right)} \\ &= \frac{\left(-\frac{P^*}{3} + \frac{6}{V^*} - \frac{3}{V^{*2}} \right)}{\left[\frac{8}{3} C_p \left(\frac{\partial T^*}{\partial V^*} \right)_{P^*} \right]} . \text{ Here the denominator is always positive} \\ &\quad \text{because } \left(\frac{\partial T^*}{\partial V^*} \right)_{P^*} > 0. \end{aligned}$$

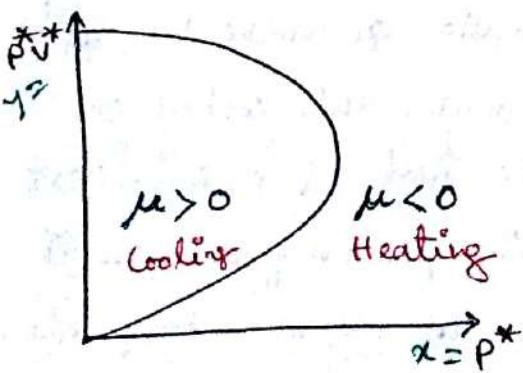
$$\therefore \begin{cases} \mu > 0 & \text{if } \frac{P^*}{3} < \frac{6}{V^*} - \frac{3}{V^{*2}} \Rightarrow P^* < \frac{9(2V^*-1)}{V^{*2}} & \xrightarrow{\text{Cooling}} \\ \mu < 0 & \text{if } P^* > \frac{9(2V^*-1)}{V^{*2}} & \xrightarrow{\text{Heating}} \end{cases}$$

Thus inversion occurs at $P^* = \frac{9(2V^*-1)}{V^{*2}}$ and in that state the gas cannot undergo a change in temperature.

Setting $P^* = x$, $P^* V^* = y$ we have $P^* V^{*2} = 9(2P^* V^* - P^*)$

$$\Rightarrow y^2 = 9(2y - x) \text{ representing}$$

a parabola. Here $\mu > 0$ means $9x < 18y - y^2$ which are points inside the curve with cooling effect & for points outside, $\mu < 0$ and heating effect takes place. The temperature of inversion is obtained by putting P^* in reduced VW state

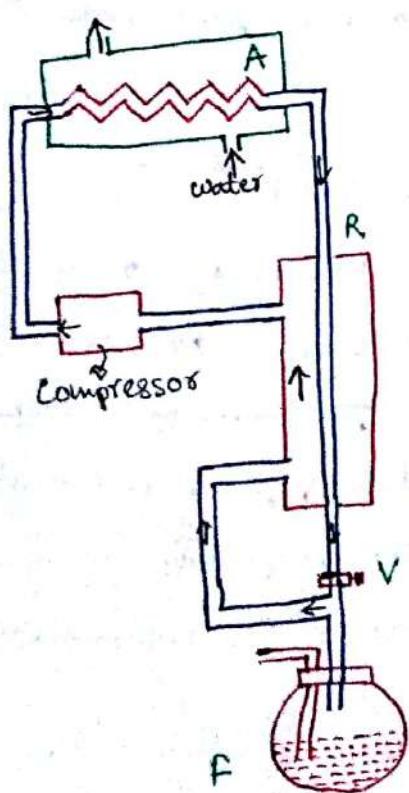


$$T_i = \frac{3}{4} \left(3 - \frac{1}{V^*} \right)^2$$

Principle of Regenerative cooling

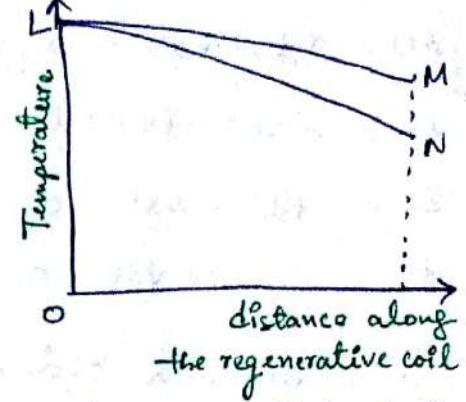
Joule-Thomson cooling that depends on the pressure difference on the sides of the porous plug is observed to be very small for most of the gases. For air at 20°C temperature with pressure on two sides at 50 atm & 1 atm, Joule-Thomson found that the temperature falls by 11.7°C only. Even using a pressure of 210 atm instead of 50 atm, the cooling was only 42°C . However the cooling effect can be intensified by employing regenerative cooling.

A portion of the gas which first suffers J-T expansion and becomes cooled is employed to cool other portions of the incoming gas before it later reaches the nozzle. The incoming gas becomes more cooled after traversing the nozzle. In this way the cooling effect can be cumulatively rendered. In this method the extra advantage is the lower the temperature, the greater is the J-T cooling.



The high pressure gas from compressor enters the spirals contained in the water cooled jacket A where the heat of compression is removed. The gas enters the regenerator R and suffers J-T expansion at valve V & gets cooled by small amount. This cooled gas returns by the outer tube & absorbs heat from the incoming high pressure gas before it reaches the compressor at the same temperature as the incoming gas at R. The gas is again compressed, cooled by A and reenters at R. In a time interval, the gas approaching V becomes cooled more & more till the J-T cooling at V is sufficiently to liquefy the gas. A portion of the escaping gas then condenses inside

the Dewar flask F. At this stage the temperature throughout the apparatus become steady. LM represents the continual decrease of temperature of the gas as we approach the nozzle V through the inner tube, while MN represents the J-T cooling. NL represents the temperature of the low-pressure gas which is less than that of the adjacent high pressure gas at each point of the coil. Thus, the low pressure gas extracts heat from the incoming gas.



Thermodynamic Potentials : Helmholtz & Gibbs free energy

There are 4 thermodynamic potentials

- ① Internal Energy : U
- ② Helmholtz free Energy : F
- ③ Enthalpy : H
- ④ Gibbs function : G

We know internal energy is the total energy of the system. Using 1st & 2nd law we know

$$dU = TdS - PdV. \quad \text{--- } ①$$

The function $F = U - TS$ is known as Helmholtz free energy function. While TS is the energy associated with disorder & unavailable so $U - TS$ energy can be extracted from the system to do work. Hence the term "free".

Any small change is $dF = dU - TdS - SdT$
and we know $dS = TdS = dU + PdV$. $\therefore dF = TdS - PdV - TdS - SdT$
or $dF = -PdV - SdT$ --- ②

Similarly total heat content is $H = U + PV$

$$\therefore dH = dU + PdV + VdP = TdS - PdV + PdV + VdP$$

$$\underline{dH = TdS + VdP} \quad \text{--- } ③$$

Similarly Gibbs function is $G = U - TS + PV = H - TS$

$$\therefore dG = dH - TdS - SdT = TdS + VdP - TdS - SdT$$

$$\underline{dG = VdP - SdT} \quad \text{--- } ④$$

$dU = TdS - pdV = 0$, isochoric adiabatic process, $U = \text{constant}$

$dF = -SdT - pdV = 0$, isochoric isothermal process, $F = \text{constant}$

$dH = TdS + Vdp = 0$, isobaric adiabatic process, $H = \text{constant}$

$dG = -SdT + Vdp = 0$, isobaric isothermal process, $G = \text{constant}$

A mechanical system is in stable equilibrium when potential energy is minimum. In thermodynamics, U, F, H, G plays the role of P.E. The direction of isothermal-isochoric process is to make F minimum. In isothermal-isobaric process G tends to be minimum & for isobaric-adiabatic process, H tends to be minimum.

Relation of T.D. potentials with their variables

$$\left(\frac{\partial U}{\partial S}\right)_V = T, \quad \left(\frac{\partial U}{\partial V}\right)_S = -P$$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S, \quad \left(\frac{\partial F}{\partial V}\right)_T = -P$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S, \quad \left(\frac{\partial G}{\partial P}\right)_T = V$$

$$\left(\frac{\partial H}{\partial S}\right)_P = T, \quad \left(\frac{\partial H}{\partial P}\right)_S = V$$

Since dU is a perfect differential

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S}\right)_V\right]_S = \left[\frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V}\right)_S\right]_V$$

$$\Rightarrow \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$$

Similarly df being a perfect differential

$$\left[\frac{\partial}{\partial V} \left(\frac{\partial F}{\partial T}\right)_V\right]_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial F}{\partial V}\right)_T\right]_V$$

$$\Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Similarly dH is a perfect differential,

$$\Rightarrow \left[\frac{\partial}{\partial P} \left(\frac{\partial H}{\partial S}\right)_P\right]_S = \left[\frac{\partial}{\partial S} \left(\frac{\partial H}{\partial P}\right)_S\right]_P \Rightarrow \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

So as dG a perfect differential, $\left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P}\right)_T\right]_P = \left[\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T}\right)_P\right]_T$

$$\Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

Four Maxwell's T.D. relation.

Relation amongst T.D. potentials, $U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V$

$$H = G + TS = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

Chemical potential and Gibbs-Duhem equation

Just like U and S , thermodynamic quantities F, H, G have the additivity property, if P & T remains constant. This means that when the amount of matter (N number of particles) is changed by a given factor, T.D. changes similarly or the T.D. quantity is a homogeneous function of first order with respect to the additive variable.

$$\therefore U = N U \left(\frac{S}{N}, \frac{V}{N} \right), \quad F = N F \left(\frac{V}{N}, T \right), \quad H = N H \left(\frac{S}{N}, P \right)$$

$G = N G (P, T)$. So we have essentially regarded N as a parameter then for a change dN , we can write

where the "chemical potential" is defined to be

$$dU = T dS - P dV + \mu dN$$

$$dF = -SdT - PdV + \mu dN$$

$$dH = T dS + V dP + \mu dN$$

$$dG = -SdT + VdP + \mu dN$$

$$\mu = \left(\frac{\partial U}{\partial N} \right)_{S,V} = \left(\frac{\partial F}{\partial N} \right)_{T,V} = \left(\frac{\partial H}{\partial N} \right)_{T,V} = \left(\frac{\partial G}{\partial N} \right)_{P,T}$$

and the general equation

$$U(S, \{x_i\}, \{N_j\}) = TS + \underbrace{\sum_i x_i x_i}_{\text{Generalized force}} + \underbrace{\sum_j \mu_j N_j}_{\text{Generalized displacement}}$$

is called "Gibbs-Duhem equation"

This is a very important equation in Chemical Thermodynamics.

for any single valued function $\phi(x_1, x_2, \dots, x_n)$ $\frac{\partial}{\partial x_i} \left(\frac{\partial \phi}{\partial x_j} \right) = \frac{\partial}{\partial x_j} \left(\frac{\partial \phi}{\partial x_i} \right)$

we recover Maxwell relations with additional Maxwell relations

$$\left(\frac{\partial S}{\partial N} \right)_{V,T} = - \left(\frac{\partial \mu}{\partial T} \right)_{V,N}, \quad \left(\frac{\partial P}{\partial N} \right)_{V,T} = - \left(\frac{\partial \mu}{\partial V} \right)_{T,N} \quad \text{from Helmholtz free energy}$$

$$\text{Similarly } \left(\frac{\partial V}{\partial N} \right)_{P,T} = \left(\frac{\partial \mu}{\partial P} \right)_{T,N}, \quad \left(\frac{\partial S}{\partial N} \right)_{P,T} = - \left(\frac{\partial \mu}{\partial T} \right)_{P,N} \quad \text{from Gibbs free energy}$$

Gibbs-Duhem equation for a single component PVT system reduces to

$$\therefore U = TS - PV + \mu N \quad \therefore G = \mu N$$

We will use this results to discuss the phase equilibria & phase transitions.

Phase Equilibria

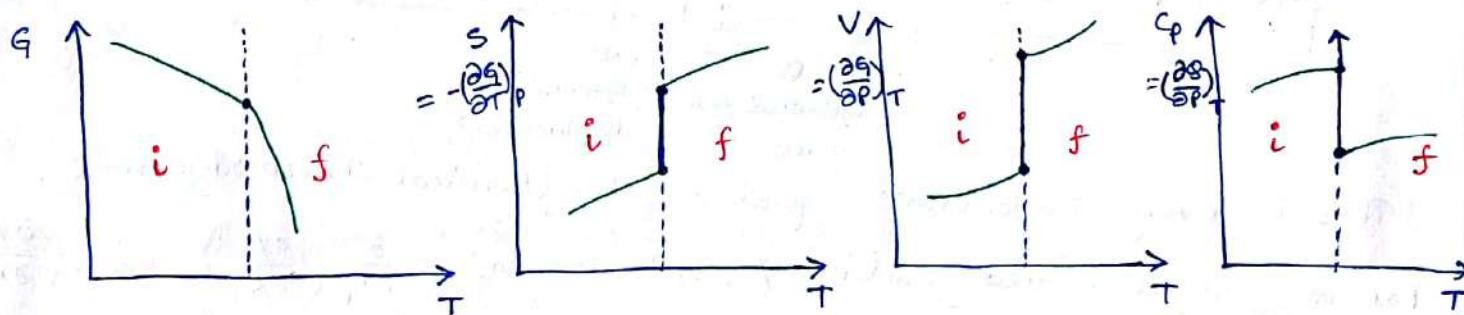
In most of the daily encountered phase transition, e.g. melting of ice, vaporization of water or sublimation, we can write down the Clausius-Clapeyron's equation $(\frac{\partial P}{\partial T})_{\text{saturation}} = \frac{L}{T(V_2 - V_1)}$.

This is classified as 1st order phase transition. This takes place at constant T and P while there is a transfer of latent heat that change the entropy and volume. As $dG = -SdT + VdP = 0$, so G is equal at two states $G^i = G^f$ and $S = -(\frac{\partial G}{\partial T})_P$, $V = (\frac{\partial G}{\partial P})_T$.

As T & P is constant, $dT = 0$ when $P = \text{constant}$

$dP = 0$ when $T = \text{constant}$

So $C_P = T(\frac{\partial S}{\partial T})_P \rightarrow \infty$, $\beta = \frac{1}{V}(\frac{\partial V}{\partial T})_P \rightarrow \infty$, $K = -\frac{1}{V}(\frac{\partial V}{\partial P})_T \rightarrow \infty$.



A 1st order phase transition is where the 1st order derivative of the Gibbs function changes abruptly at the transition point.

Using $G = \mu N$ and $dG = -SdT + VdP + \mu dN$ we obtain

$$\mu dN + N d\mu = -SdT + VdP + \mu dN$$

$$\therefore d\mu = -\frac{S}{N} dT + \frac{V}{N} dP.$$

∴ Along an isotherm $dT = 0$ means $\mu_{\text{liquid}} - \mu_{\text{gas}} = \int_{\text{gas}}^{\text{liquid}} \frac{V}{N} dP = 0$

$$\therefore \mu_{\text{L}} = \mu_{\text{g}}.$$

Note that $T-dS$ equation $TdS = Cp dT - TV\beta dP$ gives indeterminate result because $C_p \rightarrow \infty$, $dT \rightarrow 0$; $\beta \rightarrow \infty$, $dP \rightarrow 0$. However the other $T-dS$ equation $TdS = C_v dT + T \left(\frac{\partial P}{\partial T} \right)_V dV$ can be integrated along the phase transition.

$$\therefore T(S^f - S^i) = T \left(\frac{\partial P}{\partial T} \right)_V (V^f - V^i) = T \frac{dP}{dT} (V^f - V^i)$$

$$\propto H^f - H^i = T \frac{dP}{dT} (V^f - V^i)$$

$$\boxed{\frac{dP}{dT} = \frac{H^f - H^i}{T(V^f - V^i)}}$$

Clausius-Clapeyron's equation for 1st order transition

[One can reach to this conclusion starting from the fact that at constant temperature & pressure, $Q = \text{constant}$.

So applying, $q^i = q^f$ and for a change of phase from (T, P) to $(T+dT \& P+dp)$ we have $q^i + dq^i = q^f + dq^f$

$$\therefore dq^i = dq^f \quad \text{or} \quad -S^i dT + V^i dp = -S^f dT + V^f dp$$

$$\therefore \boxed{\frac{dp}{dT} = \frac{T(S^f - S^i)}{T(V^f - V^i)} = \frac{H^f - H^i}{T(V^f - V^i)}}.$$

2nd order Phase Transition

In 1st order phase transition (sublimation, vaporization, fusion) happening at a constant temperature & pressure, there is a transfer of (latent) heat & hence a change in entropy & volume. Q remains fixed and $(\frac{\partial Q}{\partial T})_P = -S$ and $(\frac{\partial Q}{\partial P})_T = V$ or the first order derivative of Q changes abruptly at the transition point.

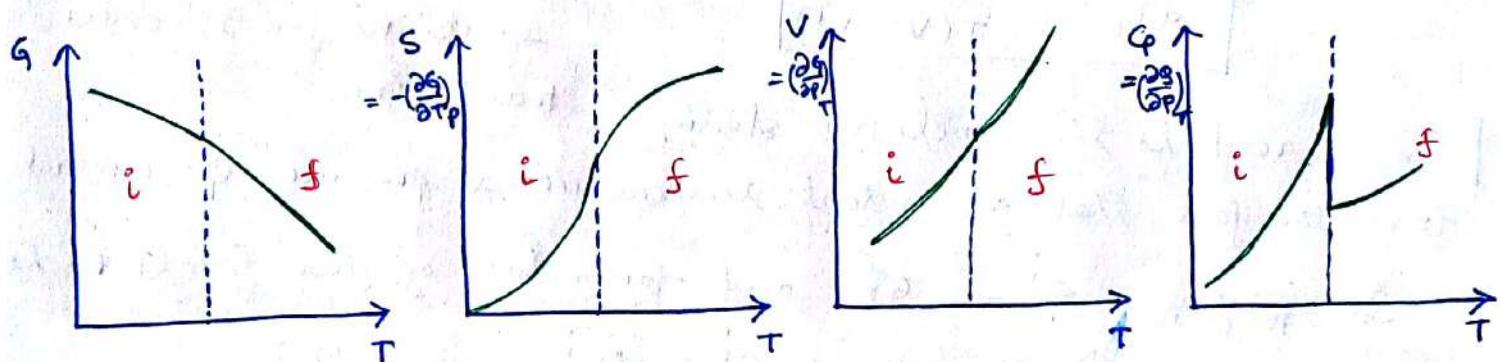
However investigation on some liquid showed no evolution of latent heat or change in volume. T, P, Q, S, V remain unchanged and therefore U, H, G etc. remain unchanged. However, finite change is seen in C_p, R and β , which are,

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p = T \frac{\partial}{\partial T} \left(- \frac{\partial G}{\partial T} \right)_p = - T \left(\frac{\partial^2 G}{\partial T^2} \right)_p$$

$$\kappa = - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = - \frac{1}{V} \left[\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial P} \right)_T \right]_T = - \frac{1}{V} \left(\frac{\partial^2 G}{\partial P^2} \right)_T$$

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P} \right)_T \right]_P = \frac{1}{V} \left(\frac{\partial^2 G}{\partial P \partial T} \right)_{T,P}$$

This led Ehrenfest to conclude that in a 1st order phase transition the 1st order derivative of G changes discontinuously while in a 2nd order phase transition, the 2nd order derivative of G changes discontinuously.



Second order phase transition is an example of continuous phase transition.

As $S = \text{constant}$, we have $ds^i = dS^f$

$$\text{from } S = S(T, P), \quad ds = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP$$

$$= \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T} \right)_P dP = \frac{C_p}{T} dT - V \beta dP$$

$$\text{we have, } \frac{C_p}{T} dT - V \beta dP = \frac{C_p}{T} dT - V \beta dP$$

$$\Rightarrow (C_p^i - C_p^f) \frac{dT}{T} = V dP (\beta^i - \beta^f)$$

$$\boxed{\frac{dP}{dT} = \frac{C_p^i - C_p^f}{TV(\beta^i - \beta^f)}}$$

Ehrenfest's first equation for 2nd order phase transition.

Similarly $V = \text{constant}$ yields $dv^i = dv^f$

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

$$= \beta V dT - kV dP \quad \text{we have}$$

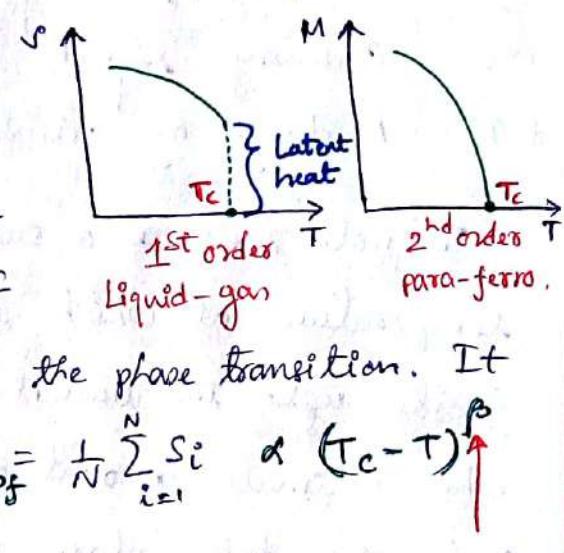
$$\beta^i V dT - k^i V dP = \beta^f V dT - k^f V dP$$

$$\Rightarrow (\beta^i - \beta^f) dT = (k^i - k^f) dP$$

$$\frac{dP}{dT} = \frac{\beta^i - \beta^f}{k^i - k^f}$$

Ehrenfest's second equation for 2nd order phase transition.

Paramagnetic to ferromagnetic transition is an example of 2nd order P.T. Ehrenfest's classification gave birth to "critical phenomena" that phase transition can be classified as nth order if nth derivative of the free energy with respect to any of its arguments yields a discontinuity at the phase transition. It was found that $\rho_{eg} \propto (T - T_c)^\beta$ and $M_p = \frac{1}{N} \sum_{i=1}^N s_i \propto (T_c - T)^\beta$

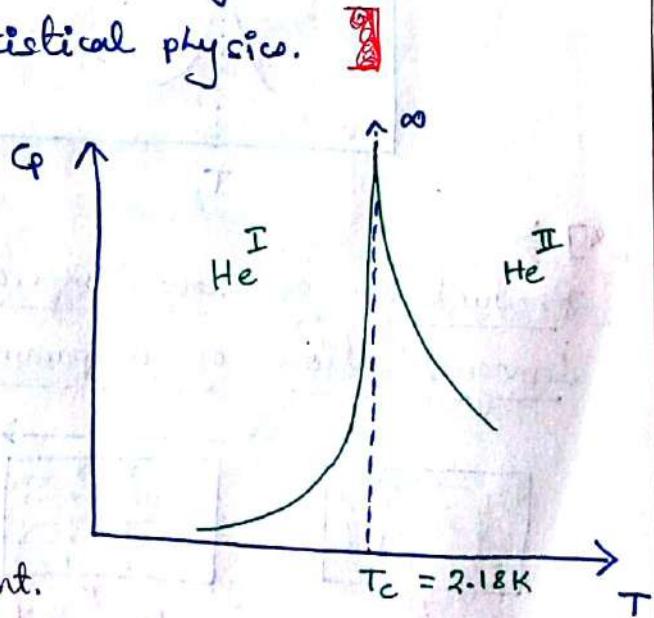


The fact that two apparently different physical systems may share precisely the same set of critical exponents is known as "universality." These led to many Nobel prizes including Landau's theory of 2nd order phase transition, Bragg-Williams theory of 1st order phase transition, Widom's scaling laws & Kadanoff's renormalisation group (RG) with two variant \rightarrow Gell-Mann-Low RG and Wilson-RG. which made the last significant contribution in the list of Nobel prizes in Statistical physics.

λ -Transition in He¹

By far the most interesting higher order phase transition that is found in Helium is the Lambda Transition, which is characterized by :

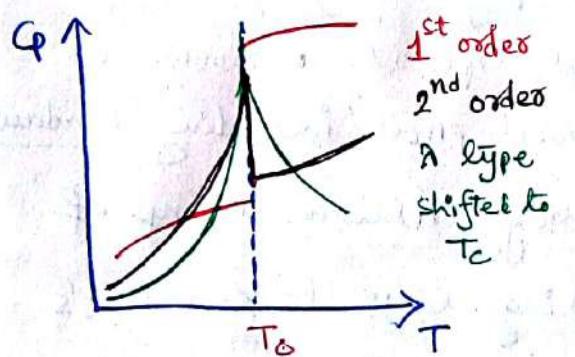
- (a) T, P, G remains constant.
- (b) S, V (also U, H, F) remains constant.
- (c) C_p, β, K tends to infinity at transition temperature.



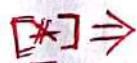
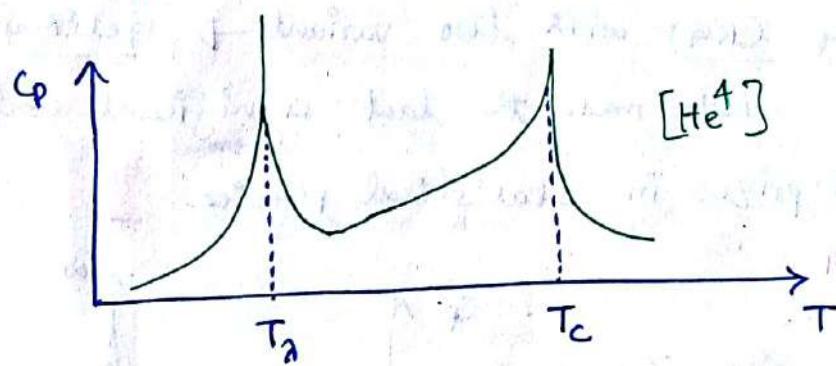
Examples of " λ "-type phase transition is

- (1) Order disorder transformation in alloys.
- (2) Onset of ferroelectricity in Rochelle salt.
- (3) Ferro to paramagnetism at the Curie point.
- (4) Ordinary liquid Helium-I to superfluid liquid Helium-II.
- (5) A change of orientation of an ion in a crystal lattice.

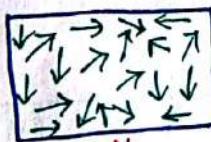
To note that as a substance in any one phase approaches the temperature at which 1st order phase transition occurs, C_p remains finite upto the transition temperature. It becomes infinite only when a small amount of the other phase is present and its behaviour before this takes place shows no evidence of the happening of the event.



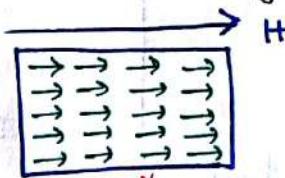
But in case of λ-type transition, C_p starts to rise before the transition point is reached and the substance anticipates the outcome of the phase transition.



[Production of low temperature using the method of adiabatic demagnetisation of a paramagnetic substance.]



$$M = \sum_i^N S_i = 0$$



$$M = \sum_i^N S_i \neq 0$$

The atoms of a paramagnetic material possess a permanent magnetic moment μ_m . In the

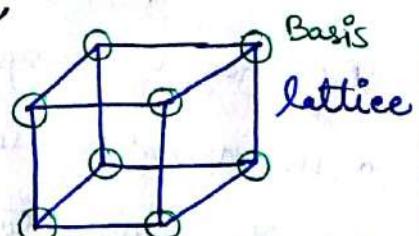
absence of an external field as a result of the thermal (Brownian) motion of the atoms, the orientation of magnetic moments is almost

random. Quantitatively disorder is confined in entropy $S = k_B \ln \Omega$ where Ω is the thermodynamic probability i.e. the number of ways N number of atoms of the paramagnetic sample can be distributed among the $(2J+1)$ sublevels into which every atomic level splits in a magnetic field. So $\Omega = (2J+1)^N$ and $\therefore S = k_B N \ln(2J+1)$

when the magnetic field is applied and its intensity is increased, more & more number of magnetic moments are oriented in the direction of the field, and the entropy is reduced. At the state of magnetic saturation, all moments are ordered & the entropy vanishes.

This process of magnetisation of a paramagnetic sample upto saturation is accompanied by the decrease of entropy. At a constant temperature T with a decrease in entropy ΔS , heat $\Delta Q = T \Delta S$ is generated & transmitted to the surrounding (immersing in a liquid Helium bath). After equilibrated, the bath is removed & the sample is left thermally insulated.

In such condition, the sample will quasistatically & adiabatically demagnetize with an increase in entropy ΔS . Heat is required to increase the entropy that is supplied by the thermal vibrations of the lattice. As the sample is thermally insulated, its temperature drops. Using this principle, it is possible to obtain temperature down to millikelvin $\sim 10^{-3} \text{ K}$.



Gibbs Phase Rule

Gibbs published a series of papers on the equilibrium of heterogeneous substance. Phase : A homogeneous, physically distinct part of a system that is separated from other parts by definite bounding surfaces is called a phase. E.g. ice-water-vapour constitute a three-phase system. Component : The smallest number of independently variable constituents by means of which the composition of each phase can be expressed. In above example, density is that variable, so water phases is one component system. Variance or d.o.f. : The number of variable factors (e.g. pressure, temperature, concentration etc) that need to be fixed in order that the condition of system at equilibrium may be completely defined is called degree of freedom (d.o.f.).

If the equilibrium between any number of phases is not influenced by external forces (electromagnetic, gravity) but only influenced by pressure, temperature and concentration, then Gibbs' phase rule provides the relation between number of d.o.f. F of the system to the components C and phases P as

$$F = C - P + 2$$

E.g. for water system, $C = 1$, $P = 3$. $\therefore F = 1 - 3 + 2 = 0$ or it is a nonvariant system. So the three phases can only exist in contact at definite temperature & pressure, which is the "triple point".

[Read more about phase rule for heterogeneous substance from Wikipedia].