

### thermodynamics (remaining)

#### Chemical potential

Change in free energy on adding 1 more mole of the substance at const. T and P.  
overall no change in composition.

May be define as the contribution per mole of each particular constituent of the mixture to the total free energy of the system under const T & P.

$$\left( \frac{\partial G}{\partial n_i} \right)_{T, P} = \mu_i = \bar{G}_i$$

$$\delta G = \left( \frac{\partial G}{\partial T} \right)_{P, N} dT + \left( \frac{\partial G}{\partial P} \right)_{T, N} dP + \mu_1 dn_1 + \mu_2 dn_2 - \dots - \mu_j dn_j$$

If  $\rightarrow \text{const}$   $\rightarrow \delta G = \mu_1 dn_1 + \mu_2 dn_2 - \dots - \mu_j dn_j$   
and  $P \rightarrow \text{const}$

If define composition having  $n_1, n_2, \dots, n_j$  mole of constituents.

then:  $G = \mu_1 n_1 + \mu_2 n_2 + \mu_3 n_3 + \dots + \mu_j n_j$

Gibbs-Duhem Equation:  $\sum (n_i \cdot d\mu_i) = 0$

Variation of chemical potential  $\Rightarrow \frac{\partial \mu_i}{\partial T}_{P, N} = -S_i$  (Partial molar entropy)

for Ideal gas

$$PV = (n_1 + n_2 + \dots + n_j) RT$$

$$\frac{\partial \mu_i}{\partial P}_{T, N} = \bar{V}_i \quad (\text{partial volume molar})$$

$$\left( \frac{\partial V}{\partial n_i} \right)_{T, P, n_1, n_2, \dots, n_j} = \bar{V}_i = \frac{RT}{P} = \left( \frac{\partial \mu_i}{\partial P} \right)_{T, N}$$

$$\cancel{\left[ d\mu_i = \frac{RT}{P} dP \right]} \rightarrow \boxed{d\mu_i = RT \ln P}$$

$$\boxed{\mu_i = \mu_{i(P)}^0 + RT \ln P_i} \rightarrow \boxed{\mu_i = \mu_{i(\infty)}^0 + RT \ln(x_i)}$$

$x_i \rightarrow$  fraction.

#### Clapeyron Equation

$$\frac{dP}{dT} = \frac{q}{T \Delta V} \quad \begin{matrix} A \\ \xrightarrow{\text{phase 1}} \\ \xleftarrow{\text{phase 2}} \\ A \end{matrix}$$

Change in pressure accompanying the change in Temp  $dT$ , & vice versa, in the case of a system containing two phases of a pure substance in eq with each other

Third law

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

at absolute temp  $T=0$   $\rightarrow \boxed{\Delta G = \Delta H}$

## Nernst heat theorem

\* only in case of pure solid

$$T \longrightarrow 0$$

$$\left( \frac{\partial \Delta G}{\partial T} \right)_P \longrightarrow 0$$

$\Delta G \approx \Delta H$ , approach each other asymptotically, as  $T \rightarrow 0$

$$\lim_{T \rightarrow 0} \left( \frac{\partial \Delta G}{\partial T} \right)_P = \lim_{T \rightarrow 0} \left( \frac{\partial \Delta H}{\partial T} \right)_P = 0$$

## Debye ( $T^3$ ) Law

at low temp  $\leftrightarrow 0 < T < 15K$

$$C_p \approx C_v \approx aT^3$$

$a$ : empirical constant

$$\boxed{S_T = aT^3}$$

$$S_T = \int_0^{T^*} aT^3 \frac{dT}{T} + \int_{T^*}^T C_p \frac{dT}{T}$$

$$\boxed{S_T = \frac{aT^3}{3bT} + \int_{T^*}^T C_p \frac{dT}{T}}$$

## Boltzmann Entropy Equation

$$S = k \cdot \ln W$$

$k$ : Boltzmann const.

$W$ : no. of micro states

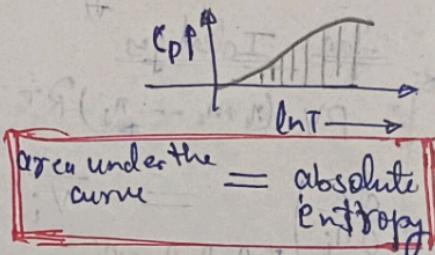
# At absolute temp zero, the entropy of every substance may become zero & it does become zero in the case of a perfectly crystalline solid.  
 $\lim_{T \rightarrow 0} S = 0$

at const  $P$

$$\int dS = \int_{T_1}^T \left( C_p / T \right) dT$$

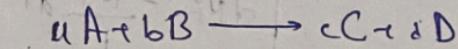
$$S = \int_{T_1}^T (C_p d\ln(T))$$

absolute entropy



area under the curve = absolute entropy

Chemical react.



$$\Delta S^\circ = \sum \delta^\circ_{\text{product}} - \sum \delta^\circ_{\text{reactant}}$$

Standard entropy change

$$[c, \delta_c^\circ + d, \delta_d^\circ]$$

$$[a, \delta_a^\circ + b, \delta_b^\circ]$$

## Effect of temp on Gibbs function.

for close system Non P work.

$$\underline{\underline{dG = TdP - \beta dT}}$$

$$\xrightarrow{\text{const } P} \frac{dG}{dT} = -\beta \quad \Leftrightarrow \theta \left. \frac{\partial G}{\partial T} \right|_P = -\beta$$

we have equation lemit

$$\left[ \frac{\partial(\Delta G/T)}{\partial T} \right]_P = -\frac{\Delta H}{T^2}$$

$$\boxed{\left[ \frac{\partial(\Delta G/T)}{\partial(1/T)} \right]_P = \Delta H}$$

$$G = H - TS$$

$$\left[ \frac{\partial G}{\partial T} \right]_P = \frac{G - H}{T}$$

$$\left. \frac{\partial G}{\partial T} \right|_P = \frac{G}{T} - \frac{H}{T} = \cancel{\frac{\partial G}{\partial T}}_P$$

$$\left[ \frac{\partial(G/T)}{\partial T} \right]_P = \frac{1}{T} \left[ \frac{\partial G}{\partial T} \right]_P + G \frac{\partial}{\partial T} \left( \frac{1}{T} \right)$$

$$\left[ \frac{\partial(G/T)}{\partial T} \right]_P = \frac{1}{T} \left[ \frac{\partial G}{\partial T} \right]_P - \frac{G}{T^2}$$

$$\left[ \frac{\partial(G/T)}{\partial T} \right]_P = \frac{1}{T} \left[ \frac{\partial G}{\partial T} \right]_P + \frac{G}{T}$$

if  $\Delta H$  independent range  
 $T_1 \rightarrow T_2$

$$\int_{T_1}^{T_2} \left[ \frac{\partial(\Delta G/T)}{\partial T} \right] = -\Delta H \int_{T_1}^{T_2} \frac{1}{T^2} dT$$

$$\boxed{\frac{\Delta G_2 - \Delta G_1}{T_2} = -\Delta H \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]}$$

$$\boxed{\left[ \frac{\partial(G/T)}{\partial T} \right]_P = -\frac{H}{T^2}}$$

$$\left[ \frac{\partial(\Delta G/T)}{\partial T} \right]_P = \left[ \frac{\partial(G/T)}{\partial T} \right]_P \times \frac{\partial(1/T)}{\partial T}$$

$$= \frac{\partial(G/T)}{\partial(1/T)} \cdot \left( -\frac{1}{T^2} \right)$$

$$\boxed{\left[ \frac{\partial(G/T)}{\partial(1/T)} \right] = -H}$$

curve

## Effect of Pressure on $G$ for Gasis

$$\Delta G = nRT \int_{P_i}^P \frac{dP}{P} = nRT \ln \left( \frac{P_f}{P_i} \right)$$

$$G_f - G_i = G_f^{\circ} + nRT \ln \left( \frac{P_f}{P_i} \right)$$

$$G_m = G_m^{\circ} + RT \ln \left( \frac{f}{P} \right)$$

$f$ : fugacity is a

$\lim_{P \rightarrow 0} f/P = 1$  at  $0^\circ$  pressure &  $T$   
and is related to  $P_f$   
by the eqn  $P = \phi P_f$   
 $\phi = 1, f = P$  where  $\phi$  is called  
the fugacity coefficient.

$\phi$  is related to the compression  
factor "z" of gases.

$$\int_{P_i}^P V_m dP = G_m - G_m^{\circ} = RT \ln \left( \frac{f}{f_i} \right)$$

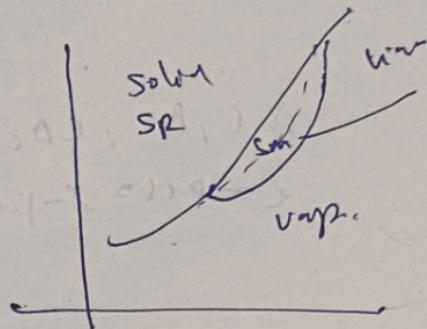
perfect gas

$$\int_{P_i}^P V_m dP = RT \ln \left( \frac{P}{P_i} \right)$$

$$\int_{P_i}^{P'} [V_m - V_m(\text{perfect})] dP = RT \left[ \ln \left( \frac{f}{f_i} \right) - \ln \left( \frac{P}{P_i} \right) \right]$$

OC: fusible curve  $F=1$

→ Metastable Curve OA'



$P_{max} = 3$  ①

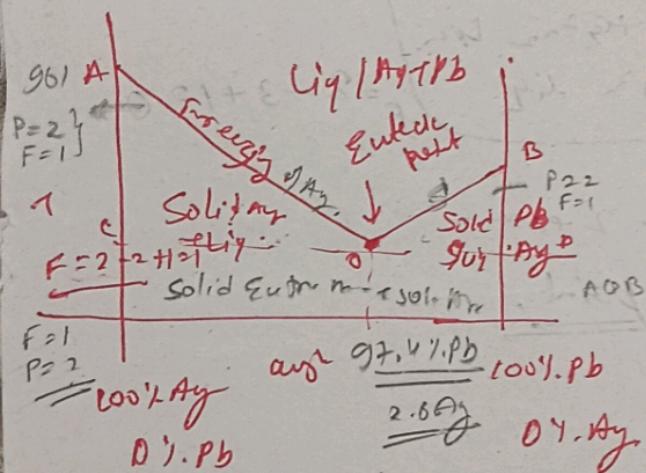
②  $P_{min} = 4$  ③

$P_{min} = 5$

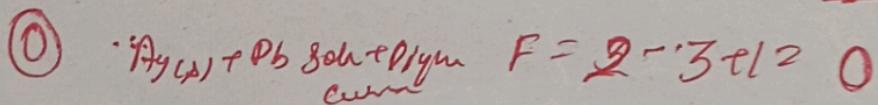
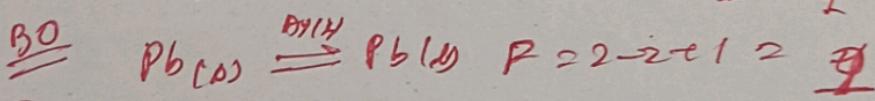
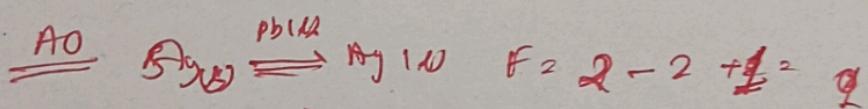
$F=0$  ~~masses~~  
for mass  
no of ph

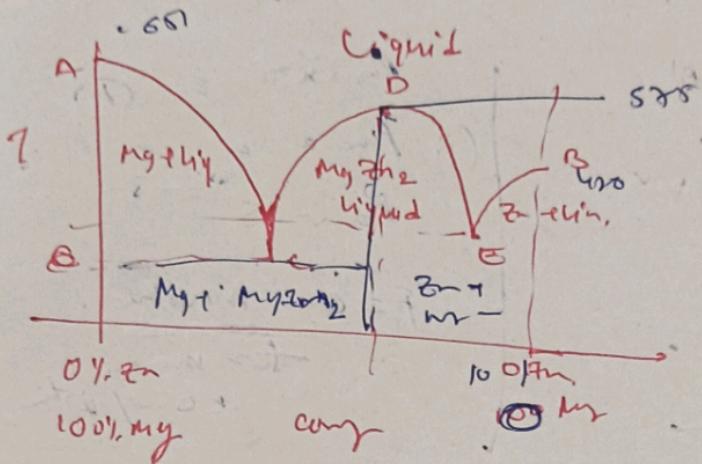
$$\ln P_2 / P_1 = \frac{\Delta H}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\frac{dP}{dT} = \frac{\Delta H}{T(V_g - V_s)}$$



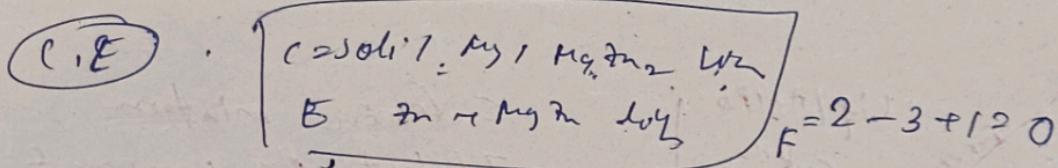
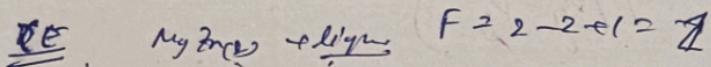
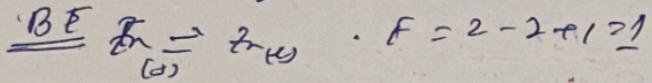
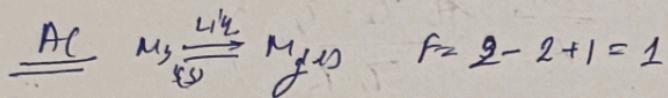
Eutectic mixture  
If both the component  
are completely miscible  
in liquid (water) & full  
insoluble in solid state  
& do not react  
with each other





$A \subset B^c, C \subset B^c$

$$C = P + 1 = 2 - 1 + 1 = 2$$



$$\text{at } D = C - P + 1 = 1 - 2 + 1 = 0$$

$\hookrightarrow$  congruent melting point.

$$\text{Phase Rule} \quad F = C - P + 2$$

$C$ : No. of components  $\rightarrow C = N - E$

$P$ : No. of phases

$F$ : No. of degrees of freedom.

$N$ : No. of chemical species

$E$ : No. of independent eqns relating the concentration of the  $N$  species.

$P$ : Phase  $\rightarrow$  ex: mix  $\text{CO}_2$ ,  $\text{O}_2$  & water vapour.  
ex: mix of miscible liquids.

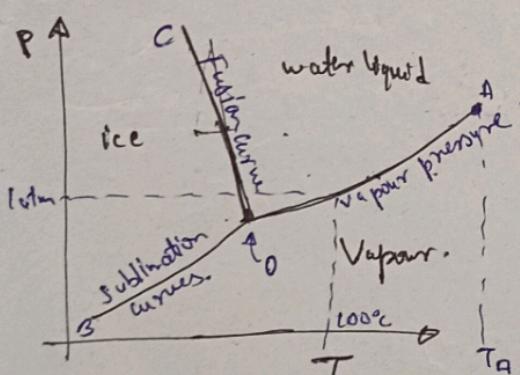
Dissolved  $\rightleftharpoons$  gas  $\rightleftharpoons$  solid  $P=3$   
 $\text{Ca(O}_2\text{)}_{(s)} \rightleftharpoons \text{CaO}_{(s)} + \text{O}_{(g)}$   $P=3$   
water + phenol  $\Rightarrow P=2$

DOF or Variance of a system is defined as the minimum number of variable factors such as temp, pressure and concentration which should be required in order to define the system completely. It is denoted by  $F$ .

- The phase rule is applicable to heterogeneous systems in equilibrium.
- So, it is of no use for such system attain slowly the eq state.
- All the phases in system must be present under same temp,  $P$ , gravity.
- Does not account electrical & magnetic.

for  $F_{\text{max}} = 2 \quad C = P = 1$ .

### Phase Diagram



$P, T$  only two variables graphically described alone component of system on approx. axis.

at  $T_c$  &  $P_c$  liquid & vapour phase can not distinguish & supercritical fluid obtain

Water vapour system Univariant.

(B) Solid  $\rightleftharpoons$  Vapour  
 $P_{\text{SL}}$   
 $F_r = C - P + 2 = 1$

Equivalent:

(D)  $F = C - P + 2$   
 $\Rightarrow 1 - 2 + 2$   
 $= 1$

$$V = RT \downarrow \partial H_i$$

## thermodynamics

### # Second law of thermodynamics

limitation of first law

→ No restriction on the direction of flow of heat.

→ Does not tell whether a specified change or a process including a chemical reaction can occur spontaneously.

→ Heat energy can't be completely converted into an equivalent amount of work.

### # AB isotherm

$$PV = \text{const.}$$

$$P_A V_A = P_B V_B$$

$$\Delta U = q + w$$

$$dU = nC_V dT \quad (\text{d}T=0)$$

duo

$$q = -w$$

$$w_{AB}^2 = -RT_2 \ln\left(\frac{V_2}{V_1}\right)$$

BC adiabatic  $\int_{T_0}^{T_c} C_V dT$

$$PVR_{2 \text{ at}} \quad \boxed{DU = w}$$

$$w =$$

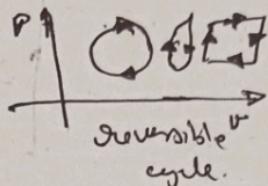
$$(W_{\text{irr}}) < (W_{\text{rev}})$$

cyclic process  $\Rightarrow (\Delta V = 0)$

process in which a system, after completing a series of changes, returns back to original state.

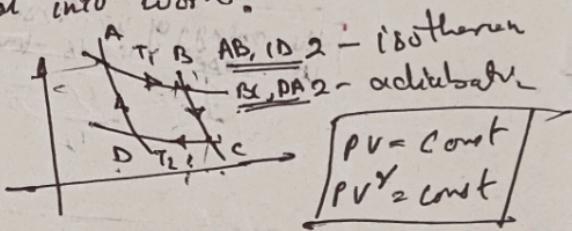
$$\Delta U = q + w$$

$$q = -w$$



### Carnot cycle

It is a reversible cyclic process in which maximum conversion of heat into work.



$$\int_{T_B}^{T_C} C_V \cdot dT$$

$$T_B = T_1$$

$$T_C = T_2$$

$$[C_V (T_2 - T_1)] = w \dots$$

$$P_c V_c = R T_2$$

$$P_B V_B = R T_1$$

$$\eta = \frac{T_2 - T_1}{T_2} \frac{q_2 - q_1}{q_2}$$

## Carnot & theorem

Efficiency of a machine working reversibly depends only on the temp of the source (and sink), independent of the nature of substance used for operation.

All periodic machines working reversibly b/w the same two temp have same efficiency

## 2<sup>nd</sup> statement

It is impossible to convert heat into work without compensation

the energy of universe is constant; the entropy of the universe tends towards a maximum.

$$1 - \frac{T_1}{T_2} = 1 - \frac{q_1}{q_2}$$

$$\frac{q_1}{T_1} = \frac{q_2}{T_2}$$

$$\frac{q_{rev}}{T} = \text{const}$$

~~Exfensive~~  
depends upon  
amount.

$$\Delta S = S_B - S_A = \int \frac{dq}{T}$$

path independent

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

J/K

for Ideal gas

$$PV = (n_1 + n_2 + \dots + n_j) R T$$

$$\Delta U = ?$$

### $\Delta S$ calculation

→ Reversible Isothermal process

$$PV = \text{const.} \quad q = -w$$

$$\Delta V = 0 \quad dW = -P_{\text{gas}} \cdot dV$$

$$P_{\text{gas}} \frac{dV}{dT} = \frac{nRT}{V}$$

$$\frac{q}{q_i} = \frac{dV}{T} \Rightarrow -\frac{dw}{T}$$

$$\Rightarrow +\frac{nRT}{T} dV$$

$$\Rightarrow +nR \ln(V_2/V_1)$$

$$\Delta S_{\text{system}} \Rightarrow -nR \ln(V_1/V_2)$$

for spontaneous  $\Delta S > 0$

$$\Delta S_{\text{system}} + \Delta S_{\text{surround}} = 0$$

$$\Delta S_{\text{surround}} = -\Delta S_{\text{system}}$$

$$\Delta S_{\text{surround}} = +nR \ln(V_1/V_2)$$

$$\Delta S_{\text{surround}} = nR \ln(V_2/V_1)$$

→  $\Delta S$  at phase change

$$\left[ \Delta S = \frac{\Delta H}{T_{\text{transition}}} \right]$$

$$\Delta S = nC_V \ln(T_2/T_1) + nR \ln(V_2/V_1)$$

$$\Delta S = nC_p \ln(T_2/T_1) + nR \ln(P_1/P_2)$$

Entropy of system in irreversible proc

$$\left[ \Delta S = - \int_{\text{system}} \frac{dq_{\text{rev}}}{T} \right]$$

$$\Delta V = Q_{\text{irr}} + w_{\text{irr}}$$

$$\Delta S_{\text{surround}} = -\frac{Q_{\text{irr}}}{T_{\text{surround}}}$$

adiabatic component  
or  
exp

$dq_{\text{rev}} = 0$  for reversible  
proc

$$\Delta S_{\text{system}} = 0$$

$$\Delta S_{\text{surround}} = 0$$

adiabatic (irr)

$$\rightarrow - \int \frac{dq_{\text{irr}}}{T} = \Delta S_{\text{system}}$$

$$0 = \Delta S_{\text{surround}}$$

$$\Delta U = \Delta H^0 + w_{\text{irr}}$$

$$\Delta U = w_{\text{irr}}$$

$$\Delta S = nC_V \ln \left[ \frac{T_2}{T_1} \right] + nR \ln \left( \frac{V_2}{V_1} \right)$$

~~for a mixture of 'de g.~~

$$\delta^2 \sum_i n_i (c_p \ln T - R \ln P_i - \mu_{\text{lim}} + \delta_0')$$

$P_T$  = Total pressure

$P_T$  Total pressure  
 $\pi_2$  mole fraction of a particular gas in the mixture

$$\Delta S_{\text{mix}} = -R \sum n_i \ln x_i$$

$\mu$  = molar fraction of that gas

$n_i^2 = \text{noy qnoleg fflat gwr}$

~~W~~ Workfunktion -  $U - t\delta = \omega \Rightarrow A$   $\rightarrow i$

$$\text{free energy} f \quad \boxed{f = H - TS}$$

$$\Delta A = \Delta U - T\Delta S$$

-14A give the maximum work that can be done by the system depends on the change

$$-DA = \omega_{\text{rev}}$$

for Ideal gas

$$PV = n_1 + n_2 + \dots + n_j$$

$$\Delta U = \Delta H - T\Delta S$$

$$\boxed{\Delta H = \Delta U + P\Delta V}$$

$$\boxed{dH = dU + dPV}$$

$$dU = dq + dw$$

$$\text{Network work} = w - P\Delta V = \Delta G$$

at const press &

$$\Delta G = \Delta U + T\Delta S$$

$$\Delta G = \Delta A + P\Delta V$$

$$\Delta G = -w + P\Delta V$$

$$\boxed{-\Delta G = w - P\Delta V}$$

work done  
by sys a

expen ent  
out P.

maxim work done  
obtained by the  
system

$$\boxed{dG = Vdp - \delta dT}$$

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_p = -\beta}$$

$$\boxed{\left(\frac{\partial G}{\partial p}\right)_T = V}$$

$$dU = Tds - Pdv$$

$$\boxed{dH = Tds + Pdv + Vdp - Pdv}$$

$$\boxed{dH = Tds + Vdp}$$

$$\boxed{dG = dH - Tds - \delta dT}$$

$$\boxed{dG = Vdp - \delta dT}$$

$$-\left(\frac{\partial G}{\partial T}\right)_p = \beta$$

$$\boxed{\Delta G = nR\gamma + P_2/V_1 - nR\gamma \ln(V_2/V_1)}$$

Sprinkler

$$\Delta S \geq 0$$

$$\Delta U \leq 0$$

$$\Delta H \leq 0$$

$$\Delta G \leq 0$$

$$\Delta A \leq 0$$

equilibrium at reversible

$$V_A = V_B = V_0$$

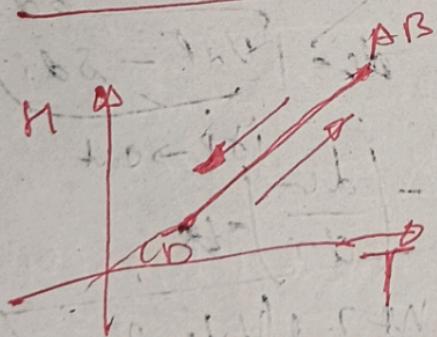
Gibbs Helmholtz equat

at const  
press

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

at const  
volume

$$\Delta A = \Delta U - T \left( \frac{\partial \Delta A}{\partial T} \right)_V$$



$$\Delta H_2 - \Delta U_1 + PV_2 - PV_1$$

(P.T.S.)

$$\Delta U = C_P \Delta T \rightarrow \left( \frac{\partial U}{\partial P} \right)_T dP$$

$$PV = (n_1 + n_2 - \dots) RT$$

$$\frac{\partial V}{\partial T}$$

Clauses

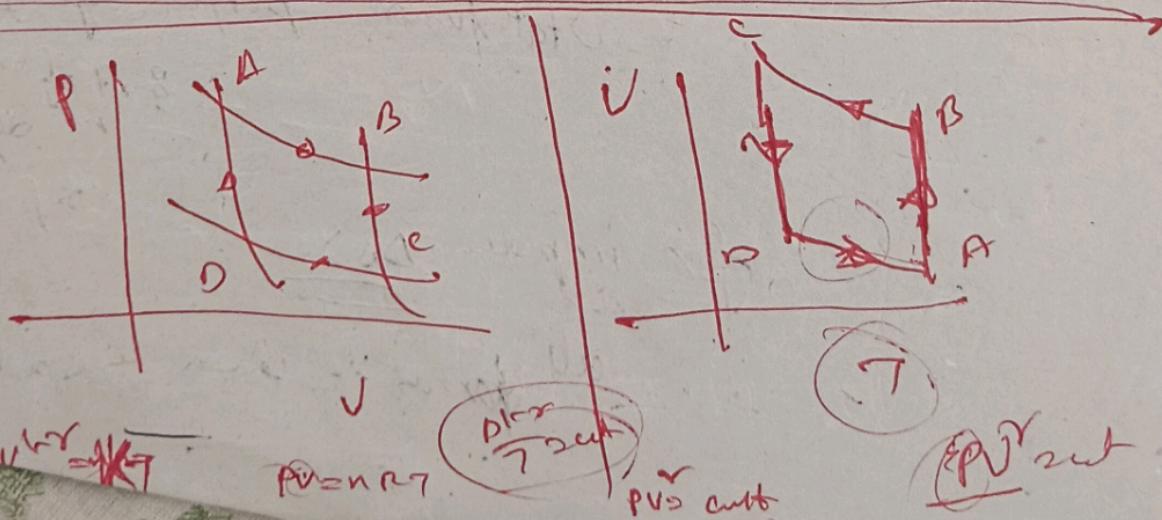
: Heat, by itself cannot pass from lower temp to higher

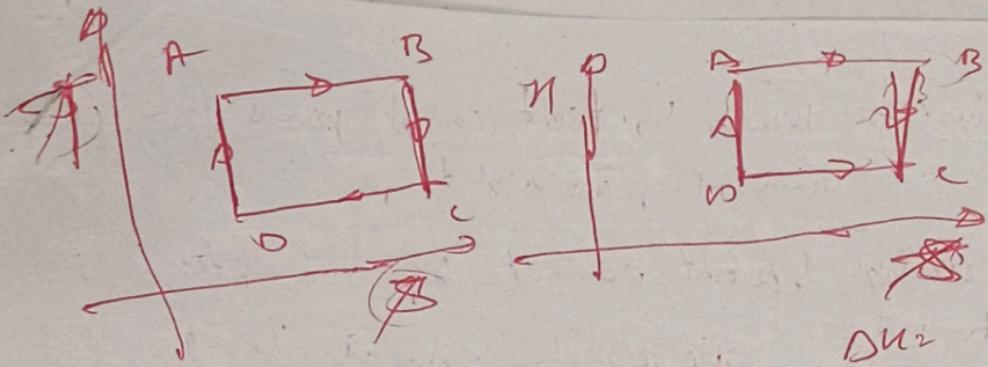
Planck's relation : Heat cannot be completely transferred ~~from work~~. If it does so, the working system will suffer upon net change.

$$\left. \begin{aligned} W_2 &= R h \left( \frac{V_2}{V_1} \right) (T_2 - T_1) \\ Q_2 &= R T_2 \ln \left( \frac{V_2}{V_1} \right) \end{aligned} \right\}$$

$$\eta = \frac{W}{Q} = \frac{R h \left( \frac{V_2}{V_1} \right) (T_2 - T_1)}{R T_2 \ln \left( \frac{V_2}{V_1} \right)}$$

$$\frac{T_2 - T_1}{T_2}$$





$$\delta Q = n R T \ln(V_2/V_1)$$

(Q5). Entropy is defined as the thermal energy of system per unit temperature which is unavailable for doing work.

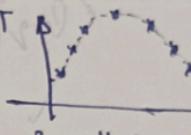
Entropy → measure of randomness of a system.

$$dS = \frac{dQ_{\text{rev}}}{T}$$

State function perfect differentiable & it does not depend on path

for irrevers.  $\sum S_i > 0$

all forces in curve is gradien

$dU = Td\delta - PdV = Td\delta - PdV$ $dH = Td\delta + VdP = dU + PdV + VdP$ $dF = -pdV - \delta dT = dU - Td\delta - \delta dT$ $dG = VdP - \delta dT = dH - Td\delta - \delta dT$	$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{\partial P}{\partial \delta}  _V \quad \left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial \delta}{\partial V}  _T$ $\left(\frac{\partial T}{\partial P}\right)_S = \frac{\partial V}{\partial \delta}  _P \quad \left(\frac{\partial V}{\partial T}\right)_P = -\frac{\partial \delta}{\partial P}  _T$ $C_p - C_v = R = T \left(\frac{\partial P}{\partial T}\right)_V \times \left(\frac{\partial V}{\partial T}\right)_P$ $= \frac{C_p}{K_T} TV^{\beta^2} = -T \left[\left(\frac{\partial V}{\partial T}\right)_T\right]^2 \left[\left(\frac{\partial P}{\partial V}\right)_T\right]$ $B = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$ $K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$
$\frac{C_p}{C_v} = \gamma = \frac{\partial P / \partial V  _S}{\partial P / \partial V  _T} = \frac{K}{K_p} = \frac{-1/V}{1/V} \left(\frac{\partial V}{\partial P}\right)_S$	<u>Joule Kelvin effect.</u> <ul style="list-style-type: none"> <li>Inversion curve</li> <li>Joule coefficient <math>M_J</math></li> </ul> <p><math>M_J &gt; 0</math> cooling region      <math>M_J &lt; 0</math> heating region</p> 
$dU = C_v dT + T \left(\frac{\partial P}{\partial T}\right)_V dV - PdV$ $[dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV]$	$\left[\frac{\partial U}{\partial V}\right]_T = T \left(\frac{\partial P}{\partial T}\right)_V - P$
<u>Clausius Clapeyron equation</u> $\frac{dP}{dT} = \frac{S^{(f)} - S^{(i)}}{V^{(f)} - V^{(i)}} = \frac{1}{T \{V^{(f)} - V^{(i)}\}}$ $P = 101.325 \exp \left[ \frac{88}{P} \left( 1 - \frac{T_b}{T} \right) \right]$	$M_J = \left[ \frac{\partial T}{\partial P} \right]_V = \frac{1}{C_p} \left[ T \frac{\partial V}{\partial T} \right]_P$ <p>For ideal gas <math>\rightarrow [M_J = 0]</math></p>
$\left(\frac{\partial x}{\partial y}\right)_f \left(\frac{\partial y}{\partial z}\right)_f \left(\frac{\partial z}{\partial n}\right)_f = 1$ $\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial z}{\partial n}\right)_y \left(\frac{\partial y}{\partial x}\right)_n = -1$ $dz = M dx + N dy$ $\frac{\partial M}{\partial y}  _m = \frac{\partial N}{\partial n}  _y$	$M_J = \frac{V}{C_p} [kT - 1] \text{ general}$ $\beta = \frac{1}{V} \frac{\partial V}{\partial T}$ <p>for ideal gas <math>\left[ \beta = 1/T \equiv M_J = 0 \right]</math></p> <p><math>\beta</math>: volume expansivity.</p>