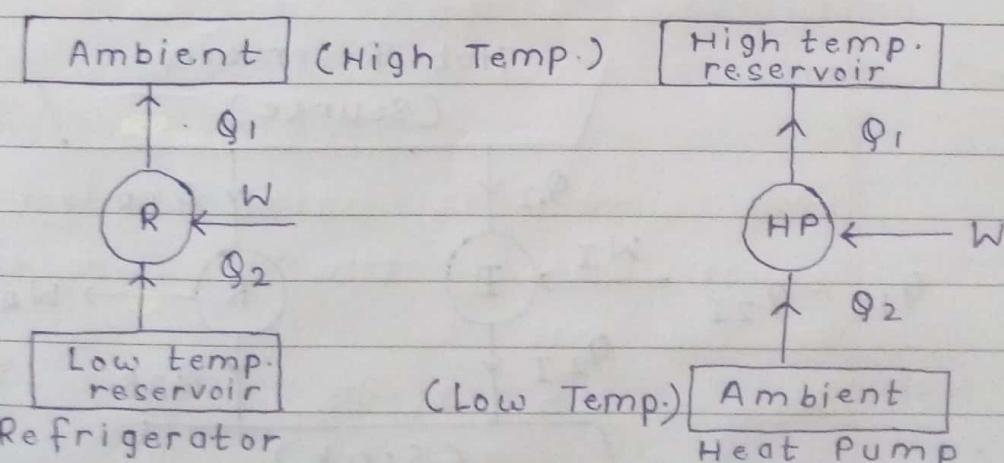
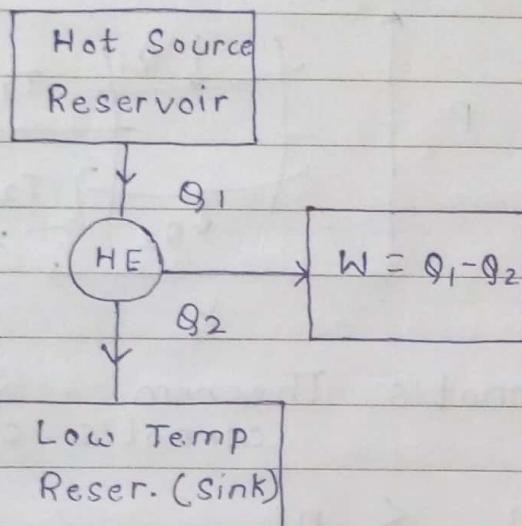


## SECOND LAW OF THERMODYNAMICS :-

All the devices are based on heat engines and heat pumps.



Effectiveness = Energy effect sought  
Energy expended

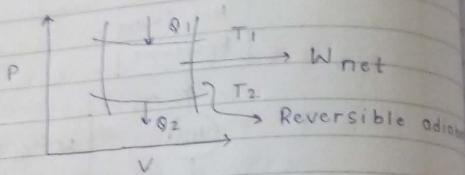
$$\eta_{HE} = \frac{W}{Q_1}$$

$$(COP)_R = \frac{Q_2}{W}; (COP) = \frac{Q_1}{W}$$

Coefficient of performance.

The purpose of HP is to keep the high temp reservoir hot and the purpose of refrigerator is to keep the temp reservoir cool.

Clausius Statement :-  
Any spontaneous process cannot reverse itself.



Carnot's Theorem - {Valid for only Carnot's cycle}

$$1. \eta_I < \eta_R$$



Assume that  $\eta_I > \eta_R$   
 $\therefore W_I > W_R$

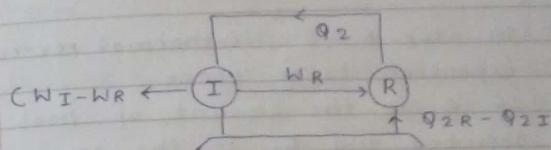
$$Q_{1I} > Q_{1R}$$

$$\text{But } Q_{1I} = Q_{1R} = Q_1$$

$$\therefore W_I > W_R \Rightarrow W_I > W_R$$

$$Q_1 > Q_1$$

∴ R is reversible, its action can be reversed and it will act like a heat pump.  
Whatever heat R is rejecting to the reservoir is picked up by I



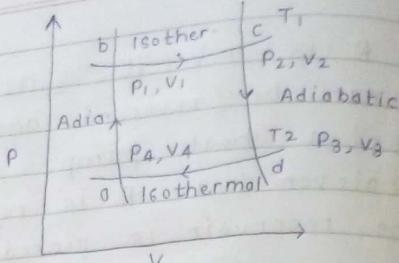
This violates Kelvin-Plank Statement  
Hence,  $W_I > W_R \Rightarrow \eta_I > \eta_R$

2. If a heat engine is operating between the same temperatures, no matter whatever be the working substance,  $\eta$  will be same.

$$\rightarrow \eta_{R1} = \eta_{R2}$$

3. If working substance is the ideal gas,  $\eta = 1 - \frac{T_2}{T_1}$

$$T_1$$



In step  $b \rightarrow c$ , isothermal reversible expansion takes place.

→ If  $Q_1$  is the amount of heat absorbed and  $Q_2$  is the amount of heat released at temp.  $T_2$

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

$$Q_1 = W_1 = nR T_1 \ln \left( \frac{V_2}{V_1} \right) - 1$$

Step  $c \rightarrow d$  is adiabatic reversible expansion of the gas. Work done by the gas

$$W_2 = nR (T_1 - T_2) \quad r-1$$

Step  $d \rightarrow a$  is isothermal compression therefore work done on the gas by the surrounding

$$W_3 = -nR T_2 \ln \left( \frac{V_3}{V_4} \right) = Q_2$$

Step  $a \rightarrow b$  is adiabatic compression of the gas. Work done on the gas

$$W_4 = -nR (T_1 - T_2) \quad r-1$$

Total work done in one complete cycle is

$$W = W_1 + W_2 + W_3 + W_4$$

$$W = nR T_1 \ln \left( \frac{V_2}{V_1} \right) - nR T_2 \ln \left( \frac{V_3}{V_4} \right)$$

Efficiency of the carnot engine

$$\eta = \frac{W}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

$$= 1 - \left( \frac{T_2}{T_1} \right) \ln \left( \frac{V_3}{V_4} \right) / \ln \left( \frac{V_2}{V_1} \right)$$

$$\text{or } \eta = 1 - \left[ \frac{T_2 \ln(V_3/V_4)}{T_1 \ln(V_2/V_1)} \right]$$

∴ points b and c lie on isotherm.

$$P_1 V_1 = P_2 V_2 - 1$$

also points c and d lie on adiabat

$$P_2 (V_2)^r = P_3 (V_3)^r - 2$$

Similarly,

$$P_3 V_3 = P_4 V_4 - 3$$

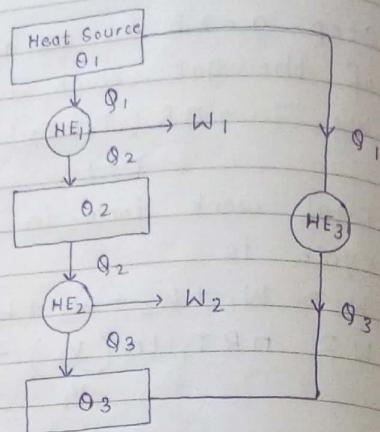
$$\text{and } P_4 (V_4)^r = P_1 (V_1)^r - 4$$

Using 1, 2, 3 and 4,  $V_3/V_4 = V_2/V_1$

$$\text{Hence, } \eta = 1 - \frac{T_2}{T_1}$$

Date 25.01.2018

(Saathi)



$$\eta_{HE_1} = \frac{W_1}{q_1} = 1 - \frac{q_2}{q_1} = F(\theta_1, \theta_2)$$

$$\Rightarrow q_2 = f(\theta_1, \theta_2)$$

q₁

$$\eta_{HE_2} = \frac{W_2}{q_2} = 1 - \frac{q_3}{q_2} = F(\theta_2, \theta_3)$$

q₂

$$\Rightarrow q_3 = f(\theta_2, \theta_3)$$

q₂

$$\eta_{HE_3} = \frac{W_3}{q_3} = 1 - \frac{q_1}{q_3} = F(\theta_1, \theta_3)$$

q₃

$$\Rightarrow q_3 = f(\theta_1, \theta_3)$$

q₁

$$q_1 = q_1/q_3 = \phi(\theta_1)\psi(\theta_3)$$

$$q_2 = q_2/q_3 = \phi(\theta_2)\psi(\theta_3)$$

$$q_1 = \phi(\theta_1)$$

$$q_2 = \phi(\theta_2)$$

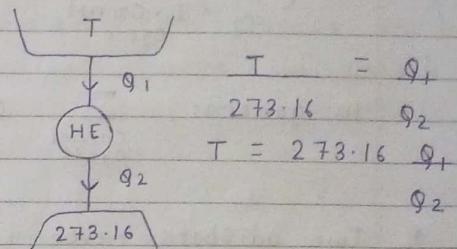
$$\phi(\theta) = 0$$

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(Saathi)

$$\frac{q_1}{q_2} = \frac{\theta_1}{\theta_2} = \frac{T_1}{T_2} \quad \{ \text{Ideal gas} \}$$

To measure any unknown temp., we design a carnot engine.



Assuming that work done by each HE is equal,

$$q_1 - q_2 = q_2 - q_3$$

$$\frac{q_1 (1 - q_2)}{q_1} = \frac{q_2 (1 - q_3)}{q_2}$$

$$\frac{q_1 (1 - T_2)}{T_1} = \frac{q_2 (1 - T_3)}{T_2}$$

$$\frac{q_1 (T_1 - T_2)}{T_1} = \frac{q_2 (T_2 - T_3)}{T_2}$$

$$\text{But } q_1 = q_2$$

$$T_1 = T_2$$

$$\therefore (T_1 - T_2) = (T_2 - T_3)$$

As all the temp. measured by this temp. scale is positive, it is also called the absolute temp. scale. Devised by Kelvin.

$$q_1 + (-q_2) = 0$$

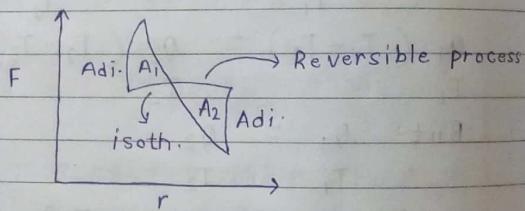
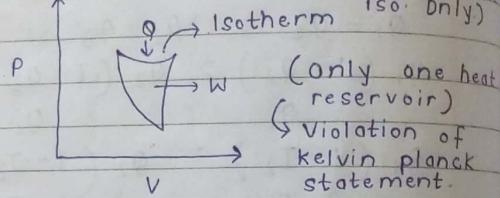
$$\frac{q_1}{T_1} - \frac{q_2}{T_2} = 0$$

$$\Rightarrow \sum \left( \frac{q_i}{T_i} \right)_{\text{Rev. Carnot cycle}} = 0$$

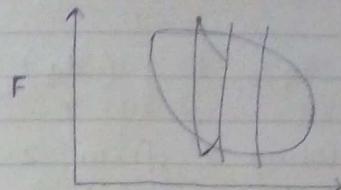
$$\sum \left( \frac{q_i}{T_i} \right)_{\text{I. Carnot cycle}} < 0$$

$$\text{In general, } \sum_{\text{Carnot cycle}} \frac{q_i}{T_i} \leq 0$$

- \* Two adiabats never intersect each other in a cyclic process. (Heat exchange will take place through the isotherm iso. Only)



Any reversible process can be replaced by two adiabats and an isotherm provided  $A_1 = A_2$

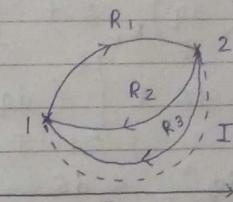


$$\oint \left( \frac{dq}{T} \right)_R = 0$$

Any reversible cyclic process can be replaced by a number of carnot cycles. If any part is irreversible,  $\oint \left( \frac{dq}{T} \right)_I < 0$

Clausius Inequality :

$$\oint \left( \frac{dq}{T} \right) \leq 0 \quad \{ \text{Cyclic process} \}$$



$$\int_{R_1}^{R_2} \left( \frac{dq}{T} \right)_{R_1} + \int_{R_2}^{R_3} \left( \frac{dq}{T} \right)_{R_2} = 0 - 1$$

Also,

$$\int_{R_1}^{R_3} \left( \frac{dq}{T} \right)_{R_1} = 0$$

$$\int_1^2 \left(\frac{dq}{T}\right)_{R1} + \int_2^1 \left(\frac{dq}{T}\right)_{R3} = 0$$

Subtracting 1. from 2. gives,

$$\int_2^1 \left(\frac{dq}{T}\right)_{R3} = \int_2^1 \left(\frac{dq}{T}\right)_{R3} = \int_2^1 dq = S_2 - S_1$$

\* Thermodynamics defines all properties as a difference.

$$\int_1^2 \left(\frac{dq}{T}\right)_{R1} + \int_2^1 \left(\frac{dq}{T}\right)_I < 0$$

$$\therefore \int_1^2 \left(\frac{dq}{T}\right)_{R1} = - \int_2^1 \left(\frac{dq}{T}\right)_{R1}$$

$$- \int_2^1 \left(\frac{dq}{T}\right)_{R1} + \int_2^1 \left(\frac{dq}{T}\right)_I < 0$$

$$- \int_2^1 ds + \int_2^1 \left(\frac{dq}{T}\right)_I < 0$$

$$\Rightarrow \left(\frac{dq}{T}\right)_I < ds$$

$$\therefore ds = \left(\frac{dq}{T}\right)_{\text{process}} + dS_G \quad \downarrow \text{Entropy generation}$$

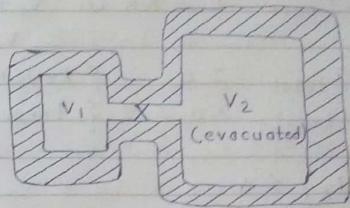
$$dS_G = 0 \quad \{ \text{Reversible Process} \}$$

$$\left(\frac{dq}{T}\right)_{\text{process}} \equiv \text{heat interaction b/w}$$

the system and surrounding during that process.

To calculate entropy change for an irreversible process, devise a reversible path connecting the initial and final states.

Free expansion :-



$$V_1 \rightarrow V_1 + V_2$$

$$q = 0$$

$$\Delta T = 0$$

Irreversible

$$dq = dU + pdV$$

$$\int dq = \int nRT dV$$

$$\int dq = nRT \ln \left( \frac{V_1 + V_2}{V_1} \right)$$

$$\left(\frac{\int dq}{T}\right)_{\text{sys}} = \frac{nR \ln (1 + v_2)}{v_1}$$

$$ds = nR \ln \left( \frac{1 + v_2}{v_1} \right) > 0$$

For an isolated system,

$$dq = 0 \quad dW = 0 \quad \therefore \frac{dq}{T} = 0$$

$$ds = dS_G$$

$$\therefore (ds)_{\text{isolated}} > 0$$

$$\begin{aligned} \delta q - \delta W &= dU^0 \\ \delta q &= \delta W \\ \int \delta q = \int pdV_{V_1+V_2} & \quad \text{Date } / / \\ \int \delta q = RT \int dv & \quad \left. \begin{array}{l} \text{Reversible} \\ \text{Isothermal expansion} \\ (V_1+V_2) \end{array} \right\} \\ \delta S_{\text{total}} = 0 & \quad \left. \begin{array}{l} \text{Assuming} \\ \text{sys. \&} \\ \text{surrounding} \\ \text{as the} \\ \text{system} \end{array} \right\} \end{aligned}$$

$$\begin{aligned} (ds)_{\text{sys}} &= NR \ln \frac{V_1+V_2}{V_1} \\ (ds)_{\text{surr}} &= -NR \ln \frac{V_1+V_2}{V_1} \\ (ds)_{\text{total}} &= 0 \quad \left. \begin{array}{l} \text{Reversible process} \\ \text{Irreversible} \end{array} \right\} \\ (ds)_{\text{total}} &> 0 \end{aligned}$$

$$1. \quad \oint \left( \frac{\delta q}{T} \right) \leq 0$$

$$2. \quad ds \geq \left( \frac{\delta q}{T} \right)$$

Adiabatic :  $\delta q = 0$

$$\rightarrow ds > 0$$

$ds = 0$  Reversible Adiabatic Process

$ds > 0$  Irreversible " "

or  $ds = dS_G$ , implies entropy is always generated and sign of  $dS_G$  is always positive

$\rightarrow$  All reversible adiabatic processes are isentropic. (No change in entropy)

Converse of the statement may not be true.

Irreversible isentropic process is also possible.

Experimentally, a liquid flowing through a pipe with friction and the heat generated is lost to the surroundings.

Any irreversible non-adiabatic process such that heat is lost and entropy is generated can be isentropic.

$$ds = \delta q + dS_G$$

$$\Rightarrow dS_G = \left( - \frac{\delta q}{T} \right) \Rightarrow ds = 0$$

For an isolated system,

$$\delta W = 0$$

$$\delta q = 0$$

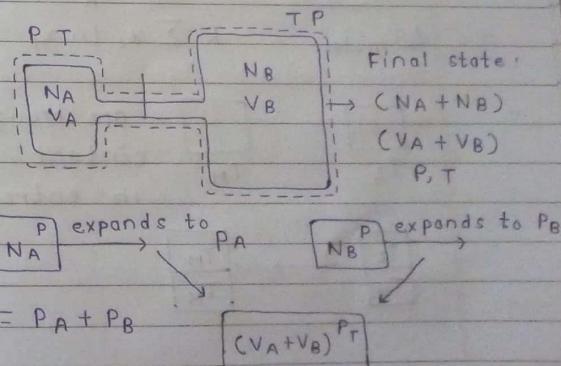
$(ds)_{\text{isolated}} \geq 0 \quad \left. \begin{array}{l} \{ (ds)_{\text{surr}} + (ds)_{\text{sys}} \} \geq 0 \end{array} \right\}$

$(ds)_{\text{iso}} > 0 \Rightarrow \text{process feasible}$

$(ds)_{\text{iso}} = 0 \Rightarrow \text{process feasible in both dir or Reversible process}$

$(ds)_{\text{iso}} < 0 \Rightarrow \text{Process infeasible in forward direction}$

### Mixing of Gases :-



Mixing of the two gases can be assumed to be made up of two reversible processes

1. Rev. Isoth Expansion of Gas  $P \rightarrow P$   
2. Diffusion of Gas 1 at  $P_1$  through a Spar

$$\Delta S_{sys} = \Delta S_{gas A} + \Delta S_{gas B} + \Delta S$$

For isothermal process,  $V_A + V_B$

$$dq_A = \int_{V_A}^{V_A+V_B} p dV = \int_{V_A}^{V_A+V_B} n_A R T dV$$

$$dq_A = n_A R T \ln \left( \frac{V_A+V_B}{V_A} \right)$$

$$dq_A = n_A R \ln \left( \frac{V_A+V_B}{V_A} \right)$$

$$\Delta S_{gas A} = n_A R \ln \left( \frac{V_A+V_B}{V_A} \right)$$

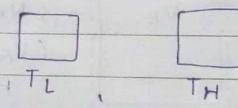
$$\Delta S_{gas B} = n_B R \ln \left( \frac{V_A+V_B}{V_B} \right)$$

$$\Delta S_{sys} = n_A R \ln \left( \frac{V_A+V_B}{V_A} \right) + n_B R \ln \left( \frac{V_A+V_B}{V_B} \right)$$

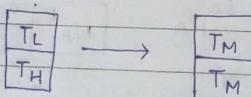
$$\ln \left( \frac{V_A+V_B}{V_B} \right)$$

$$\Delta S_{sys} = n_A R \ln \left( \frac{P}{P_A} \right) + n_B R \ln \left( \frac{P}{P_B} \right)$$

$$\Delta S_{motor} = -R \sum x_i \ln x_i$$



are brought in contact. Find change in entropy.



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(Saathi)

Let us assume that the two blocks are identical in all aspects and have the same specific heat capacity  $S$ .

When the two blocks are brought together, heat transfer takes place but this is an irreversible process. We need to devise a reversible path. To do this we imagine a large number of heat reservoirs at varying temperatures in the range  $T_H - dT \dots dT + T_L$ . The bricks are put in contact with them sequentially to raise the temp. of one and lower the temp. of the other in a reversible manner.

Heat exchange at any step is given by  $dq = CdT$ .

Now,

Assume after thermal equilibrium they have temp.  $\neq T_M$ .

$$\begin{aligned} \Delta S_{hot block} &= \int_{T_H}^{T_M} C dT = C \ln T \Big|_{T_H}^{T_M} \\ &= C \ln \left( \frac{T_M}{T_H} \right) < 0 \end{aligned}$$

$$\Delta S_{\text{cold brick}} = \int_{T_L}^{T_M} C dT = C \ln T \Big|_{T_L}^{T_M} \\ = C \ln \left( \frac{T_M}{T_L} \right) > 0$$

The total entropy change of the two blocks is

$$\Delta S_{\text{blocks}} = c \ln \left( \frac{T_M}{T_H} \right) + c \ln \left( \frac{T_H}{T_L} \right) \\ = c \left\{ \ln \left( \frac{T_M}{T_H} \right) + \ln \left( \frac{T_H}{T_L} \right) \right\} \\ = c \ln \left( \frac{T_M^2}{T_H T_L} \right)$$

Assuming that heat lost by one block is gained by the other block completely,

$$mS(T_H - T_M) = mS(T_M - T_L)$$

$$T_H - T_M = T_M - T_L$$

$$T_H + T_L = 2T_M$$

2

Substituting  $T_M$  in ①

$$\Delta S_{\text{blocks}} = c \ln \left\{ \frac{(T_H + T_L)^2}{4 T_H T_L} \right\} > 0$$

Date 02/02/2018

From Combined First and Second Law

$$dU = dq - dw \quad (\text{Closed System, Any Process})$$

$$dq = dU + PdV \quad (\text{For only PV work})$$

$$TdS \geq dq \quad (\text{Closed system, any process})$$

$$TdS \geq dq$$

Assuming only PV work  $dq = dU + pdV$   
(System and surroundings are in thermal equilibrium).

1. At const. volume : -  $dV = 0$

$$TdS \geq (dU)_V$$

For constant S and V

$$(dU)_{S,V} \leq 0$$

2. At const. pressure : -  $dP = 0$

$$TdS \geq dU + d(PV)$$

$$TdS \geq (dH)_P$$

At constant S and P

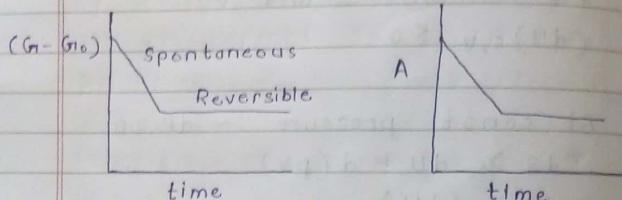
$$(dH)_{S,P} \leq 0$$

Criteria of spontaneity :-

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$$\begin{aligned}
 TdS &> dq \\
 d(TS) - SdT &> dU + pdV \\
 &> dU + d(pV) - Vdp \\
 &> d(U + pV) - Vdp \\
 &> dH - Vdp \\
 d(H - TS) &> Vdp - SdT \\
 (dG)_{T, P} &\leq 0 \quad \{ \text{constant } T \text{ and } P \}
 \end{aligned}$$

$$\begin{aligned}
 d(TS) - SdT &> dU + pdV \\
 d(TS) - SdT &> dU + pdV \\
 - SdT - pdV &\geq d(U - TS) \\
 \text{At constant } T \text{ and } V \\
 d(U - TS) &\leq 0 \\
 (dA)_{T, V} &\leq 0 \quad \{ \text{Helmholtz free energy} \}
 \end{aligned}$$



$$\Delta g_{vap} \Big|_{100^\circ C} = 0.03 kJ \quad \{ \text{reversible} \}$$

$$\Delta g_{vap} \Big|_{90^\circ C} = 1.092 kJ \quad \{ \text{condensation} \}$$

$$\Delta g_{vap} \Big|_{110^\circ C} = -1.085 kJ \quad \{ \text{vapourisation} \}$$

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$$G_f = H - TS$$

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

At higher and higher temp., it's the entropy (or randomness) that matters. Processes non-spontaneous at <sup>low</sup> temp. becomes possible at high temp.

If non P-V work also occurs -

$$dq = dU + pdV + dW_{\text{non-pV}}$$

$$TdS \geq (dU)_V + dW_{\text{non-pV}}$$

For constant V and S,

$$(dU)_{S, V} + dW_{\text{non-pV}} \leq 0 \quad -1$$

At constant S and P,

$$(dH)_{S, P} + (dW_{\text{non-pV}}) \leq 0 \quad -2$$

$$(dA)_{T, V} + dW_{\text{non-pV}} \leq 0 \quad -3$$

$$(dG)_{T, P} + dW_{\text{non-pV}} \leq 0 \quad -4$$

The four eq's give the maximum non PV work.

$$(dG_f + dW_{\text{non-pV}}) \leq 0$$

$$(dG_f) \leq -dW_{\text{non-pV}}$$

$$(-dG_f) \geq dW_{\text{non-pV}}$$

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- Work done by system is either greater than (irreversible) or equal to (reversible) decrease in Gibbs free energy for constant T and P, e.g. in exothermic process.

- Work done on system is either greater than (irreversible) or equal to (reversible) increase in Gibbs free energy for constant T and P, e.g. in endothermic process.

→ Applicable only to closed systems.

By analogy with mechanics, U, H, A, G can be termed as thermodynamic potentials.

### Properties of Thermodynamic Potentials

- Are extensive (additive in nature)
- Decides the criteria of spontaneity
- Gives the useful non PV work.

From 1<sup>st</sup> Law:-

$$dU = dq - dw$$

For a reversible process with only

P-V work : (Closed system)  
 $dU = TdS - pdV$  { depends only on the initial and final equilibrium states. Valid for both reversible and irreversible processes }

$$dH = TdS + Vdp$$

$$dG = - SdT + Vdp$$

These are the Maxwell's relations

$$P(x,y) : dP = Mdx + Ndy$$

$$\frac{\partial^2 P}{\partial x \partial y} = \frac{\partial^2 P}{\partial y \partial x}$$

$$\left( \frac{\partial M}{\partial y} \right)_x = \left( \frac{\partial N}{\partial x} \right)_y$$

$$\left( \frac{\partial M}{\partial T} \right)_P = -S$$

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

$$G = H - TS$$

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

$$= -\frac{H}{T^2} + \frac{C_p}{T} - \left( \frac{\partial H}{\partial T} \right)_P \left( \frac{\partial S}{\partial T} \right)_P$$

$$= -\frac{H}{T^2} + \frac{C_p}{T} - \frac{C_p}{T}$$

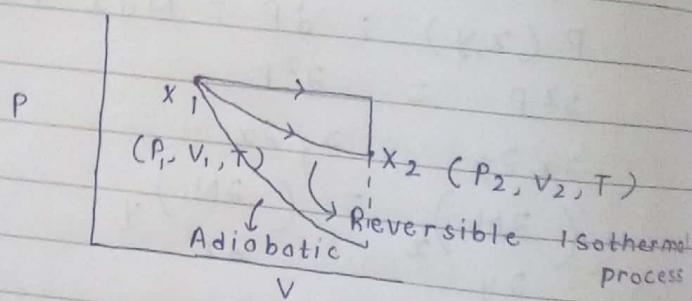
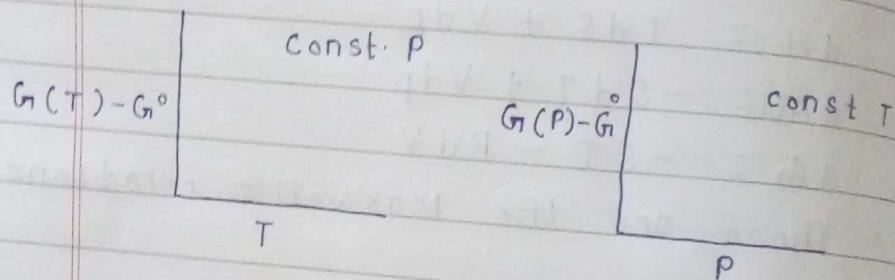
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$$\left[ \frac{\partial (G/T)}{\partial T} \right]_P = -\frac{H}{T^2}$$

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

→ Gibbs Helmholtz Eq<sup>n</sup>.



All processes are reversible. Ideal gas.

Find  $\delta q$  and  $\delta q/T$ .

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$$ds = \left(\frac{\partial s}{\partial v}\right)_T dv + \left(\frac{\partial s}{\partial T}\right)_v dT$$

$$ds = \left(\frac{\partial p}{\partial T}\right)_v dv + \frac{C_v}{T} dT$$

$$TdS = T \left(\frac{\partial p}{\partial T}\right)_v dv + C_v dT$$

$$* TdS = C_v dT + \frac{B}{K} T dv$$

$$ds = \left(\frac{\partial s}{\partial p}\right)_T dp + \left(\frac{\partial s}{\partial T}\right)_p dT$$

$$ds = -\left(\frac{\partial v}{\partial T}\right)_p dp + \frac{C_p}{T} dT$$

$$TdS = -T \left(\frac{\partial v}{\partial T}\right)_p dp + C_p dT$$

$$* TdS = C_p dT - v \beta T dp$$

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

$$dU = T \left(\frac{\partial p}{\partial T}\right)_V dv + C_v dT - pdv$$

$$dU = C_v dT + \left[T \left(\frac{\partial p}{\partial T}\right)_V - p\right] dv$$

$$* dU = C_v dT + \left[\frac{T \alpha - P}{K}\right] dv$$

Maxwell's eqn has been used.

For ideal gas,

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

$$\left(\frac{\partial U}{\partial P}\right)_T = 0$$

$$dU = C_v dT$$

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$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T} \quad \left(\frac{\partial S}{\partial P}\right)_T = \frac{C_P}{T}$$

Molar quantities.

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$$PV = RT$$

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

$$T \left(\frac{\partial P}{\partial T}\right)_V = RT = P$$

$$dU = C_v dT + \left[T \left(\frac{\partial P}{\partial T}\right)_V - P\right] dv$$

$$\therefore dU = -C_v dT + T \left(\frac{\partial P}{\partial T}\right)_V dv$$

$$dU = T ds - P dv$$

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

$$= T \left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\left(\frac{\partial U}{\partial V}\right)_T = RT - P = P - P = 0$$

$$dU = T dS - P dv$$

$$\left(\frac{\partial U}{\partial P}\right)_T = T \left(\frac{\partial S}{\partial P}\right)_T - \frac{\partial (P dv)}{\partial P}$$

$$= T \left(-\frac{\partial v}{\partial T}\right)_P - \frac{\partial (P dv)}{\partial P}$$

$$= -RT - \frac{\partial (P dv)}{\partial P}$$

$$= -v + v$$

$$= 0$$

$$\left(\frac{\partial U}{\partial P}\right)_T = 0$$

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From the  $\left(\frac{\partial u}{\partial p}\right)_T \left(\frac{\partial p}{\partial v}\right)_T = \left(\frac{\partial u}{\partial v}\right)_T$

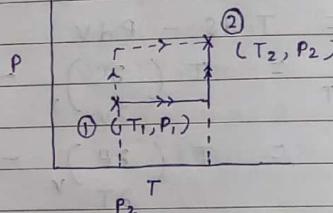
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$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP$$

$$dh = Cp dT + \left(T \left(\frac{\partial s}{\partial P}\right)_T + v\right) dP$$

$$dh = Cp dT + \left(-T \left(\frac{\partial v}{\partial T}\right)_P + v\right) dP$$

\*  $dh = Cp dT + v(1 - \beta T) dP$



$$(h_2 - h_1) = \int_{P_1}^{P_2} \left[ v - T \left(\frac{\partial v}{\partial T}\right)_P \right] dP + \int_{T_1}^{T_2} (C_p) dT$$

$$(h_2 - h_1) = \int_{T_1}^{T_2} (C_p) dT + \int_{P_1}^{P_2} \left[ v - T \left(\frac{\partial v}{\partial T}\right)_P \right] dP$$

$$\begin{aligned} \left(\frac{\partial C_p}{\partial T}\right)_P &= \left[ \frac{\partial}{\partial P} \left( \frac{\partial h}{\partial T} \right)_P \right]_T \\ &= \left[ \frac{\partial}{\partial T} \left( \frac{\partial h}{\partial P} \right)_T \right]_P \\ &= \left[ \frac{\partial}{\partial T} \left[ v - T \left(\frac{\partial v}{\partial T}\right)_P \right]_T \right]_P \end{aligned}$$

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$$\begin{aligned} &= \left(\frac{\partial v}{\partial T}\right)_P - T \left(\frac{\partial^2 v}{\partial T^2}\right)_P - \left(\frac{\partial v}{\partial T}\right)_P \\ * \quad \left(\frac{\partial C_p}{\partial P}\right)_T &= -T \left(\frac{\partial^2 v}{\partial T^2}\right)_P \\ C_p|_{P_1} - C_p|_{P_0} &\stackrel{\text{known}}{=} - \int_{P_0}^{P_1} T \left(\frac{\partial^2 v}{\partial T^2}\right)_P dP \end{aligned}$$

$$\begin{aligned} h_2 - h_1 &= \int_{P_1}^{P_0} \left(\frac{\partial h}{\partial P}\right)_{T=T_1} dP + \int_{T_1}^{T_2} C_p dT \\ &\quad + \int_{P_0}^{P_2} \left(\frac{\partial h}{\partial P}\right)_{T=T_2} dP \end{aligned}$$

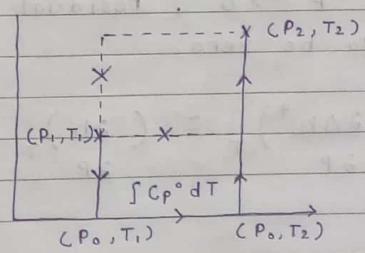
Measurable Properties: - T, P, v, β, K

Unmeasurable → : - s, h, g, a, u

$$TdS = Cp dT - T \left(\frac{\partial v}{\partial T}\right)_P dP$$

$$TdS = Cv dT + T \left(\frac{\partial P}{\partial V}\right)_T dV$$

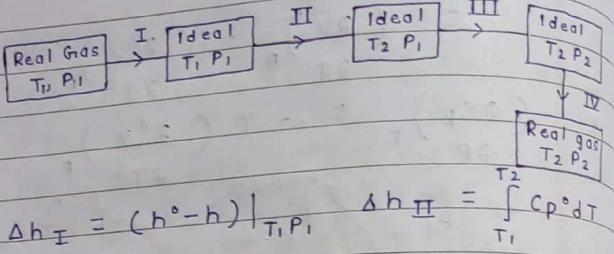
$$dh = Cp dT + \left[v - T \left(\frac{\partial v}{\partial T}\right)_P\right] dP$$



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$$\Delta h_{III} = h^\circ_{T_2, P_2} - h^\circ_{T_1, P_1} = 0 \quad \Delta h_{IV} = (h - h^\circ)$$

$$h_2 - h_1 = (h^\circ - h)|_{T_1, P_1} + \int_{T_1}^{T_2} C_p^\circ dT + (h - h^\circ)$$

$$\Delta h^*_{T, P} = (h - h^\circ)|_{T, P} \quad \text{Residual properties}$$

$$h_2 - h_1 = -\Delta h^*|_{T_1, P_1} + \Delta h^*|_{T_2, P_2} + \int_{T_1}^{T_2} C_p dT$$

$$s_2 - s_1 = -\Delta s^*|_{T_1, P_1} + \int_{T_1}^{T_2} C_p^\circ dT - \int_{P_1}^{P_2} R dP$$

$$+ \Delta s^*|_{T_2, P_2}$$

$$\Delta g^*|_{T, P} = (g - g^\circ)|_{T, P} = \Delta h^* - T \Delta s^*$$

$$\Delta G^*|_{T, P} = \Delta H^* - T \Delta s^*$$

\* If  $P \rightarrow 0$ , residual properties will also be zero.

$$\left( \frac{\partial \Delta h^*}{\partial P} \right)_T = \left( \frac{\partial h}{\partial P} \right)_T - \left( \frac{\partial h^\circ}{\partial P} \right)_T$$

$$\Delta h^* = \int_0^P \left( \frac{\partial h}{\partial P} \right)_T dP$$

$$\Delta h^* = \int_0^P [V - T(\frac{\partial V}{\partial T})_P] dP$$

$$= \int_0^P V dP - T \int_0^P \left( \frac{\partial V}{\partial T} \right)_P dP$$

$$\Delta s^* = S - S^\circ$$

$$\left( \frac{\partial \Delta s^*}{\partial P} \right)_T = \left( \frac{\partial s}{\partial P} \right)_T - \left( \frac{\partial s^\circ}{\partial P} \right)_T$$

Using Maxwell's relations gives,

$$= -\left( \frac{\partial V}{\partial T} \right)_P - R$$

$$\Delta s^* = - \int_0^P \left[ \left( \frac{\partial V}{\partial T} \right)_P + R \right] dP$$

$$V dP = d(PV) - P dV$$

$$\Delta h^* = \int_{RT}^{PV} d(PV) - \int_{V=V_\infty}^V P dV - T \int_{0}^P \left( \frac{\partial V}{\partial T} \right)_P dP$$

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

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

$$\Delta h^* = (PV - RT) - \int_{V_\infty}^V P dV + T \int_{V_\infty}^V \left( \frac{\partial P}{\partial T} \right)_V dV$$

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$$\Delta S^* = \int_{V_\infty}^V \left[ \left( \frac{\partial P}{\partial T} \right)_V - \frac{R}{P} \right] dV$$

For eq<sup>n</sup>  $v = ZRT$

$$\left( \frac{\partial v}{\partial T} \right)_P = ZR + RT \left( \frac{\partial z}{\partial T} \right)_P$$

$$\Delta h^* = \int_p^p ZRT dp - \int_p^p (ZRT + RT^2 \frac{\partial z}{\partial T}) dp$$

$$\Delta h^* = - \int_p^p RT^2 \left( \frac{\partial z}{\partial T} \right)_P dp$$

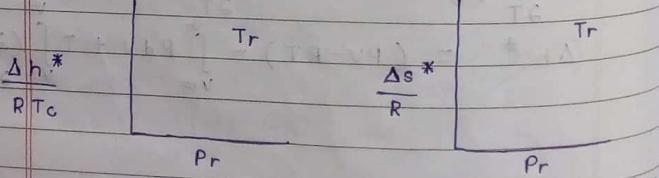
$$\Delta h^* = - \int_{P_r}^{P_r} R T_r^2 T_c^{-1} \left( \frac{\partial z}{\partial T_r} \right)_{P_r} dP_r$$

$$\Delta h^* = - \int_{P_r}^{P_r} R T_r^2 T_c^{-1} \left( \frac{\partial z}{\partial T_r} \right)_{P_r} dP_r$$

$$\Delta h^* = - \int_{R T_c}^0 T_r^2 \left( \frac{\partial z}{\partial T_r} \right)_{P_r} dP_r$$

( Reduced departure function (also follows the Law of Corresponding states). )

$$\Delta S^* = f^n(z, T_r, P_r)$$



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All departure f<sup>n</sup>'s can be expressed as a unique f<sup>n</sup> of reduced properties (Tr and Pr).

$\Delta C_P^*$  also follows Law of corresponding states.

$$\Delta S^* = - \int_p^p \left( \frac{\partial v}{\partial T} \right)_P dp + R \int_p^p \frac{dp}{P}$$

$$v = ZRT ; \left( \frac{\partial v}{\partial T} \right)_P = ZR + RT \left( \frac{\partial z}{\partial T} \right)_P$$

$$\Delta S^* = - \int_p^p \left( (ZR + RT \left( \frac{\partial z}{\partial T} \right)_P) + R \right) dp$$

$$\Delta S^* = - \int_p^p \left( Z + T \left( \frac{\partial z}{\partial T} \right)_P + 1 \right) dp$$

$$\Delta S^* = - Tr \int_{P_r}^0 \left( \frac{\partial z}{\partial T_r} \right)_{P_r} dP_r - \int_{P_r}^0 (z-1) dP_r$$

$$d(\Delta U^*) = T(d\Delta S^*) - Pd(\Delta V^*)$$

All the eq<sup>n</sup>'s are applicable to total as well as residual properties.

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Value of  $(C_p - C_v)$  for Real Gas

$$T dS = Cv dT - T \left( \frac{\partial P}{\partial T} \right)_V dV$$

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

$$(C_p - C_v) dT = \left[ \left( \frac{\partial V}{\partial T} \right)_P dV + \left( \frac{\partial P}{\partial T} \right)_V dP \right]$$

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

$$C_p - C_v = \frac{C_p - C_v}{C_p - C_v}$$

$$\text{But, } T \left( \frac{\partial V}{\partial T} \right)_P dP = \left( \frac{\partial T}{\partial P} \right)_V dP$$

Comparing 1. and 2. gives

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

Also,

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

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

Now,  $PV = RT$

$$\therefore \left( \frac{\partial V}{\partial T} \right)_P = \frac{R}{P}, \quad \left( \frac{\partial P}{\partial V} \right)_T = -\frac{R}{V^2}$$

Substituting this in the boxed eq

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

+ive ↓      -ive ↓

∴ The whole RHS will be +ive.

1.  $C_p > C_v$  { always }
2. For ideal gas,  $C_p - C_v = R$

3. At 0 K,  
 $C_p = C_v$

$C_p = C_v$  also  
possible if  $\left( \frac{\partial V}{\partial T} \right)_P = 0$   
i.e.,  $V = V_{\min}$  or  
 $P = P_{\max}$

Water at 4°C,  $C_p = C_v$

\*  $dS = 0$  (isentropic)

$$(C_p dT)_s = T \left( \frac{\partial V}{\partial P} \right)_s dP_s$$

$$(C_v dT)_s = -T \left( \frac{\partial P}{\partial T} \right)_V (dV)_s$$

$$\left( \mu_s = \left( \frac{\partial I}{\partial P} \right)_s = T \left( \frac{\partial V}{\partial T} \right)_P \right)$$

isentropic coefficient.

\*  $dh = 0$

$$dh = C_p dT + \left[ V - T \left( \frac{\partial V}{\partial T} \right)_P \right] dP$$

$$\left( \mu_H = \left( \frac{\partial H}{\partial P} \right)_T = \frac{1}{C_p} \left[ T \left( \frac{\partial V}{\partial T} \right)_P - V \right] \right)$$

Joule Thomson Coefficient.

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

$$\Rightarrow \frac{\mu_H}{\mu_S} > 1 \quad \text{and} \quad \left(\frac{\partial T}{\partial P}\right)_H > \left(\frac{\partial T}{\partial P}\right)_S$$

For ideal gas,

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

$$\therefore \frac{\mu_H}{\mu_S} = \frac{T}{P} - \frac{V}{C_p} = \frac{V}{C_p} - \frac{V}{C_p} = 0$$

Under isentropic condition ( $dS=0$ )  
 $C_p/C_v$  (for real gases).

$$C_p = \frac{1}{V} \frac{\partial V}{\partial T} dP$$

$$C_v = \frac{-P}{T} \frac{\partial T}{\partial V} dP$$

$$\Rightarrow \frac{C_p}{C_v} = -V K \left(\frac{\partial P}{\partial V}\right)_S$$

$$\Rightarrow \frac{C_p}{C_v} = \left(\frac{\partial V}{\partial P}\right)_T \left(\frac{dP}{dV}\right)_S$$

Now,

$$dh = T ds - V dp \Rightarrow \left(\frac{\partial h}{\partial P}\right)_S = -V$$

$$du = T ds + pdV \Rightarrow \left(\frac{\partial u}{\partial V}\right)_S = P$$

By definition,

$$r_s = \left(\frac{\partial h}{\partial u}\right)_S$$

Exponent of an isentropic process

$$\gamma = -V \left(\frac{\partial P}{\partial V}\right)_S$$

For an ideal gas,

$$r_s = -V \left(\frac{\partial P}{\partial V}\right)_S = \frac{C_p}{C_v}$$

Q. The longitudinal velocity of sound  
 $u = \sqrt{\left(\frac{\partial P}{\partial V}\right)_S}$

Prove for ideal gas,  
 $u = \sqrt{r P}$

$\because S$  is constant, adiabatic process.  
 $P V^\gamma = K$  (ideal gas)

From definition,

$$V = M/P$$

$$\therefore P (M)^\gamma = K$$

$$\Rightarrow P P^{-\gamma} = K$$

$$\ln P - \gamma \ln P = \ln K$$

$$\frac{dp}{P} - \gamma \frac{dp}{P} = 0$$

$$\frac{dp}{P} = \gamma \frac{dp}{P}$$

$$\left(\frac{\partial P}{\partial V}\right)_S = \gamma P$$

$$* \left( \frac{\partial C_p}{\partial P} \right)_T = -T \left( \frac{\sigma}{\partial T^2} \right)_P$$

$$C_{p,0}(P, T) = C_p^0(P=0, T) - T \int_{P=0}^P \left( \frac{\partial^2 C_p}{\partial T^2} \right)_P dP$$

$$\therefore u = \sqrt{rP}$$

Concept of Chemical Potential  
- Homogeneous Open Systems

For an open system;

$$dU = \left( \frac{\partial U}{\partial S} \right)_{V,n} dS + \left( \frac{\partial U}{\partial V} \right)_{S,n} dV +$$

$$\left( \frac{\partial U}{\partial n} \right) \neq u$$

$$dH = \dots + \left( \frac{\partial H}{\partial n} \right) \neq n$$

$$dA = \dots + \left( \frac{\partial A}{\partial n} \right) \neq a$$

$$dG = \left( \frac{\partial G}{\partial T} \right)_{P,n} dT + \left( \frac{\partial G}{\partial P} \right)_{T,n} dP +$$

$$\left( \frac{\partial G}{\partial n} \right) = g$$

$$U = un$$

$$\left( \frac{\partial U}{\partial n} \right)_{S,V} = u + n \left( \frac{\partial u}{\partial n} \right)_{S,V}$$

$$\left( \frac{\partial U}{\partial n} \right)_{S,V} \neq u$$

$$dU = TdS - pdV$$

$$\Rightarrow (dU)_{S,V} = 0 \quad \{ \text{if } s \text{ and } v \text{ are constant} \}$$

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$$S = ns, V = nv$$

$$\left( \frac{\partial U}{\partial n} \right)_{S,V} \neq \left( \frac{\partial U}{\partial n} \right)_{S,V} \neq u$$

$$G = ng$$

$$\left( \frac{\partial G}{\partial n} \right)_{T,P} = g + n \left( \frac{\partial g}{\partial n} \right)_{T,P}$$

$$dg = -SdT + Vdp$$

$$(dg)_{T,P} = 0$$

$$\therefore \left( \frac{\partial g}{\partial n} \right)_{T,P} = 0$$

$$\therefore \left( \frac{\partial G}{\partial n} \right)_{T,P} = g$$

$$dU = TdS - pdV$$

$$dU = d(TS) - SdT - [d(pV) - Vdp]$$

$$dU = ndu + udn$$

$$= n[Tds - vdp] + udn$$

$$dU = [Td(ns) - Tsdn] - [P(d(nv)) - pdn]$$

$$= Tds - Tsdn - pdV + pdn + udn$$

At constant T and P,  $(dG)_{T,P} = 0$

$$dG = (\partial G) dn_1 + (\partial G) dn_2 = 0$$

$\rightarrow \mu_1 \rightarrow \mu_2$

$$\sum n_i \mu_i = 0$$

$$TdS = dU + pdV - \mu dn$$

$$d(TS) - SdT = dU + d(pV) - Vdp$$

$+ -d(n\mu) - nd\mu$

$$d(U + PV - TS) = -SdT + Vdp + nd\mu$$

$-d(n\mu)$

$$dG^{\circ} = -SdT + Vdp + \cancel{nd\mu} - \cancel{dG^{\circ}}$$

$\left( -SdT + Vdp + nd\mu = 0 \right)$

Gibbs Duhem Equation for 1 component.

For multi-component system,

$$-SdT + Vdp + \sum n_i d\mu_i = 0$$

All P, T and potential cannot be changed simultaneously.