Thermodynamic system

① **Open System**

Matter and energy both exchange

② **Closed System**

only energy exchange

③ **Isolated**

neither matter or neither energy exchange

④ → **Homogeneous**

Single Phase

→ **Hetrogeneous**

More than one Phase

Thermodynamics Propertiet

Intensive

* Not depend on Mass or quantity of System
  - → Density, [illegible]
  - → Temp., Pressure
  - → Heat, Refective Index
  - → Surface tension.

Extensive

* depend on quantity of System

Mass, Volume, energy, enthalpy entropy, etc.

* Some Intensive property derive from extensive property
  e.g. specific Volume, specific Heat, density

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* If X and Y intensive then $X+Y$, XY, $\frac{X}{Y}$, $\frac{\partial X}{\partial Y}$ will also intensive

* If X and y extensive then $X+Y$ will be extensive But $\frac{X}{Y}$ and $\frac{\partial X}{\partial Y}$ are Intensive

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Thermodynamic Process

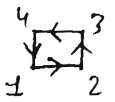
① Isothermal $\boxed{dT=0}$

② Isobaric Process $\boxed{dP=0}$

③ Isochoric $\boxed{dV=0}$

④ Adiabatic $\boxed{dQ=0}$
or (~~Isentric process~~)
(~~Isentropic~~)

④ Cyclic $\boxed{dU=0}$, $\boxed{dH=0}$



1→2→3→4 ↑ $\boxed{\text{All Point function changes are zero}}$

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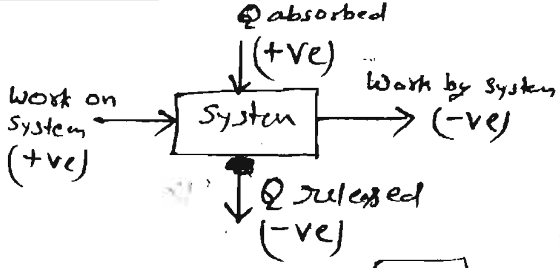
* Reversible process is ideal not in actual, it take Infinite time for completion, maxmium work obtained in this type process.

⇒ **First Law of Thermodynamic**

$$\Delta U = Q + W$$



Sign conversion

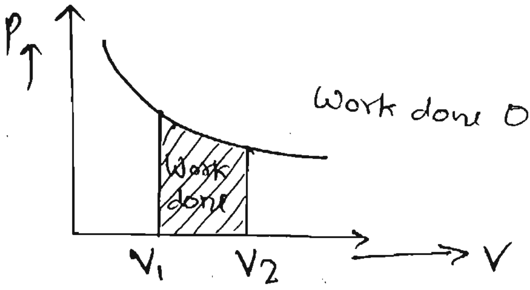
① for Work done on the system $\boxed{W}$ take $\boxed{+ve}$

② for work done by system $\boxed{W}$ take $\boxed{-ve}$

③ Heat absorbed by system $\boxed{Q}$ take $\boxed{+ve}$

④ Heat released by System $\boxed{Q}$ take $\boxed{-ve}$

⇒ **Work done** If gas enclosed in a Volume change its from V_1 to V_2, workdone $\boxed{W = \int_{V_1}^{V_2} P\,dV}$



Work done on P-V graph

⇒ **Point function** Property Value depend on Intial & final Stage. Internal energy, enthalpy, entropy

⇒ **Path function** change in property Value depend on path
e.g, work, heat.

⇒ **Thermodynamics criteria for irreversible process**

$$(\Delta G)_{T,P} < 0$$
$$(\Delta A)_{T,V} < 0$$
$$(\Delta U)_{S,V} < 0$$
$$(\Delta H)_{S,P} < 0$$

=> Limitation of first Law

① I^{st} Law does not tell the direction of Heat flow
" It say that the heat extracted from a cold object by further reducing its temp. But it does not say that we actually need an external Machine for doing so "

② It does not deny that all Heat converted in to work. while any Machine does not give 100% efficiency

③ It does not tell the difference b/w spontaneous and Non spontaneous process and why Natural spontaneous Process are irreversible.

④ It does not tell why certain chemical reach do not proceed to completion.

=> Heat capacity Relation

$$\boxed{\text{Heat capacity} = \frac{\Delta Q}{\Delta T}}$$

Required energy for 1°C change in temp

at const Volume

$$C_V = \frac{Q_V}{\Delta T}$$

$$\Delta U = Q + W = Q + \int P dV$$

$\boxed{\Delta U = Q}$ so $\boxed{C_V = \frac{\Delta U}{\Delta T}}$

at const pressure

$$C_P = \frac{Q_P}{\Delta T}, \quad H = U + PV$$

$$C_P = \frac{\Delta H}{\Delta T}$$

$w = -\int P dV$ in expansion

$$\Delta U = Q + W = Q - \int_{V_1}^{V_2} P dV$$

$$\Delta U = Q - P(V_2 - V_1)$$

$$U_2 - U_1 = Q - PV_2 + PV_1$$

$$(U_2 + PV_2) - (U_1 + PV_1) = Q$$

$$H_2 - H_1 = Q$$

$\Delta H = Q_P$ at cons P

then

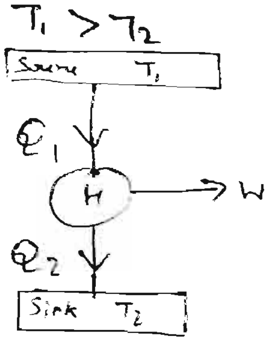
$$\boxed{C_V = \left(\frac{\partial U}{\partial T}\right)_V} \quad \boxed{C_P = \left(\frac{\partial H}{\partial T}\right)_P}$$

$$\boxed{\gamma = \frac{C_P}{C_V}} \quad \boxed{C_P - C_V = R}$$

⇒ Heat Engine

Performance of Heat engine measured by its efficiency

$$\eta = \frac{\text{Work output}}{\text{Heat Input}} = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$



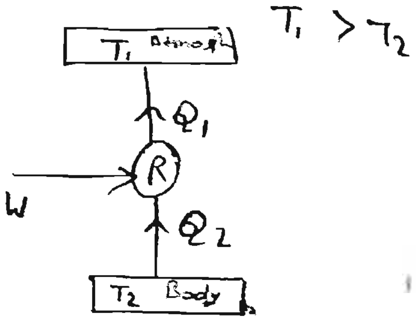
$$\boxed{\eta = 1 - \frac{Q_2}{Q_1}}$$

Since $Q \propto T$

$$\boxed{\eta = 1 - \frac{T_2}{T_1}}$$

⇒ Refrigerator

$$(COP)_R = \frac{\text{Heat removed}}{\text{Work Input}} = \frac{Q_2}{W}$$



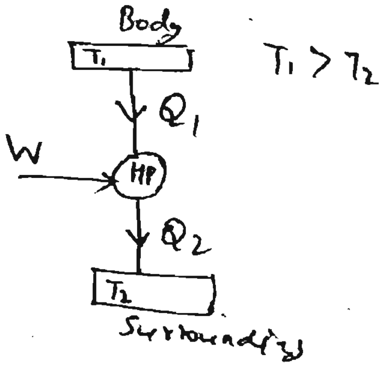
Now energy balance

$$W + Q_2 = Q_1 \Rightarrow W = Q_1 - Q_2$$

$$\boxed{(COP)_R = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}}$$

⇒ Heat pump

$$\boxed{(COP)_H = \frac{Q_1}{W} = \frac{Q_1}{Q_1 - Q_2} = \frac{T_1}{T_1 - T_2}}$$



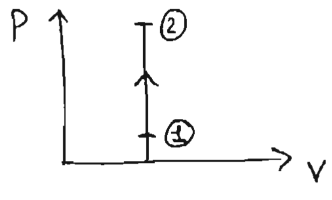
$H = R + 1$

$P_1V_1 = nRT_1$
$P_2V_2 = nRT_2$

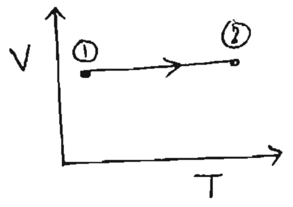
⇒ Isochoric Process ($dV = 0$)

* Work done $\boxed{W = \int P dV = 0}$

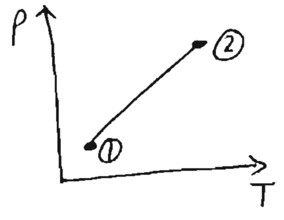
* Graph of Isochoric process



P-V graph



V-T graph



* Internal energy change $\Delta U = Q + W = Q_V + 0$

$$\boxed{\Delta U = nC_V \Delta T}$$

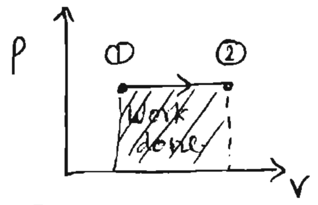
2

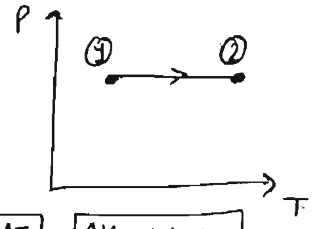
⇒ Isobaric Process ($dP = 0$)

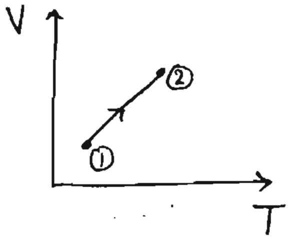
* Work done $W = \int P dV = P\int dV = P\,\Delta V$ where $\Delta V = V_2 - V_1$

$\boxed{W = nR\Delta T}$ $\boxed{\Delta T = T_2 - T_1}$

* Graph of Isobaric Process







* Internal energy $\boxed{\Delta U = nC_V \Delta T}$ $\boxed{\Delta H = nC_p \Delta T}$

⇒ Isothermal Process ($dT = 0$)

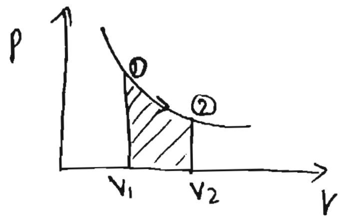
* $\boxed{\Delta U = nC_V \Delta T = 0}$, $\boxed{\Delta H = 0}$

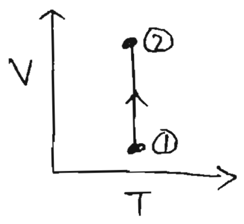
* $\Delta U = Q + W$ But $\Delta U = 0$ then $Q = -W$

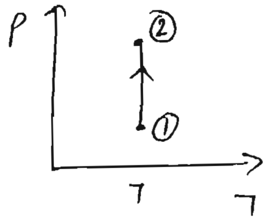
* $W = -nRT \ln\left(\frac{V_2}{V_1}\right) = RT \ln\left(\frac{P_2}{P_1}\right)$ Where $V_2 > V_1$

* $W = nRT \ln\left(\frac{V_1}{V_2}\right) = nRT \ln\left(\frac{P_2}{P_1}\right)$ Where $V_1 > V_2$

* Curve of Isothermal Process







Adiabatic Process (dQ = 0) (Reversible process) (expansion)

⊛ $\Delta U = Q + W = W$

⊛ work done $\boxed{W = \Delta U = nC_V\Delta T}$

But $W = -P\Delta V = -PdV$

then $C_V\,dT = -PdV = -\frac{RT\,dV}{V}$ (from $PV = RT$)

$$\int_1^2 \frac{dT}{T} = -\frac{R}{C_V}\int_1^2 \frac{dV}{V}$$

$$\ln\frac{T_2}{T_1} = -\frac{R}{C_V}\ln\frac{V_2}{V_1} = \frac{R}{C_V}\ln\frac{V_1}{V_2}$$

But $C_p - C_V = R \Rightarrow \frac{C_p}{C_V} - 1 = \frac{R}{C_V} \Rightarrow (\gamma - 1) = \frac{R}{C_V}$

then $\ln\frac{T_2}{T_1} = (\gamma - 1)\ln\frac{V_1}{V_2}$

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

and also $\boxed{PV^{\gamma} = \text{const}}$

$$\boxed{W = C_V\Delta T = \frac{R}{\gamma-1}\Delta T = \frac{R(T_2 - T_1)}{\gamma-1} = \frac{P_2V_2 - P_1V_1}{\gamma-1}}$$

⇒ Irreversible, Adiabatic, expansion. workdone

$\Delta U = W = 0$ when external pressure zero

$W = -P_{ext}(V_2 - V_1)$ when, $P_{external} < P_{gas}$

Important Points (All for Reversible, Closed, Ideal gas System)

① Adiabatic workdone $= C_v \Delta T = \frac{R\Delta T}{\gamma - 1} = \frac{R(T_2 - T_1)}{\gamma - 1} = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$

② $\Delta U = W$ in Adiabatic, $\boxed{P(V)^\gamma = \text{const}}$ $\gamma = \frac{C_p}{C_v}$

$\boxed{C_p - C_v = R}$

③ In Isochorohic Process Workdone $= 0$

④ In Isothermal $W = nRT \ln \frac{V_1}{V_2} = nRT \ln \frac{P_2}{P_1}$

⑤ In Throttling Process these condition apply

a) Adiabatic $P(V)^\gamma = \text{const}$

b) $\Delta H = 0$, $W = 0$, $Q = 0$

c) Isenthalpic, Irreversibble

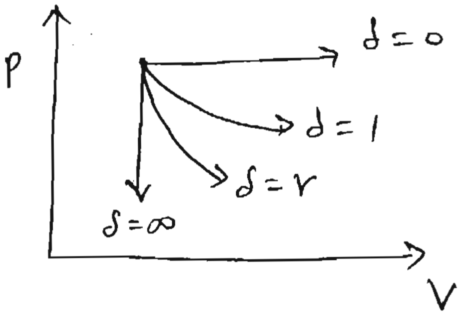
⑥ Polytropic Process $\boxed{P(V)^\delta = \text{const}}$

i) when $\delta = 0$ ⇒ Isobaric

ii) when $\delta = 1$ ⇒ Isothermal

iii) when $\delta = \gamma$ ⇒ Adiabatic

iv) when $\delta = \infty$ ⇒ Isochoric

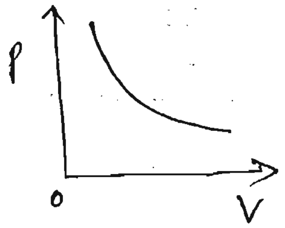


Workdone $W = \frac{P_2V_2 - P_1V_1}{\delta - 1}$

Heat Q $\quad Q = \left(\frac{\delta - \gamma}{\delta - 1}\right) nC_v (T_2 - T_1)$

⇒ Workdone in Polytropic

$$P(V)^{\delta} = \text{const} = k$$



$$W = -\int P\,dV$$

$$= -\int_1^2 \frac{k}{V^{\delta}}\,dV = -\int_1^2 k V^{-\delta}\,dV$$

$$= -k\left[\frac{V^{-\delta+1}}{-\delta+1}\right]_{V_1}^{V_2}$$ [illegible]

$$= -k\left(\frac{V^{1-\delta}}{1-\delta}\right)_{V_1}^{V_2} = \frac{-k}{1-\delta}\left(V_2^{1-\delta} - V_1^{1-\delta}\right)$$

[illegible] $$= \frac{-k}{1-\delta}\left(\frac{V_2}{V_2^{\delta}} - \frac{V_1}{V_1^{\delta}}\right)$$

$$= \frac{-k}{1-\delta}\left(\frac{V_2P_2}{k} - \frac{V_1P_1}{k}\right) = \frac{-1}{1-\delta}\left(P_2V_2 - P_1V_1\right)$$

$$\boxed{W = -\left(\frac{P_2V_2 - P_1V_1}{1-\delta}\right)}$$

Where $\delta \neq 1$
Its not apply for Isothermal

⇒ Q (Heat) $\Delta U = Q + W$

V.Imp

$$Q = \Delta U - W$$ [illegible]

$$\boxed{W = \left(\frac{P_2V_2 - P_1V_1}{\delta - 1}\right)} = \frac{nR(T_2 - T_1)}{\delta - 1}$$

$$C_p - C_v = R$$
$$\frac{C_p}{C_v} - 1 = \frac{R}{C_v}$$
$$(\gamma - 1) = \frac{R}{C_v}$$
$$C_v = R/(\gamma - 1)$$

then $$Q = nC_v\Delta T - nR\frac{(T_2 - T_1)}{\delta - 1}$$

$$= nC_v(T_2 - T_1) - nC_v\frac{(\gamma - 1)(T_2 - T_1)}{\delta - 1}$$

V.V Imp

$$= nC_v(T_2 - T_1)\left[1 - \frac{\gamma - 1}{\delta - 1}\right]$$

$$\boxed{Q = \left(\frac{\delta - \gamma}{\delta - 1}\right) nC_v(T_2 - T_1)}$$

Joule Thomson effect

* Joule thomson coeff.

$$\boxed{\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p}\left(\frac{2a}{RT} - b\right)}$$

* This process is isenthalpic process.

* the temp at which μ change sign its known as Inversion temp. of the gas.

* $\mu > 0$ Gas will show cooling effect in exapansion

$\mu < 0$ Gas will show warming effect in exapansion

* For an ideal gas $\mu = 0$

* for real gas μ take any value including zero ($-\infty$ to $+\infty$)

* At Inversion temp $\mu = 0$ then $b = \frac{2a}{RT_i}$

OR $\boxed{T_i = \frac{2a}{Rb}}$

Entropy (unit J/K-mol)

* Entropy is state function, Extensive property.

* Entropy is randomness or disorder of Molecules in System

* Difficult to determine the actual entropy of System becuz randomness is not a fixed Parameter.

* Entropy change at absolute temp (T)

$$\boxed{\Delta S = \int \frac{dq_{rev}}{T}}$$

Heat absorbed $Q \rightarrow +ve$ then $\Delta S = +ve$
Heat released $Q \rightarrow -ve$ then $\Delta S = -ve$

* By ↑se temp → Randomness ↑se → Entropy ↑se

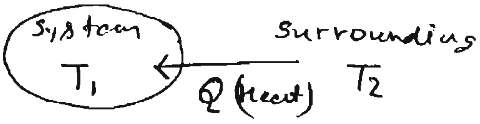
* In solid Molecules are fixed, so no randomness and entropy will be zero at ($T = 0K$) III^rd Law

* $\Delta S_{total} > 0$ for spontaneous, $\Delta S_{total} < 0$ for Nonspontaneous

(*) II^nd Law $\Delta S_{total} \geq 0$ | V. Imp

(*) In Irreversible

$\boxed{\Delta S > 0}$



$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$$

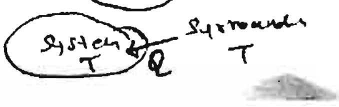
$$= +\frac{Q}{T_1} - \frac{Q}{T_2} = Q\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$\Delta S > 0$

(*) Reversible $\Delta S_{total} = 0$ $\Delta S_{total} = \Delta S_{system} + \Delta S_{surrounding}$

must $T_1 = T_2$

$$= +\frac{Q}{T} - \frac{Q}{T} = 0$$



⊛ When entropy is function of T, V

$$\boxed{\Delta S = nC_v \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{V_2}{V_1}\right)} \quad \text{———} ①$$

⊛ When entropy is function of T, P

$$\boxed{\Delta S = nC_p \ln\left(\frac{T_2}{T_1}\right) + nR\ln\left(\frac{P_1}{P_2}\right)} \quad \text{———} ②$$

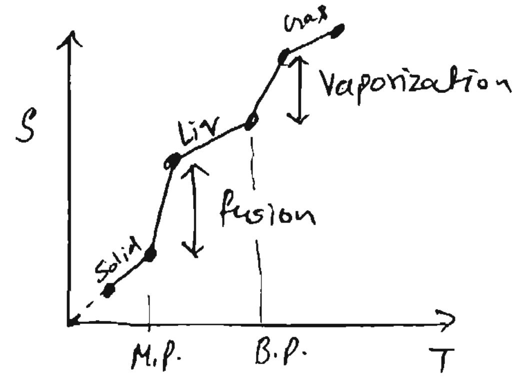
⊛ Entropy {↑se in expansion
↓se in compression}

⊛ Entropy change of Mix of Gas

$$\boxed{\Delta S_{mix} = -\sum R\, n_i \ln n_i}$$

$$\boxed{\Delta S_{\frac{mix}{mole}} = -\sum R\, n_i \ln n_i}$$

⇒ Tephigraph (Variation of Entropy V/S Temp.)



⊛ S ↑se with T

⊛ Entropy sudden ↑se during Phase change

$$\boxed{\text{Moiler diagram is H V/S S}}$$

PVT Relation

- Ideal gas Law $\boxed{PV = nRT}$
- at low pressure, high temp gas is considered Ideal
- Vanderwalls eqn $\boxed{\left(P + \frac{a}{V^2}\right)(V-b) = RT}$
- At critical condition $(T = T_c, P = P_c)$

$$\left(\frac{\partial P}{\partial V}\right)_T = \left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0$$

- Compressibility factor

$$\boxed{Z = \frac{PV}{RT}}$$

- Viral eqn $\boxed{Z = 1 + \frac{B}{V} + \frac{C}{V^2}}$
- Another form of Viral eqn

$$\boxed{Z = 1 + B'P + c'P^2}$$

=> First Law $\Delta U = Q + W$

=> work done in reversible process $W = -\int P dV$

=> Work done in irreversible process $W = -P_r \Delta V$, $(\Delta V = V_2 - V_1)$

=> Heat capacities $C = \frac{dQ}{dT}$

=> Heat capacities at const. volume $C_V = \left(\frac{\partial U}{\partial T}\right)_V$ where $dQ = dU$

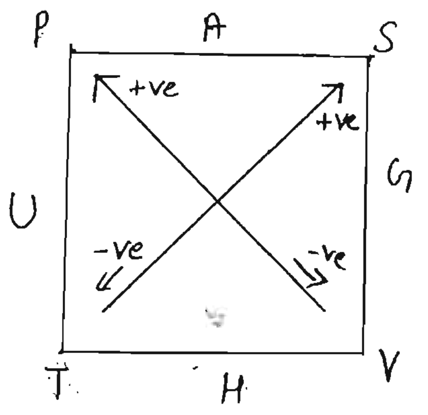
=> Heat capacities at const. pressure $C_P = \left(\frac{\partial H}{\partial T}\right)_P$ where $dQ = dH$

Thermodynamics Relation

⇒ Gibbs free energy $G = H - TS$

⇒ Helmholtz free Energy $A = U - TS$

⇒ Fundamental Property relation



$$dU = +T\,dS - P\,dV$$

$$dH = +T\,dS + V\,dP$$

$$dG = +V\,dP - S\,dT$$

$$dA = -S\,dT - P\,dV$$

⇒ Short Method $\boxed{(U\ H\ G\ A)}$

$\boxed{PASGVHTU}$

$dU = dW + dQ$ — Ist Law.

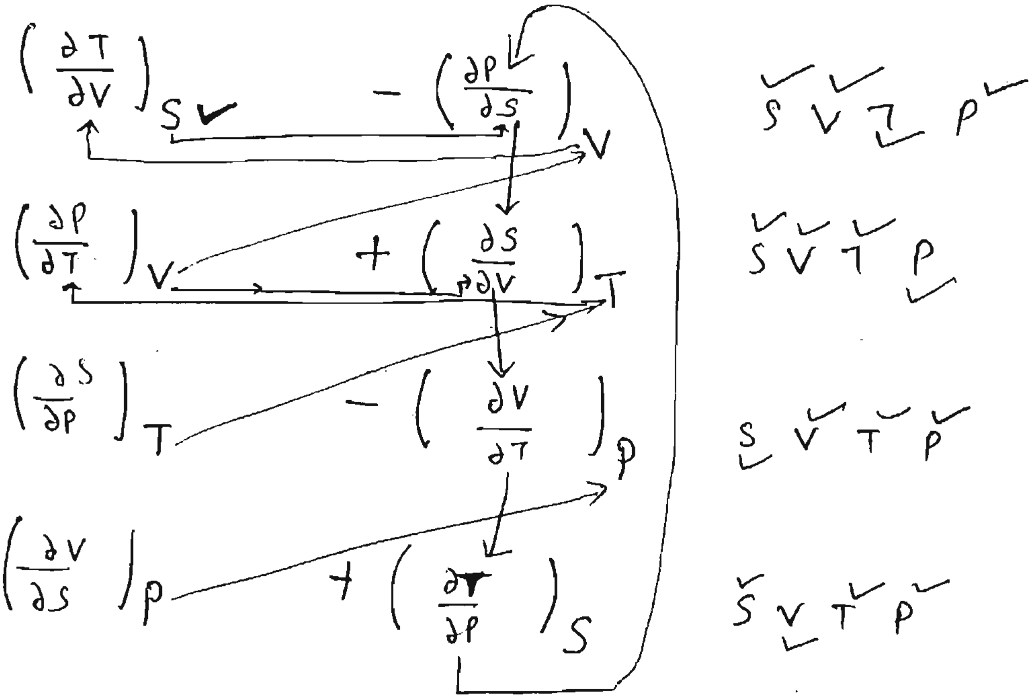
$$dU = -P\,dV + T\,dS$$

$$dH = T\,dS + V\,dP$$

$$dG = V\,dP - S\,dT$$

$$dA = -S\,dT - P\,dV$$

⇒ Short trick for write Maxwell eqn $(S\ V\ T\ P)$



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

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

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

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

(T V S P) Maxwell eqn

Best Method

↓

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

↓

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

↓

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

↓

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

⇒ For Real gas workdone in Adiabatic expansion

$$\boxed{W = nRT\ln\left(\frac{V_1 - nb}{V_2 - nb}\right) + an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right)}$$

* Change in Internal energy

$$\boxed{\Delta U = an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right)}$$

* Heat $\boxed{Q = nRT\ln\left(\frac{V_2 - nb}{V_1 - nb}\right)}$

⇒ For Isobaric, Isochoric workdone is same for Ideal gas.

⇒ Mach Number = $\frac{\text{Velocity of fluid}}{\text{Velocity of Sound in fluid}}$

* For a Closed system

$$d(nG) = (nV)\,dP - (nS)\,dT$$

* For open system of constant or variable composition

$$d(nG) = (nV)\,dP - (nS)\,dT + \Sigma \mu_i dn_i$$

where $\mu_i = \left(\frac{\partial (nG)}{\partial n_i}\right)_{P, T, n_j}$

* during Phase change P, T, and G are constant.

* Clapeyron Equation (where two phase are in equilibrium then it apply) $\boxed{\frac{dP^*}{dT} = \frac{\Delta H^{lv}}{T\,\Delta V^{lv}}}$ $\boxed{\frac{dP}{dT} = \frac{\Delta H}{T(V_2 - V_1)}}$

* Clausius - Clapeyron Equation (Valid for approximate on low pressure)

Assumption $\Delta V^{lv} = V^v = \frac{RT}{P^*}$

$$\boxed{\frac{dP^*/P^*}{dT/T^2} = \frac{\Delta H^{lv}}{R}} \text{ i.e. } \boxed{\ln\left(\frac{P_2^*}{P_1^*}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

* Antoine Equation $\ln P^* = A - \frac{B}{T+C}$

* Mollier diagram H-S graph of Water

* Residual property for gas

* Excess property for liq

* Isothermal compressibility $\boxed{\alpha = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T}$

* coefficient of volume expansion $\boxed{\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P}$

~~[illegible]dT − αdP~~

$$\boxed{\frac{dV}{V} = \beta\,dT - \alpha\,dP}$$

Residual Property

* Residual Property $(\underbrace{V^R, U^R, H^R, S^R, G^R}_{\text{extensive}})$ for gas only

* $$M^R = M - M^{ig}$$

$M \downarrow$ actual Value of Thermodynamics Property of Substance at given (T, P)

$M^{ig} \rightarrow$ Value of Thermodynamic Property of an Ideal gas at same T, P

for example (Volume)

$$V^R = V - V^{ig} = V - \frac{RT}{P} \qquad \left(\begin{array}{c} PV = RT \\ \text{Ideal} \end{array}\right)$$

But for real gas

$\boxed{V = \frac{ZRT}{P}}$ eqn of State

$$V^R = \frac{ZRT}{P} - \frac{RT}{P} \Rightarrow \boxed{V^R = \frac{RT}{P}(Z-1)}$$

* $\frac{G^R}{RT} = \int_0^P (Z-1)\frac{dP}{P}$ ✓

* $\frac{G^R}{RT} = Z - 1 - \ln Z + \frac{1}{RT}\int_\infty^V \left(\frac{RT}{V} - P\right) dV$ for real gas

* $U^R = \int_\infty^V \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$ ✓ All relation from $\boxed{PV = ZRT}$ eqn of state

* $H^R = \int_0^P \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dP + RT(Z-1)$ ✓

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

Residual Property from Viral Eqⁿ

* $$\frac{H^R}{RT_c} = P_r\left[\left(0.083 - \frac{1.097}{T_r^{1.6}}\right) + \omega\left(.139 - \frac{.894}{T_r^{4.2}}\right)\right]$$

* $$\frac{S^R}{R} = -P_r\left[\frac{.675}{T_r^{2.6}} + \omega\left(\frac{.722}{T_r^{5.2}}\right)\right]$$

Residual property from cubic Eqⁿ of state

Vander Waals

* $$\boxed{U^R = \frac{-a}{V}}$$ $$\boxed{S^R = R \ln \frac{P(V-b)}{RT}}$$

* $$\boxed{H^R = \frac{bRT}{V-b} - \frac{2a}{V}}$$

=> Partial Molar properties

$$\bar{M}_i \equiv \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_j}$$

$\bar{M}_i$ = Partial properties

M = Solution properties

M_i = Pure species Properties

=> Relation b/w Molar and partial Molar property

$$nM = f(T, P, n_1, n_2 -- n_i)$$

$$d(nM) = \left(\frac{\partial(nM)}{\partial P}\right)_T dP + \left(\frac{\partial(nM)}{\partial T}\right)_P dT + \sum_i \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_j} dn_i$$

at Const T, P and Binary Sol^n

$$d(nM) = ndM + Mdn \quad \text{and} \quad n_i = x_i n$$

$$dn_i = x_i dn + n dx_i$$

then

$$ndM + Mdn = n\left(\frac{\partial M}{\partial P}\right)_{T,n} dP + n\left(\frac{\partial M}{\partial T}\right)_{P,n} dT + \sum \bar{M}_i (x_i dn + n dx_i)$$

$$\underbrace{\left[dM - \left(\frac{\partial M}{\partial P}\right)_{T,n} dP - \left(\frac{\partial M}{\partial T}\right)_{P,n} dT - \sum \bar{M}_i dx_i\right]}_{\text{zero}} n + \underbrace{\left[M - \sum x_i \bar{M}_i\right]}_{\text{zero}} dn = 0$$

$$\boxed{dM = \left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT + \sum \bar{M}_i dx_i} \quad \text{—— ①}$$

$$\boxed{M = \sum x_i \bar{M}_i} \Rightarrow \boxed{dM = \sum x_i d\bar{M}_i + \sum \bar{M}_i dx_i} \quad - ②$$

from ① & ②

$$\boxed{\left(\frac{\partial M}{\partial P}\right)_{T,x} dP + \left(\frac{\partial M}{\partial T}\right)_{P,x} dT - \sum x_i dM_i = 0}$$

at const T, P $\boxed{\sum x_i dM_i = 0}$ V. Imp

$$\Rightarrow \quad \bar{M}_i = \left[\frac{\partial(nM)}{\partial n_i}\right]_{P,T,n_j}$$

which yields partial properties from total properties

$$\Rightarrow \quad M = \sum n_i \bar{M}_i$$

which yields total properties from partial properties

⇒ Method to find partial properties

$$M = x_1\bar{M}_1 + x_2\bar{M}_2 \quad \text{—— A}$$

$$dM = \underline{x_1\, d\bar{M}_1} + \bar{M}_1\, dx_1 + \underline{x_2\, d\bar{M}_2} + \bar{M}_2\, dx_2$$

But $\sum x_i\, dM_i = 0$ at const. T, P

$$\boxed{dM = \bar{M}_1\, dx_1 + \bar{M}_2\, dx_2} \quad \text{and} \quad \boxed{x_1\, d\bar{M}_1 + x_2\, d\bar{M}_2 = 0}$$

$$x_1 + x_2 = 1 \Rightarrow \boxed{dx_1 = -dx_2}.$$

$$dM = -\bar{M}_1\, dx_2 + \bar{M}_2\, dx_2 = dx_2(\bar{M}_2 - \bar{M}_1)$$

$$\frac{dM}{dx_2} = \bar{M}_2 - \bar{M}_1 \quad \text{—— (B)}$$

Now eqⁿ (A) $M = (1-x_2)\bar{M}_1 + x_2\bar{M}_2$

$$= \bar{M}_1 + \bar{M}_2(x_2) - \bar{M}_1(x_2)$$

$$M = \bar{M}_1 + x_2(\bar{M}_2 - \bar{M}_1)$$

$$\boxed{M = \bar{M}_1 + x_2\frac{dM}{dx_2}}$$

$$M = x_1\bar{M}_1 + (1-x_1)\bar{M}_2 = x_1(\bar{M}_1 - \bar{M}_2) + \bar{M}_2$$

$$M = -x_1\frac{dM}{dx_2} + \bar{M}_2 = \bar{M}_2 + x_1\frac{dM}{dx_1} \qquad \boxed{dx_2 = -dx_1}$$

$$\boxed{M = \bar{M}_2 + x_1\frac{dM}{dx_1}} \quad \& \quad \boxed{M = \bar{M}_1 + x_2\frac{dM}{dx_2}}$$

* In Ideal Gas Mixture

① $\bar{H}_i^{ig} = H_i^{ig}$

② $\bar{S}_i^{ig} = S_i^{ig} - R\ln y_i$ and $\bar{G}_i^{ig} = \bar{H}_i^{ig} - T\bar{S}_i^{ig}$

③ $\bar{G}_i^{ig} = G_i^{ig} + RT\ln y_i$

④ $H^{ig} = \sum y_i H_i^{ig}$

⑤ $S^{ig} = \sum y_i S_i^{ig} - R\sum y_i \ln y_i$

⑥ $G^{ig} = \sum y_i G_i^{ig} + RT\sum y_i \ln y_i$

⑦ $G_i^{ig} = \Gamma_i(T) + RT\ln P$

⑧ $\bar{G}_i^{ig} = \Gamma_i(T) + RT\ln(y_i P) = \mu_i$ (Chemical Potential)

Chemical Potential, (Intensive Property)

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

Chemical Potential is partial derivative of H, A, G of ith component with respect to composition

⑨ Effect of pr on chemical potential

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

⑩ Effect of temp on μ

$$-\bar{S}_i = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_j}$$

Ideal gas Mixture Model

$$\Delta M = \sum x_i (\bar{M}_i - M_i^\circ)$$

① Entropy change of Mixing

$$\Delta S_{mix} = -nR \sum x_i \ln x_i$$

② Gibbs free energy change of mixing

$$\Delta G_{mix} = nRT \sum x_i \ln x_i$$

③ Enthalpy change of Mixing for Ideal gas Mix.

$$\Delta H_{mix} = 0$$

④ Volume change of Mixing for Ideal gas Mix

$$\Delta V_{mix} = 0$$

⑤ Molar free energy of gas

$$\mu_i = \mu_i^\circ + RT \ln x_i$$

⑥ $\Delta U_{mix}^{ideal} = 0$

Fugacity

is fictitious pressure which is used for real gas

We know that for ideal gas, closed system

$$dG^{ig} = VdP - SdT$$

at const. temp. $\left(\frac{\partial G^{ig}}{\partial P}\right)_T = V$

$$(dG^{ig})_T = V\,dP = \frac{nRT}{P}dP = nRT\,d(\ln P) \quad \text{— ①}$$

Integrating this eq^n

$$G = G^\circ + nRT\ln P \quad \text{— ②}$$

But its apply on real gas so eq^n ① introduced new variable for real gas

$$dG = nRT\,d(\ln f) \qquad f = \text{fugacity} \quad \text{— ③}$$

from eq^n ② − ①

$$d(G - G^{ig}) = nRT\,d(\ln f) - nRT\,d(\ln P)$$

$$\boxed{dG^R = RT\,d\ln\left(\frac{f}{P}\right)} \qquad G^R = G - G^{ig}$$

Residual

$$\boxed{\text{Fugacity coeff: } \phi = \frac{f}{P}} \qquad dG^R = RT\,d(\ln\phi)$$

on Integration $G - G^{ig} = G^R = RT\ln\phi + C$

Put $\phi = 1$, $G^R = 0$ then $C = 0$ So

$$G^R = RT\ln\phi \Rightarrow \boxed{\frac{G^R}{RT} = \ln\phi}$$

$$\boxed{\frac{G^R}{RT} = \ln\phi = \sum n_i \ln\bar{\phi}}$$

Scanned by CamScanner

⇒ Fugacity Coeff from Compressibility factor

$$Z = \frac{PV}{RT} = 1 + \frac{BP}{RT}$$

$$Z - 1 = \frac{BP}{RT}$$

$$\boxed{\ln \phi = \int_0^P \frac{Z-1}{P}\, dP}$$

⇒ from viral eq^n of state

$$\ln \phi = \ln \frac{f}{P} = \int_0^{P_r} (Z-1) \frac{dP_r}{P_r} = (B^0 + \omega B^1) \frac{P_r}{T_r}$$

⇒ Gibbs Dhuem Eq^n

① $\sum n_i d\bar{M}_i = 0$

② $\sum n_i d\mu_i = 0$

③ $\sum x_i d\mu_i = 0$

④ $\sum n_i d(\ln \hat{f}_i) = 0$

⑤ $\sum n_i d(\ln a_i) = 0$

⑥ $\sum n_i d(\ln \gamma_i) = 0$

⇒ Fugacity of gas Mix

$$\ln \phi = \sum n_i \ln \bar{\phi}_i$$

⇒ +ve deviation $\gamma_i > 1$

−ve deviation $\gamma_i < 1$

No deviation $\gamma_i = 1$

Excess property of Mixture

[Actual Property of sol^n at given at T, P] − [Property it would have as an ideal gas at same T, P] = Excess property of sol^n at given T, P

$$M - M^{id} = M^E$$

⟹ Excess free Energy

$$\boxed{\frac{G^E}{RT} = \sum x_i \ln \gamma_i} = \sum x_i \frac{\bar{G}^E}{RT}$$

V. Imp.

$$\boxed{\ln \gamma_i = \frac{\bar{G}^E}{RT} = \left[\frac{\partial(n G^E/RT)}{\partial n_i}\right]_{T, P, n_j}}$$

⟹ Criteria for Equilibrium

① Isolated System $dS)_{U,V} \leq 0$ ④

② at const T, V $dA \leq 0$

③ at const T, P $dG)_{T,P} \leq 0$

⟹ criteria for Phase

① Chemical Potential in each phase equal

② fugacity in each Phase equal of al component of Mix.

③ $dG = 0$

⇒ Phase rule for Non reacting system

① Phase Rule $\boxed{F = C - P + 2}$ where F = no. of Independent intensive variable.

* In this Phase rule only Intensive Variable include.

* '2' is show that Temp, Pressure $\rightarrow$ Intensive.

* $\boxed{DOF = \text{No. of Variable} - \text{No. of Eq}^n}$

* If F = 1 that is one independent intensive property is required to be specified

* at Triple point F = 0 It implie that none of the Properties of a pure substance at triple point can be varied.

② DUHEM'S Theorem

In this Extensive + intesive both consider.

no. of Intensive Variable = $P(C-1)+2$

no. of Extensive " = $P\begin{bmatrix}\text{mass in} \\ \text{each Phase}\end{bmatrix}$

total Variable = $P(C-1)+2+P$

$= 2 + CP$

no. of Intensive eqⁿ relation = $(P-1)C$

no. of extensive " " = C

total " " = $(P-1)C + C$

$$DOF = [2+CP] - [(P-1)C + C]$$
$$= 2 + CP - [PC - C + C]$$
$$= 2$$

Acco. to this only two independent Variable are required to define state

③ Phase rule derive

consider system (closed) with P = Phase, C = component

In Closed System required only (C−1) component composition, other one is remainder. so

no of composition Variable in 'P' Phase $= P(C-1)$

two variable is T & P

$\boxed{\text{total Variable} = P(C-1)+2}$

In P-Phase, C-component only $(P-1)C$ no of Equilibrium Phase eqn so

$\boxed{\text{no. of Eq}^n = (P-1)C}$

$$F = N_V - N_E = P(C-1)+2 - (P-1)C$$
$$= PC - P + 2 - PC + C$$
$$\boxed{F = C - P + 2}$$

at least one Variable extensive ←	F = 1
both must be extensive ←	F = 0

VLE Point

⇒ If ① = Higher Volatile , ② = less Volatile than allways

$y_1 > x_1$ and $y_2 < x_2$

⇒ Raoult's Law

* for liq Phase composition

$\boxed{\Sigma y_1 = 1}$ $\boxed{P = x_1 P_1^* + x_2 P_2^*}$ and $\boxed{y_1 P = x_1 P_1^*}$

* for Vapor Phase System

$$\boxed{\frac{1}{P} = \frac{y_1}{P_1^*} + \frac{y_2}{P_2^*}} \quad \boxed{\Sigma x_i = 1}$$

⇒ Modified Raoult's law

Vapor = Ideal
Liq = Real $\boxed{y_i P = x_i \gamma_i P_i^*}$ γ_i = Activity coeff

Vapor = Real
Liq = Real $\boxed{y_i \phi_i P = x_i \gamma_i P_i^*}$ ϕ_i = Fugacity coeff.

⇒ Deviation from Raoult's Law

+ve deviation	−ve deviation
① $P_{total} > P_{Raoult\ Law}$	① $P_{total} < P_{Raoult\ law}$
② $p_A > p_A^\circ x_A$	② $p_A < p_A^\circ x_A$
③ $\underbrace{A - - B}_{\text{(Adhesive force)}} < \underbrace{A - - A, B - - B}_{\text{cohesive force}}$	③ $\underbrace{A - - B}_{\text{Adhesive}} > \underbrace{A - - A, B - - B}_{\text{cohesive force}}$
④ $\Delta H > 0$ Endothermic process	④ $\Delta H < 0$ Exthermic process
⑤ $\Delta S > 0$, $\Delta V > 0$	⑤ $\Delta S < 0$, $\Delta V < 0$
example MeOH + H_2O etOH + H_2O ACitone + CS_2	example HCl + H_2O HNO_3 + H_2O $CHCl_3$ + H_2O Aceton + $CHCl_3$

Azetrope [Constant Boiling Mixture]

⇒ Each Azetrope has a characterstic boiling Point.

* B.P. of Azetrope > Boiling Point of its every consituents for (−ve) Azetrope
Maxma boiling Mix

* B.P. of Azetrope < B.P. of its every consituents for (+ve Azetrope)
Minimum boiling Mix.

⇒ Maximum boiling Mixture	⇒ Minimum boiling Mixture
① $(B.P.)_{AZ} > (B.P.)_{Pure\ component}$	$(B.P.)_{AZ} < (B.P.)_{Pure\ component}$
② B.P. $\propto \frac{1}{V.P}$ so $(V.P)_{AZ} < (V.P.)_{Pure\ Component}$	$(V.P.)_{AZ} > (V.P.)_{Pure\ component}$
3) Large −ve deviation	Large +ve deviation
④ −ve Azetrope	+ve Azetrope
⑤ $\ln \gamma_i < 0$, $\gamma_i < 1$	$\ln \gamma_i > 0$, $\gamma_i > 1$
⑥ e.g. (HCl + water) 20.2% 79.8%	eg. Pyridine + water 59% 41%.

⇒ Margules eqn (3- suffix)

$$\ln \gamma_1 = x_2^2 [A + 2(B-A)x_1]$$

$$\ln \gamma_2 = x_1^2 [B + 2(A-B)x_2]$$

⇒ Margules eqn (2-suffix)

$$\ln \gamma_1 = A x_2^2 , \quad \ln \gamma_2 = A x_1^2$$

⇒ VLE at High pressure (K-Value)

$$\boxed{K = \frac{y_i}{x_i} = \frac{P_i^*}{P}}$$

for Modified Raoult's Law $\boxed{K = \frac{\gamma_i P_i^*}{P}}$

⇒ For Binary Mixture, the ration two k-Values of two component is called relative Volatility

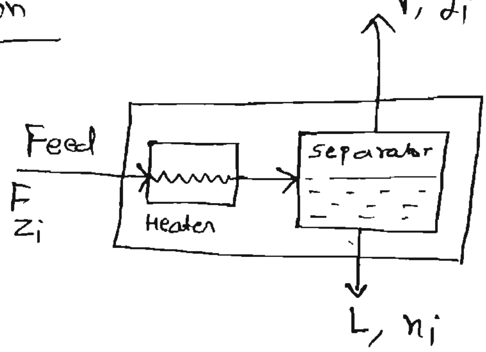
$$\alpha = \frac{k_i}{k_j} = \frac{\frac{y_i}{x_i}}{\frac{y_j}{x_j}}$$

⇒ At 100% Relative Humidity [dew point = current temp]

⇒ Dew point is also known Saturation point

⇒ When dew point temp falls below freezing it is often Called frost point

Flash Calculation



Consider a binary Mixture, feed rate F mol/h

total Material balance

$$F = V + L$$

Material Balance for component

$$Fz_i = Vy_i + Lx_i$$

Put $y_i = k_i x_i$ then

$$Fz_i = Vk_i x_i + Lx_i$$
$$= x_i (Vk_i + L)$$

$$x_i = \frac{Fz_i}{L+Vk_i}$$

$\Sigma x_i = 0$ then

$$\boxed{\sum \frac{Fz_i}{L+Vk_i} = 1}$$

Put $x_i = \frac{y_i}{k_i}$ then

$$Fz_i = Vy_i + \frac{Ly_i}{k_i} = y_i\left[V + \frac{L}{k_i}\right]$$

$$y_i = \frac{Fz_i}{\left[V + \frac{L}{k_i}\right]} \qquad \Sigma y_i = 1$$

then

$$\boxed{\sum \frac{Fz_i}{\left[V + \frac{L}{k_i}\right]} = 1}$$

Chemical reach Equilibria

⟹ RXN Coordinate (ε)

* It represent progress of chemical reach along a path way

* This is one dimensional coordinate

$$P + 3Q \rightarrow 2R \quad [\text{single reaction}]$$

$$V_R = 2, \; V_P = -1, \; V_Q = -3$$

$$\left[\begin{array}{ll} \text{Product} & +\text{ve} \\ \text{Reactant} & -\text{ve} \\ \text{Inert} & \text{zero} \end{array}\right]$$

$$\frac{dn_i}{V_i} = d\varepsilon \Rightarrow \int_{n_{i0}}^{n_i} dn_i = \int_0^{\varepsilon} V_i \, d\varepsilon$$

$$n_i - n_{i0} = V_i \varepsilon \Rightarrow \boxed{n_i = n_{i0} + V_i \varepsilon}$$

total Mole $n = \sum n_i = \sum n_{i0} + \varepsilon \sum V_i$

$$\boxed{n = n_0 + \varepsilon V} \quad \text{Where } \boxed{V = \sum V_i}$$

$$\boxed{n_0 = \sum n_{i0}}$$

$$\boxed{y_i = \frac{n_i}{n} = \frac{n_{i0} + V_i \varepsilon}{n_0 + \varepsilon V}}$$

* In Multireaction

$$y_i = \frac{n_i}{n} = \frac{n_{i0} + \sum_j V_{i,j} \varepsilon_j}{n_0 + \sum_j V_j \varepsilon_j}$$

i = component

j = reaction

① Equilibrium crition of a chemical rxn

$$(dG)_{T,P} \le 0$$

② At equilibrium

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

③ Equilibrium constant K_c is depend on only temp.

④ $\alpha A + \beta B \rightleftharpoons \sigma S + z T$

① $K_c = \frac{[C_S]^{\sigma} [C_T]^{z}}{[C_A]^{\alpha} [C_B]^{B}}$ (in terms of concn)

② $k_a = \frac{a_S^{\sigma} a_T^{z}}{a_A^{\alpha} a_B^{\beta}} = \Pi (a_i)^{V_i}$ - (in terms of activity)

③ $k_f = \Pi \left(\frac{\bar{f_i}}{f_i^{\circ}} \right)^{V_i}$ (in terms of fugacity)

④ $k_p = \Pi (\bar{P_i})^{V_i}$ (in terms of Partial Pr)

⑤ $k_p = k_c (RT)^{\Delta n}$ (where Δn = mol of Product − mol of reactant)

⑥ If $A + B \rightleftharpoons C$ equilibrium const $= k_c$

then $C \rightleftharpoons A + B$ Equilibrium const $= \frac{1}{k_c}$

$2A + 2B \rightleftharpoons 2C$ Eqᵘ const $= (k_c)^2$

① Equilibrium Constant K_c in terms of concn

② Equilibrium Constant K_p in terms of Partiatal Pr

③ $K_p = K_c (RT)^{\Delta n}$

④ $K_a = \Pi(a_i)^{V_i}, = \Pi\left(\frac{\bar{f}_i}{f_i^\circ}\right)^{V_i} = \Pi(\bar{f}_i)^{V_i} = K_f$

$= \Pi(\bar{p}_i)^{V_i} = K_p$

$$\boxed{\begin{array}{l} K_a = K_f = K_p \\ \text{for ideal system } K_c = K_a \text{ becuz activity coeff} = 1 \end{array}}$$

⇒ Homogenous gas Phase RXN ($P^\circ = 1$)

$K_a = K_p = K_f = K_y P^{\Sigma V_i}$ (Kp and Kc both find)

and $K_y = \Pi(y_i)^{V_i}$ $\boxed{K_p = K_c (RT)^{\Delta n}}$

⇒ Homogenous liq Phase (only Kc find) $\boxed{K_a = K_x = \Pi(x_i)^{V_i}}$

⊛ Activity of Solid component = one

⇒ Hetrogenous Phase (find Kp) (only gas Phase term consider)

⇒ $\boxed{\Delta G^\circ = -RT \ln K}$

⇒ Van't Hoff eqn (effect of temp on K)

$\boxed{\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$ $\boxed{\frac{\partial(\ln K)}{\partial T} = \frac{\Delta H^\circ}{RT^2}}$

(*) Isentropic process means

① reversible ② Adiabatic ③ entropy constant

④ used for cooling ⑤ used for real + Ideal gas

⑥ $\mu_s = \left(\frac{\partial T}{\partial P}\right)_s$

(*) Isenthalpic Process Means (Joule Thomson effect)

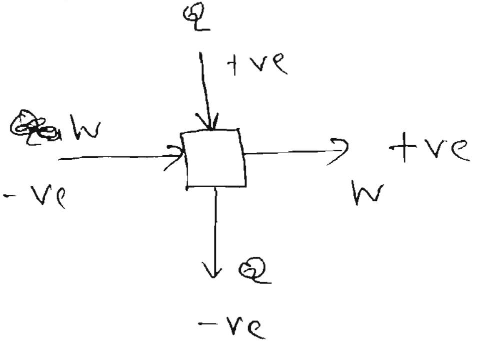
① enthalpy const.

② Intial temp. should < Inversion temp for cooling

③ Adiabatic

④ used for real gas. only

⑤ $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_{\partial H}$



(*) Adiabatic

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

$TV^{\gamma-1} = \text{const} \Rightarrow$ ~~[illegible]~~

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

$\boxed{T^{\gamma} \propto P^{\gamma-1}}$

These are for

Rev and Adiabatic

Isentropic

than used 1st Law of

$$\boxed{\Delta U = Q - W}$$

$$W_{ad}\Big|_{rev} = \frac{R(T_2 - T_1)}{1-\gamma} = C_v(T_1 - T_2)$$

$$\Delta U\Big|_{rev,\,adiabatic} = C_v(T_2 - T_1)$$

$dQ = 0$