[redacted]

physical

sem I Thermodynamics.

Thermodynamics means flow of Heat. It a branch of physical chemistry which deals with the study of quantitative relationship between Heat & other form of energy

Thermodynamics is based upon two imp nt generations known as first & second low of the system

Importance

1) It helps to lay down criteria for predict feasibility or ~~of~~ spontaneity of a process i.e whether given process is possible under given set of conditions or not.

2) It also helps to determine the extent to which a process can proced before obta ing a state of equilibrium.

* Limitations of thermodynamics

1) It is only applicable ~~only~~ to the bulk of the matter and not to the individual atom or molecule.

ii) It does not consider time element

iii) It only considers initial and final state of system not mechanism.

iv) It can give the direction of change & not the rate of change.

v) It deals with properties like pressure tem

* Basic Concepts

① system :-

A part of the universe which is under thermodynamic consideration is known as a system.

② open system

system which exchange both matter & energy with the surrounding is called as open system.

③ closed system

system which exchange only energy & not matter with surrounding is called as closed system

④ Isolated system

system which exchange neither energy nor matter with the surrounding is known as isolated system.

⑤ state function

A thermodynamics property which depends only on initial & final state of system & not on the path followed by the system is called as state function.

⑥ Macroscopic properties

The properties associated with the macroscopic system [i.e a system consisting of large no: of particles] are called as macroscopic properties.

⑦ Homogenous system

A system is said to be homogenous, when consist of only one phase or which is uniform througout.

⑧ Heterogenous system

when a system consist of two or more phases or when it is not uniform throughout then it is said to be heterogenous system.

⑨ surrounding

A part of universe excluding the system & which can exchange matter & energy with the system is known as surrounding

⑩

A state of a system can be defined as completly by four variables. ~~of~~ state i.e variables of state. These are composition, pressure, volume & temp.

A state of system is also known as macroscopic or thermodynamics state.

⑪ Thermodynamics equilibrium.

A system in which the macroscopic properties like temp., pressure, volume etc. do not undergo any change with time is said to be in thermodynamics equilibrium.

For thermodynamics studies, system must be in three parts of equilibrium, which can must exist simultaneously.

i) Thermal equilibrium : Temp. constant.

ii) chemical equilibrium : same molecule composition.

iii) mechanical equilibrium :- mechanical properties uniform.

⑫ Intensive property.

A property whose value does not depend upon the quantity of matter, present in the system is called intensive property.

The property depends upon nature of substance & its composition or constitution.

eg. Temp., pressure, density, surface tension, viscosity.

⑬ Extensive property

A property whose value depend upon the quantity of matter present in the system is known as extensive property.

⑭ Process.

A path of an operation by which a system changes from one form to another is called as process.

⑮ Isothermal process.

If the temp. of a system remains constant during each step of a process, then the process is known as isothermal process.

⑯ Adiabatic process

A process which neither absorbs heat from the surrounding nor it can give heat to the surrounding is called as an adiabatic process.

⑰ Thermodynamic reversible process

A process in which the driving force is only infinitesimally greater than the opposing force & which can be reversed by infinitesimal increase in opposing force is called as thermodynamic reveriable process.

⑱ Irreversible process

A process in which driving force is much greater than opposing force & which can not be reversed by infinitesimal increase in opposing force is known as thermodyamic irreversible process.

⑲ Cyclic process

A process in which, any system after completing a series of operations, returns to its original state is called as cyclic process.

⑳ Internal energy of a system

The sum of different forms of energies associated with atoms or molecules of a system required for their motions & transformations is called as in internal energy of a system.

㉑ Enthalpy ($\Delta H = \Delta E + P\Delta V$)

The total energy content of a system inclusive of pressure, volume & internal energy is called as heat content of energy or a system or enthalpy of a system at constant pressure

㉒ Heat capacity

The amount of heat in calories required to raise temp. of whole system through one degree, centigrade under given set of conditions is called as heat capacity.

㉓ Heat capacity at constant volume (C_v)

The amount of heat is required to raise temp. of one mole of gas through 1°C, when the volume is kept constant & pressure is allowed to increase is know as heat capacity for one mole or molar heat capacity at constant volume

㉔ Isochoric process (constant volume)

A process which is carried out at constant volume is known as Isochoric process.

㉕ Isobaric process

A process which is carried out at constant pressure is called as isobaric proce

㉖ specific Heat :-

The amount of heat required to raise temp. of 1 gm of substance through 1°c is called as specific heat

Derive maxwell relation.

Maxwell Relation (I)

① Variation of entropy with pressure and volume

⇒ we know that, 2nd law of thermodynamics:

$E = q + W$

$\therefore W = -PV$

$\therefore E = q - PV$

For small changes,

$dE = dq - Pdv$ — ①

Rearranging eqn ① we get,

$dq = dE + Pdv$

$\frac{dq}{T} = \frac{dE + Pdv}{T}$

$ds = \frac{dE + Pdv}{T} \quad \left(\because \frac{dq}{T} = ds\right)$

$Tds = dE + Pdv$ — ②

Heat capacity at constant volume is given by,

i.e $C_v = \left(\frac{dq}{dT}\right)_v$

From eqn ①

$dE = dq - Pdv$

At constant volume i.e $dv = 0$

i.e $dE = dq$

i.e $C_v = \left(\frac{dq}{dT}\right)_v = \left(\frac{dE}{dT}\right)_v$ — ③

Eqn ② becomes,

$Tds = dE + Pdv$

$ds = \frac{dE + Pdv}{T}$

For integrally small changes,

$\partial s = \frac{\partial E + P\partial v}{T}$

$\partial s = \frac{\partial E}{T} + \frac{P\partial v}{T}$

At constant volume i.e $\partial v = 0$

$\partial s = \frac{\partial E}{T}$

$\left(\frac{\partial s}{\partial E}\right)_v = \frac{1}{T}$

$\left(\frac{\partial s}{\partial T}\right) \Big/ \left(\frac{\partial E}{\partial T}\right) = \frac{1}{T}$

$$\left(\frac{\partial s}{\partial T}\right)_V \Big/ C_V = \frac{1}{T} \qquad [\because \text{from eq}^n \text{③}]$$

$$\left(\frac{\partial s}{\partial T}\right)_V = \frac{C_V}{T} \qquad ④$$

~~But $C_V = \frac{\partial E}{\partial T}$~~

Eq^n ② becomes,

$$Tds = dE + Pdv$$

$$Pdv = Tds - dE$$

By applying the condition from constant temp is given by,

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

Diff. w.r.t T at constant volume.

$$\left(\frac{\partial P}{\partial T}\right)_V = T\left(\frac{\partial^2 s}{\partial V \partial T}\right)_T + \left(\frac{\partial s}{\partial V}\right)_T - \left(\frac{\partial^2 E}{\partial V \partial T}\right)_T \quad ⑤$$

Eq^n ④ becomes,

$$\left(\frac{\partial s}{\partial T}\right)_V = \frac{C_V}{T}$$

But $C_V = \left(\frac{\partial E}{\partial T}\right)_V$

i.e $\left(\frac{\partial s}{\partial T}\right) = \frac{1}{T}\left(\frac{\partial E}{\partial T}\right)$

Diff. w.r.t V at constant T

$$\left(\frac{\partial^2 s}{\partial V \partial T}\right)_T = \frac{1}{T}\left(\frac{\partial^2 E}{\partial V \partial T}\right)_T$$

$$\left(\frac{\partial^2 E}{\partial V \partial T}\right)_T = T\left(\frac{\partial^2 s}{\partial V \partial T}\right)$$

putting this value in eq^n ⑤

$$\left(\frac{\partial P}{\partial T}\right)_V = T\left(\frac{\partial^2 s}{\partial V \partial T}\right)_T + \left(\frac{\partial s}{\partial V}\right)_T - T\left(\frac{\partial^2 s}{\partial V \partial T}\right)$$

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial s}{\partial V}\right)_T} \quad \text{Ⓘ}$$

Eq^n Ⓘ is nothing but the maxwell 1st relation. It gives variation of pressure with temp. at constant volume is equal to variation of entropy with volume at constant T.

(II) Relations Maxwell (II) Relation

→ According to enthalpy,

$H = E + PV$

Diff. above eq^n we get,

$dH = dE + pdv + vdp$

i.e $dH = Tds + vdP$ $(\because dE + Pdv = Tds)$

$vdP = dH - Tds$

~~At constant~~ By applying condition from constant temp. is given by.

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

Diff. w.r.t T at constant P

$$\left(\frac{\partial v}{\partial T}\right) = \left(\frac{\partial^2 H}{\partial P \partial T}\right)_T - T\left(\frac{\partial^2 s}{\partial p \partial T}\right)_T \left(\frac{\partial s}{\partial P}\right)_P \text{ ———— } ①$$

Let, Heat capacity at constant pressure is given by,

$$C_P = \left(\frac{dq}{dT}\right)_P$$

we know that

$dH = dE + Pdv + vdP$

At constant P i.e $dP = 0$

$\therefore dH = dE + Pdv$

$\therefore dH = dq$ $(\because dE + Pdv = dq)$

Hence $C_P = \left(\frac{dq}{dT}\right)_P = \left(\frac{dH}{dT}\right)_P$

we also know that,

$dH = Tds + vdP$

At constant P

$dH = Tds$

$$\left(\frac{\partial H}{\partial s}\right)_P = T$$

$$\left(\frac{\partial s}{\partial H}\right)_P = \frac{1}{T}$$

$$\left(\frac{\partial s}{\partial T}\right)_P \Big/ \left(\frac{\partial H}{\partial T}\right)_P = \frac{1}{T}$$

$$\left(\frac{\partial s}{\partial T}\right)_P \Big/ C_P = \frac{1}{T}$$

$$\left(\frac{\partial s}{\partial T}\right)_p = \frac{C_p}{T} \quad ②$$

But $C_p = \left(\frac{\partial H}{\partial T}\right)_p$

$$\left(\frac{\partial s}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_p$$

Diff. w.r.t P at constant T.

$$\left(\frac{\partial^2 s}{\partial T}\right) = \frac{1}{T}\left(\frac{\partial^2 H}{\partial T \partial P}\right)$$

$$\left(\frac{\partial^2 H}{\partial T \partial P}\right) = T\left(\frac{\partial^2 s}{\partial T \partial p}\right)$$

putting this value in eqⁿ ① we get,

$$\left(\frac{\partial v}{\partial T}\right) = T\left(\frac{\partial^2 s}{\partial T \partial p}\right)_T \; T\left(\frac{\partial^2 s}{\partial T \partial p}\right) \; \left(\frac{\partial s}{\partial p}\right)_T$$

$$\boxed{\left(\frac{\partial v}{\partial T}\right)_p = -\left(\frac{\partial s}{\partial p}\right)_T} \text{ — Ⅱ}$$

Eqⁿ Ⅱ gives maxwell relation 2

* Maxwell Ⅲ Relation.

→ From 2nd law of thermodynamics.

$$dE = Tds - pdv$$

At constant volume i.e $dv = 0$

$$dE = Tds$$

i.e $\left(\frac{\partial E}{\partial s}\right)_v = T$

Diff. w.r.t volume at constant entropy,

$$\left(\frac{\partial^2 E}{\partial s \partial v}\right) = \left(\frac{\partial T}{\partial v}\right)_s \text{ — ①}$$

Similarly,
At constant entropy $ds = 0$

$$dE = -pdv$$

$$\left(\frac{\partial E}{\partial v}\right)_s = -p$$

Diff. w.r.t. s at constant volume.

$$\left(\frac{\partial^2 E}{\partial v \partial s}\right) = -\left(\frac{\partial p}{\partial s}\right)_v \text{ — ②}$$

Comparing eqⁿ ① & ② we get,

$$\boxed{\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial p}{\partial s}\right)_v}$$

Eq^n (III) is nothing but maxwell III relation
It gives variation of T with volume at contant s is equal to negative variation of P with s at constant V.

* Maxwell (IV) Relation

→ According to enthalpy

$$dH = Tds + vdp$$

At constant pressure [$dp=0$]

$$\left(\frac{\partial H}{\partial s}\right)_p = T$$

Diff. w.r.t pressure at constant S.

$$\left(\frac{\partial^2 H}{\partial s . \partial P}\right) = \left(\frac{\partial T}{\partial p}\right)_s \quad \text{①}$$

At constant entropy [$ds=0$].

$$\left(\frac{\partial H}{\partial P}\right)_s = V$$

Diff. w.r.t entropy at constant P.

$$\left(\frac{\partial^2 H}{\partial p \partial s}\right) = \left(\frac{\partial v}{\partial s}\right)_p \quad \text{②}$$

compairing eq^n ① & ②

we get,

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial v}{\partial s}\right)_P}$$

Eq^n IV is nothing but maxwell IV relati
It gives variation of temp with pressu
at constant s is equal to variation o
volume with entropy at constant pressure

✓* Maxwell Equations

① $\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ —— (I)

② $\left(\frac{\partial v}{\partial T}\right)_P = -\left(\frac{\partial s}{\partial P}\right)_T$ —— (II)

③ $\left(\frac{\partial T}{\partial v}\right)_S = -\left(\frac{\partial P}{\partial s}\right)_V$ —— (III)

④ $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial v}{\partial s}\right)_P$ —— (IV)

✱ Maxwell Relation proved by mathematical method.

$$dz = Mdx + Ndy \quad ---- ①$$

where z, M & N are functions of x & y

Theorom :-

If relation exist between x, y & z. The z-may be expressed in terms of x&y

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad --- ②$$

compairing eq^n ① & ②

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

By def^n of M

$$M = \left(\frac{\partial z}{\partial x}\right)_y$$

Diff. w.r.t y at constant x

$$\left(\frac{\partial M}{\partial y}\right) = \left(\frac{\partial^2 z}{\partial x \partial y}\right) \quad --- ③$$

similarly for N

$$N = \left(\frac{\partial z}{\partial y}\right)_x$$

Diff. w.r.t. x at constant y

$$\left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial^2 z}{\partial x \partial y}\right) \quad --- ④$$

compairing eq^n ③ & ④

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

1) we know that,

$$H = E - TS$$

Diff. above eq^n

$$dH = dE - Tds - sdT$$

$$dH = -Pdv - sdT \quad --- ① \quad (\because dE = Tds - Pdv)$$

$$dz = Mdx + Ndy \quad --- ②$$

compair eq^n ① & ②

$$H = z, \; M = -P, \; N = -S, \; x = V, \; T = y.$$

Putting these values in eq^n Ⓐ

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

$$\boxed{\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial s}{\partial v}\right)_T} \quad ⓐ$$

(ii) we know that,

$G = H - TS$

Diff. above ~~re~~equation,

$dG = dH - Tds - sdT$

But $dH = Tds + Vdp$

$dG = Tds + Vdp - sdT - Tds$

i.e $dG = Vdp - sdT$ ----- ①

$d\cancel{H} = Mdx + Ndy$ ---- ②

compair eq^n ① & ②

$G = Z$, $V = M$; $N = -S$, $x = P$, $y = T$

Putting these values in eq^n Ⓐ

$$\boxed{\left(\frac{\partial v}{\partial T}\right)_P = \left(-\frac{\partial s}{\partial P}\right)_T} \quad ⓑ$$

(iii) we know that,

$dE = Tds - Pdv$ ---- ①

$dz = Mdx + Ndy$ ---- ②

compair eq^n ① & ②

$Z = E$, $M = T$, $N = -P$, $x = S$, $y = V$

putting these values in eq^n Ⓐ we get,

$$\boxed{\left(\frac{\partial T}{\partial v}\right)_S = -\left(\frac{\partial P}{\partial s}\right)_V} \text{ ---- } ⓒ$$

(iv) we know that,

$dH = Tds + vdp$ ---- ①

$dz = Mdx + Ndy$ ---- ②

compair eq^n ① & ②

$Z = H$, $M = T$, $N = V$, $x = S$, $y = P$

putting these values in eq^n Ⓐ we get,

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial v}{\partial s}\right)_P} \text{ --- } ⓓ$$

eq^n ⓐ ⓑ ⓒ & ⓓ are the Maxwell eq^{ns}

* [redacted]

Ideal solution is defined as,

'The one is which the activity of each component is equal to its mole fraction. under all condition of temp, pressure & conc.

i.e $a_i = x_i$

For ideal solution,

we know that,

$$\frac{\partial \mu_i}{\partial p_i} = \frac{\partial \mu_i}{\partial n_i} = \overline{V_i} = \text{partial molar volume}$$

For ideal gas,

$$PV = nRT, \quad V = \frac{nRT}{P}$$

$$\overline{V} = \frac{\partial V}{\partial n} = \frac{RT}{P}$$

$$\therefore \frac{\partial \mu_i}{\partial p_i} = \frac{RT}{p_i}$$

$$\therefore \partial \mu_i = RT \frac{\partial p_i}{p_i}$$

Integrating above eq^n w.r.t limit

$$\int_{\mu_i}^{\mu_i^\circ} d\mu_i = RT \int_{i=1}^{p_i} \frac{\partial p_i}{p_i}$$

$$\therefore \mu_i - \mu_i^\circ = RT \ln p_i$$

$$\boxed{\therefore \mu_i = \mu_i^\circ + RT \ln p_i}$$

This eq^n for ideal gas using chemical potential. where μ_i = chemical potential

μ_i° = standard chemical potential.

consider two component liquid sol^n in eq^n with it's vapour assumed ideal.

since for a system in eq^n the chemical potential of a component 'A' is same in the liquid and the gas phases.

$$\mu_{A(l)} = \mu_{i(g)}^\circ + RT \ln P_A^\circ \quad \text{—— ①}$$

for pure liquid

$$\mu_{A(l)} = \mu_{A(g)}^\circ + RT \ln P_A^\circ \quad \text{—— ②}$$

Add & substracte $RT \ln P_A^\circ$ on the right hand side of eq^n ①.

$$\therefore \mu_{A(l)} = \mu_{A(g)}^\circ + RT \ln P_A + RT \ln P_A^\circ - RT \ln P_A$$

$$\therefore \mu_{A(l)} = \mu_{A(g)}^\circ + RT \ln$$

*

Qu. Derive

* [redacted]

The change of any thermodynamic property is due to a change in the state of the system and not to the addition or removal of matter.

In the study of such system consisting two or more phase it is necessary to consider open system where composition and mass may vary. In this connection the concept of partial molar properties as devolped by G.N Lealls in 1907.

consider any thermodynamic extensive property (x) such as volume, free energy entropy energy content etc. whose value depends upon state of system as well as amount of various constituent present (i.e no. of moles of each constituent)

$$x = f(P, T, n_1, n_2, n_3 ---- n_i)$$

where x = Any extensive property

$n_1, n_2 --- n_i$ = no. of moles of the respectiv constituent.

For small change,

$$dx = \left(\frac{\partial x}{\partial T}\right)_{P, n_1, n_2 -} dT + \left(\frac{\partial x}{\partial P}\right)_{T, n_1, n_2} dP + \left(\frac{\partial x}{\partial n_1}\right)_{T, P, r}$$

$$+ ----- + \left(\frac{\partial x}{\partial n_i}\right)_{T, P, n_1 --- n_j} \partial n_i$$

$\therefore \left(\frac{\partial x}{\partial n_i}\right)_{P, T, n_1 -- n_j}$ is called as partial molar properties. It is represeted by $\overline{x}$.

$$dx = \left(\frac{\partial x}{\partial T}\right)_{P, n_1 --- n_j} d_1 + \left(\frac{\partial x}{\partial P}\right)_{T, n_1 --- n_j} dP$$

$$+ \overline{x}_1 dn_1 + \overline{x}_2 dn_2 + ---- \overline{x_i}\, dn_i$$

At conc. P and T

$$dx = \overline{x}_1 dn_1 + \overline{x}_2 dn_2 + ----- + \overline{x_i}\, dn_i \text{ —— } ①$$

Integrating eq^n ①

$$x = \overline{x}_1 n_1 + \overline{x}_2 n_2 + ----- * \overline{x}_i n_i \text{ —— } ②$$

Diff. at constant temp & pressure

$$d\bar{x} = \bar{x}_1 dn_1 + n_1 d\bar{x}_1 + \bar{x}_2 dn_2 + n_2 d\bar{x}_2 + \bar{x}_i dn_i + n_i d\bar{x}_i \quad \text{——} ③$$

compair eqⁿ ④ & ④ compair eqⁿ ① & ②

$$\bar{x}_1 dn_1 + \bar{x}_2 dn_2 + \cdots \bar{x}_i dn_i = \bar{x}_1 dn_1 + n_1 d\bar{x}_1 + \bar{x}_2 dn_2$$

$$\therefore n_1 d\bar{x}_1 + n_2 d\bar{x}_2 + n_i d\bar{x}_i = 0$$

$$\boxed{\therefore \Sigma n_i dx_i = 0} \quad \text{——} ④$$

Eqⁿ ④ is nothing but the Gibb's duhem eqⁿ

This simple relationship is basis of the important Gibb's Duhem eqⁿ first derived by J.W. Gibb's and later independanly by P. Duhem.

$$\left(\frac{\partial G}{\partial n_i}\right) = \mu = \text{chemical potential}$$

* Significance of Gibb's Duhem equations

Derivation for partial molar volume.

$$\left(\frac{\partial V}{\partial n_i}\right) = \bar{V}_i$$

$$\Sigma n_i d\mu_i = 0 \quad \text{——} ①$$

where μ_i = chemical potential

we know that,

$$G = \mu_1 n_1 + \mu_2 n_2 + \cdots$$

Differentiating eqⁿ

$$dG = n_1 d\mu_1 + \mu_1 dn_1 + n_2 d\mu_2 + \mu_2 dn_2 + \cdots$$

$$dG = \mu_1 dn_1 + \mu_2 dn_2 \cdots \Sigma \mu_i dn_i + n_1 d\mu_1 + n_2 d\mu_2 \cdots \Sigma n_i d\mu_i.$$

$$\text{i.e } dG = \mu_1 dn_1 + \mu_2 dn_2 \cdots \Sigma \mu_i dn_i$$

(∵ from eqⁿ ①)

At constant temp. & pressure

$$\left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP = 0 \;,\quad \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT = 0$$

$$\boxed{\text{i.e } \Sigma \mu_i dn_i = 0}$$

Derivation for partial molar enthalpy. (Hi)

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

$$G = H - TS$$

Diff. eq^n.

$$dG = dH - Tds - sdT \quad \text{——} ①$$

For $G(P,T,n_i)$

small change in energy

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_j} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_j} dP + \Sigma n_i d\mu_i$$

$$\therefore dG = -s\,dT + V\,dP + \Sigma n_i d\mu_i \quad \text{——} ②$$

compairing eq^n ① & ②

$$dH - Tds - sdT = -sdT + VdP + \Sigma \mu_i dn_i$$

$$\therefore dH = Tds + VdP + \Sigma \mu_i dn_i$$

$$\text{i.e}\ \boxed{\left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_i \cdots n_{i-1}} = \overline{H_i}}$$

Derivation for partial molar Energy [Ei]

$$G = H - TS$$

$$G = E + PV - TS$$

Diff. eq^n.

$$dG = dE + Pdv + vdP - Tds - sdT \quad \text{——} ①$$

For $G(T,P,n_i)$

small change in energy,

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

$$dG = -s\,dT + V\,dP + \Sigma \mu_i dn_i \quad \text{——} ②$$

compairing eq^n ① & ②

$$dE + Pdv + \cancel{vdP} - Tds - \cancel{sdT} = -\cancel{sdT} + \cancel{vdP} + \Sigma \mu_i dn_i$$

$$\therefore dE = Tds - Pdv + \Sigma \mu_i dn_i$$

$$\text{i.e}\ \boxed{\left(\frac{\partial E}{\partial n_i}\right)_{S,V,n_i \cdots n_{i-1}} = \overline{E_i}}$$

Derivation for partial molar Helmoltz free energy ($\bar{A_i}$)

$$G = A + PV$$

Diff. eq^n

$$dG = dA + Pdv + vdP \quad — ①$$

At $G(P, T, n_i)$

For small change in energy,

$$\partial G = \left(\frac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_i} dP + \Sigma \mu_i dn_i$$

$$dG = -SdT + V\,dP + \Sigma \mu_i dn_i \quad — ②$$

comparing eq^n ① & ②

$$dA + Pdv + vdP = -SdT + vdP + \Sigma \mu_i dn_i$$

$$\text{i.e. } dA = \cancel{Pd} - Pdv - SdT + \Sigma \mu_i dn_i$$

$$\text{i.e. } \boxed{\left(\frac{\partial A}{\partial n_i}\right)_{V,T,n_i} = \bar{A_i}}$$

* All of the above equation

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_i} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_i} = \left(\frac{\partial E}{\partial n_i}\right)_{S,V,n_i} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_i}$$

* "Change in extensive property of the system when one mole of substance is added to the very large amount of the system, so that there will be no change in composion."

Qu. Derive an expression for various form of chemical poten

Qu. Derive an expression for chemical potenia [redacted] with pressure;

Qu. Derive expression for chemical potenitial with temperat re

The chemical potential or partial molar free energy is most important partial molar property in physical chemistry.

The chemical potential of a substance is defined as, "The change in free energy of a system results from one mole of that particular substance at constant temp. & pressure into a such a large quantity of a system that there is no appreciable change in composition of the system.

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,\ldots n_j} = \bar{G_i} = \mu_i$$

μ_i = chemical potential of i^{th} constituent.

The chemical potential is given as the rate of change of internal energy per unit change of mass

OR.

The only chemical potential that is def.ⁿ at constant T & P is the partial molar Gibb's free energy.

* [redacted]

[redacted]

From definition of chemical potential.

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

diff. w.r.t T at constant P & composition N

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

we know that,

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S \qquad \left(\because \partial G = Vdp - SdT \text{ at cons. } P \quad \left(\frac{\partial G}{\partial T}\right)_P = -S\right)$$

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

$$\therefore \left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = \frac{\partial}{\partial n_i}(-S)_{T,P,n_j}$$

$$\therefore \left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = -\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_j}$$

$$\therefore \boxed{\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = -\bar{S}_i} \quad \text{—— ①}$$

where $\bar{S}_i$ represents partial molar property of the component.

It def.ⁿ variation of chemical potential with temp. The rate of change of chemical potential with temp.

$$S^S < S^L < S^G \qquad (\because S = \text{solid}, L = \text{li}\ldots, G = \text{Gas})$$

The chemical potential affects on temp change, it express to Gibb's-Helmoltz eqⁿ. Free energy is given by,

$$G = H - TS$$

~~At constant T~~ For small change

$$\partial G = \partial H - T\partial S$$

Diff. w.r.t ni keeping T, P & molarities of the constituent ith except ith constituent is constant,

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1 \ldots} = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n_1 \ldots} - T\left(\frac{\partial S}{\partial n_i}\right)_{P,T,n_j \ldots} \quad ②$$

where $\left(\frac{\partial H}{\partial n_i}\right) = \overline{H_i}$ (partial molar term of property)

$$\left(\frac{\partial G}{\partial n_i}\right) = \overline{G_i} = \mu_i$$

eq^n ② becomes,

$$\mu_i = \overline{H_i} - Ts_i$$

but from eq^n ① $-\overline{s_i} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,N}$

$$\therefore \mu_i = \overline{H_i} + T\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N}$$

$$\therefore \overline{H_i} = \mu_i - T\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N}$$

Dividing by T^2 on both sides,

$$\frac{\overline{H_i}}{T^2} = \frac{\mu_i}{T^2} - \frac{1}{T}\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N}$$

Rearranging above eq^n

has general applicability to physical as well as chemical changes occurring at constant pressure.

(ii) It can be also used in calculating electromotive forces of reversible cells.

$$\frac{\overline{H_i}}{T^2} = \frac{\mu_i}{T^2}\left[\left(\frac{\partial}{\partial T}\right)\left(\frac{\mu_i}{T}\right)\right]$$

But $\frac{\mu_i}{T^2} = 0$

$$\therefore \frac{\overline{H_i}}{T^2} = -\frac{\partial}{\partial T}\left(\frac{\mu_i}{T}\right)$$

i.e. $$\boxed{\frac{-\overline{H_i}}{T^2} = \frac{\partial}{\partial T}\left(\frac{\mu_i}{T}\right)} \quad ③$$

eq^n ③ is nothing but the Gibb's-Duhem eq^n in terms of partial molar quanties.

② <u>Variation of chemical potential with pressure</u>

From def^n of chemical potential,

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

Diff. w.r.t P at constant T & N

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

$$\therefore \left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \left[\frac{\partial}{\partial n_i}\left(\frac{\partial G}{\partial P}\right)_{T,N}\right]_{T,P,n_j} \quad \text{①}$$

But $\left(\frac{\partial G}{\partial P}\right)_{T,N} = V$ $\quad \left[\because \partial G = V\partial P - S\partial T\right.$

At const. T

$\left.\left(\frac{\partial G}{\partial P}\right)_T = V\right]$

$\therefore$ eq^n ① becomes,

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \left[\frac{\partial}{\partial n_i}(V)_{T,N}\right]_{T,P,n_j}$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \left[\frac{\partial V}{\partial n_i}\right]_{T,P,n_j}$$

i.e $\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \overline{V_i}$ --- ($\because$ partial molar volume)

For ideal gas of a system

$\therefore PV = RT$

i.e $V = \frac{RT}{P}$

For n mole of gas,

$$V = \frac{nRT}{P}$$

i.e $V = (n_1 + n_2 + \cdots)\frac{RT}{P}$

Diff. w.r.t n_i keeping all the constitue constant $n_j \neq n_i$

$$\left(\frac{\partial V}{\partial n_i}\right)_{n_1+n_2\cdots n_j} = \frac{RT}{P}$$

$$\therefore \overline{V_i} = \frac{RT}{P}$$

Now we know that,

$$\overline{V_i} = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} \quad \text{②}$$

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{T,N} = \frac{RT}{P}$$

$$\therefore \partial \mu_i = RT\frac{\partial P}{P}$$

$$\therefore \partial \mu_i = RT\, d\log P$$

$$\int_{\mu_i^\circ}^{\mu_i} \partial \mu_i = RT\int_{P_i^\circ}^{P_i} d\log P$$

$\left[\log P\right]_{P_i^\circ}^{P_i}$

$$\mu_i - \mu_i^\circ = RT\ln\frac{P_i}{P_i^\circ}$$

$= \log P_i - \log$

$= \log\frac{P_i}{P_i^\circ}$

$$\boxed{\mu_i = \mu_i^\circ + RT\ln\frac{P_i}{P_i^\circ}}$$

* For ideal system

$$p_i^\circ = 1$$

$$\therefore \mu_i = \mu_i^\circ + RT \ln p_i$$

* For non ideal system

$$f_i = \frac{p_i}{p_i^\circ}$$

$$\text{But } f_i = \gamma a$$

$$\therefore \mu_i = \mu_i^\circ + RT \ln(\gamma a)$$

$$\mu_i = \mu_i^\circ + RT \ln \gamma_i a$$

Imp

* **Application of chemical potential**

① Phase rule – Qu. Derive phase rule.

Consider a closed system containing no. of phases a, b, c ---- p (P) composed of component 1, 2, 3 ----- c (C)

The degree of freedom which must be satisfied in order to define system completely.

The composition of each of present phase is expressed by (C-1) intensive variables of conc. only (C-1) mole fraction are variables.

$$\because \sum_i N_i = 1$$

N_i are the various mole fraction. Thus with respective the compostion, each phase posses (C-1) variable since there are 'P' phases. the entire system has P(C-1) constant variable. Additional variables, such as the temp. & pressure of each phase should also be given when temp & press. are the same in all phases, the total no. of intensive variable is,

$$P(C-1) + 2$$

Not all the intensive variables are however, indep. the eqⁿ condition i.e

$$\mu_{i(a)} = \mu_{i(b)} \text{------} \mu_{i(P)}$$

reduce the no. of the intensive variables by (P-1) for each component & by C(P-1) for all the component in the system.

No. of variable = Total no. of variable – fixed no. of variable

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

$$= C - P + 2$$