Unit-I

Thermodynamics

Entropy

• We will introduce a new thermodynamic function, entropy (S), that is dependent on heat flow between the system and surroundings and temperature. It will be used to determine spontaneity.

• Entropy is a function of state (does not depend on the path)

• Entropy is an additive function : the entropy of a universe is a sum of entropies of a system and its surroundings:

$S_{univ} = S_{sys} + S_{sur}$, $\Delta S_{univ} = \Delta S_{sys} + \Delta S_{sur}$

If surroundings are much larger than the system then

$T_{sur} \approx$ const and we define the change of entropy in surroundings as:

$\Delta S_{sur} = q_{sur}/T_{sur}$ ($q_{sur} = - q_{sys}$)

- **Spontaneous process:** the system is far from equilibrium and the process is directed towards the equilibrium: infinitesimal action cannot stop the process.

- **Non-spontaneous process:** improbable. Non-spontaneous process may become spontaneous only by redefining a universe, e.g. including in a universe something that can change equilibrium.
- **Reversible process:** the system is at equilibrium: infinitesimal action can move the process in any direction from the equilibrium (extremely important for determination ΔS_{sys}).

Free Energy (Gibbs Function, G)

We can multiply both parts of the last expression by T: $T \Delta S_{univ} = T \Delta S - \Delta H = -(\Delta H - T \Delta S)$ Definition: Free energy function is: $G = H - T S$ Free energy change is: $\Delta G = - T \Delta S_{univ} = \Delta H - T \Delta S$ ΔG connects the change of entropy in the universe, ΔS_{univ}, with thermodynamic parameters of the system only, ΔH, ΔS, and T.

ΔG can be used to determine spontaneity From $\Delta G = - T \Delta S_{univ}$ the sign of ΔG is opposite to that of ΔS_{univ}. Therefore, the following criteria can be used to determine spontaneity of a process:

ΔS_{univ}	ΔG (P = const, T = const)	Process
> 0	< 0	Spontaneous
< 0	> 0	Nonspontaneous
$= 0$	$= 0$	Equilibrium

Examples

Reaction	ΔH	ΔS	ΔG
$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$	< 0	> 0	< 0 (all T)
$H_2O(l) \rightarrow H_2O(s)$	< 0	< 0	< 0 (low T) > 0 (high T)
$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$	> 0	> 0	< 0 (high T) > 0 (low T)
$3O_2(g) \rightarrow 2O_3(g)$	> 0	< 0	> 0 (all T)

Entropy as a measure of unavailable energy

When a quantity of heat is supplied to a work substance, a portion of this energy is used for doing work, this portion of energy is called available energy and the remaining portion of energy is called unavailable energy.

The entropy is a measure of unavailable energy which may be written as,
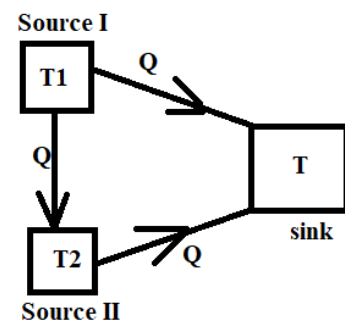
Unavailable energy = Entropy x Temperature

$$= SxT$$

To show that, Entropy as a measure of unavailable energy of a system

Consider two reservoirs of heat at a temperature T_1 and T_2 ($T_1 > T_2$) respectively and a sink at a temperature T.

Let there be a reversibility between the source-1 and sink T.

Let Q calories of heat flows into engines, maximum amount of work obtained is given by,

$$W_1 = \left[\frac{T_1 - T}{T_1}\right] \text{ or } Q\left[1 - \frac{T}{T_1}\right] \quad \text{-----1}$$

Now let us transfer Q calories of heat from source I to II and then to the engine, now as the engine works between T_2 and T_1

Maximum work obtained is given by

$$W_2 = Q\left[1 - \frac{T}{T_2}\right] \text{------}2$$

$$W_1 > W_2 \text{ as } T_1 > T_2$$

Due to the flow of heat from source I to II amount of unavailable work is given by W_1-W_2.

$$\Delta W = W_1 - W_2$$

$$= Q\left[1 - \frac{T}{T_1}\right] - Q\left[1 - \frac{T}{T_2}\right]$$

$$= \left[Q - \frac{TQ}{T_1} - Q + \frac{TQ}{T_2}\right]$$

$$\Delta W = TQ\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\Delta W = TQ\left[\frac{T_1 - T_2}{T_2 T_1}\right]\text{------}3$$

Due to the flow of heat from source I to II, The change in entropy is given by

$$\Delta S = \left[\frac{Q}{T_2} - \frac{Q}{T_1}\right]$$

$$= Q\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$= Q\left[\frac{T_1 - T_2}{T_1 T_2}\right]\text{----}4$$

Dividing equation 3 by 4

$$\frac{\Delta W}{\Delta S} = TQ\left[\frac{T_1 - T_2}{T_2 T_1}\right] X \left[\frac{T_1 T_2}{T_1 - T_2}\right]$$

$$\frac{\Delta W}{\Delta S} = T$$

$$\Delta W = T\Delta S\text{--------}5$$

This is the entropy and work relationship equation to measure the unavailable energy.

Entropy change during a spontaneous process

o During any spontaneous process, entropy of the system increases, this can be mathematically established as follows.

o Consider two vessels separated by stopper containing 1 mole of an ideal gas, enclosed in a vessel of volume V_1, being connected to another vessel having volume V_2.

o On opening stop cark, the gas in vessel A spontaneously flows into vessel B for this process, we have an entropy change as

$$dS = \frac{dq}{T} \text{--------1}$$

WKT, dq= dE+Pdv

At isothermal conditions dT=0 {dE=Cv.dt, dt=0 and dE=0}

$$dS = \frac{dE+pdv}{T} \text{--------2}$$

For 1 mole of an ideal gas PV=RT

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

Substitute P value into eqn.2

$$dS = dE + \frac{dv}{v}R \text{ ------------3}$$

Since dE=0
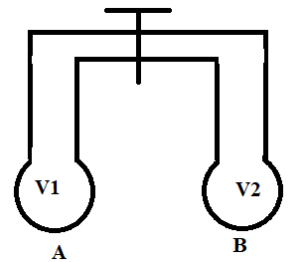
$$dS=R \frac{dv}{v} \text{--------4}$$

Total change in entropy during spontaneous isothermal change, when its volume changes from V_2 V_1+V_2 is given by

$$\delta S=\int_{v_1}^{v_2} R \frac{dv}{v} \text{--------5}$$

$$\Delta S= R \ln\frac{v_1+v_2}{v_1} \text{--------6}$$

As V_1+V_2 is greater than V_1 ie $V_1+V_2 \gg V_1$

dS>0   Therefore $\Delta S>0$,

So, Entropy of system increases during spontaneous process.
As all process occurring in nature are spontaneous process, the entropy of universe must be continuously increasing.

Helmholtz and Gibbs Free energy change:

A= E-T.S----------------1

G=H-T.S----------------2

A and G are the differential and state functions for a reversible cyclic process

$\oint dA = 0$-------3

$\oint dG = 0$-------4

Relation between A &G

G= H-T.S

G=E+PV-T.S

G=E-T.S+PV

G=A+PV--------5

Free energy functions for isothermal conditions change in G, when a system changes from one state to another under isothermal T=0,

$\Delta G = G_2 - G_1$

$=(H_2 - T S_2)-(H_1 - TS_1)$

$=H_2 - H_1 - T(S_2 - S_1)$

$= \Delta H - T \Delta S$

Thus, for infinite change, under dT=0

G=H-T.S--------6

dG=dH-T.dS-S.dT

dG=dH-T.dS--------7

Similarly

A=E-T.S

dA=dE-T.dS--------8

$\Delta A = \Delta E - T\Delta S$--------9

Substract equation 9 from 7

dG-dA=dH-dE or $\Delta G - \Delta A = \Delta H - \Delta E$

$\{\Delta H = \Delta E + P\Delta V, \Delta H - \Delta E = P\Delta V\}$

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

$\Delta G = \Delta A + P\Delta V$----------10

In reversible process $\Delta S = \dfrac{Q_{rev}}{T}$, substitute ΔS to eqn. 9

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

$\Delta A = \Delta E - Q_{rev}$ ------------------11

$\Delta E - Q_{rev} = -W_{rev}$ ---------------12   (According to 1st law of TD)

Substitute equation 12 in 11

$\Delta A = -W_{rev}$ or $-\Delta A = W_{rev}$--------------------13

WKT

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

$\Delta G = -W_{rev} + P\Delta V$

$-\Delta G = W_{rev} + P\Delta V$--------------------14

(Gibbs free energy Network function)

In a reversible process, the decrease in free energy (-ΔG) is equal to Net work done.

WKT,

dA=dE-T.dS –S.dT------------------15

We have , dS = $\frac{dq}{T}$ = dE+ $\frac{PdV}{T}$

T.dS= dE+ PdV

dE-T.dS=-PdV

In Equation 15

dA= - PdV-S.dT----------------16

dG=VdP-SdT--------17

Effect of P,V,T on free energy change

Similarly, Effect of T,P,V on free energy.

   i)   For isothermal condition,dT=0

         Equation 16 dA= - Pdv   or $\left(\frac{\partial A}{\partial V}\right)_T$ = -P --------18

         Equation 17 dG=VdP   or $\left(\frac{\partial G}{\partial P}\right)_T$ = V----------19

   ii)   For isobaric condition (dP=0)

         dA= - SdT   or $\left(\frac{\partial A}{\partial T}\right)_P$ = -S

         dG = -S.dT   or $\left(\frac{\partial G}{\partial T}\right)_p$ = -S   ----------------20

   iii) For isochoric process dv=0

         dA=-S.dT   or $\left(\frac{\partial A}{\partial T}\right)_V$ = -S---------------21

$$\left(\frac{\partial A}{\partial T}\right)_V = \frac{A-E}{T} \quad \text{or} \quad \frac{A-E}{T} \qquad \{A=E-T.S, \ -S=\frac{A-E}{T}\}$$

Comparing equation 20 and 21

$$\left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_p$$

Helmholtz and Gibbs energies as criteria of spontaneity and equilibrium, their variations with P,V and T.

o   We have seen earlier that the net entropy change of a process determines whether the process would proceed irreversibly (i.e., spontaneously) or not.

o   If there is net increase in the entropy of the system and the surroundings taken together, the process would proceed irreversibly, i.e., it would be thermodynamically feasible.

o   If there is no net change in the entropy of the system and the surroundings put together, the process will be reversible, i.e., the system will remain in a state of equilibrium.

o   We can express the criteria for reversibility and irreversibility in terms of entropy of the system (alone) as well as in terms of other fundamental thermodynamic properties, namely U, H, A and G.

o   It was stated earlier that change of entropy for a given change of state is definite quantity, independent of the fact whether the change is brought about reversibly or irreversibly. But, mathematically, it is given (for a small change) by the equation

o   The state of equilibrium is represented by a balance of driving and opposing forces, and the system is incapable of undergoing any change in this state.

o   Thus the gradients of temperature, pressure and volume are zero at equilibrium.

$$\text{i.e } dT = 0 = dP = dV$$

We shall consider the two cases below.

(i)   Criteria for equilibria at constant T and V, under this condition the equilibrium condition can be expressed in terms of Helmholtz free energy A.

$A = E\text{-}T\,S$

$dA = dE - T.dS - S\,dT$

But for a reversible process

$dE = dq_{rev} - PdV = T\,dS - PdV$

Therefore, $dA = -SdT - PdV$------------1

At constant temperature and volume

$(dA)_{T,V} = 0$

For finite changes we will have

$(\Delta A)_{T,V} = 0$----------------------------2

In an irreversible process (Spontaneous changes) the work done by the system is less then that in a reversible process.

i.e., $(PdV)_{irr} < PdV_{rev}$---------------3

Equation (2) for irreversible process can be written as

$dA < (SdT + P\,dV_{irr})$

At constant T and V, dT=0=dV,

$(dA)_{T,V} < 0$

For spontaneous process

For finite changes

$(\Delta A)_{T,V} < 0$----------------------4

Thus spontaneous processes are accompanied by a decrease of work function and this function does not change at equilibrium.

This can be restated in the following form:

"The Helmholtz free energy decreases in natural (Spontaneous) Processes. When it reaches a minimum value, the system reaches equilibrium".

This statement is obvious from the definition of $A = E-TS$
Since at equilibrium E is minimum and S is maximum naturally the difference must be a minimum.

ii) Criteria for equilibrium at constant T and P.

For this case we consider the Gibbs free energy function.

$G = H - T.S$

$G = E + PV - TS$

Diff.

$dG = dE + PdV + Vdp - TdS - SdT$ ------------- 5

For a reversible change

$dE = TdS - PdV$ ------------------------- 6

Subtract equation 5 in 6

Therefore, $dG = -SdT + VdP$ ------------- 7

At constant temperature and pressure $dT = 0 = dP$

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

For finite changes

$(\Delta G)_{T,P} = 0$ ----------------------------------- 8

For irreversible (Spontaneous) changes

$TdS > dq_{irr}$

$dq_{irr} - TdS > 0$

$dE + PdV_{irr} - TdS < 0$ ---------------------- 9

$TdS > dE + PdV_{irr}$ ----------------------- 10

From equation 7 and 9, we get

$dG < -SdT + VdP + (dE + P \, dV_{irr} - T \, dS)$

11

At const. T and P for an isolated system

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

For finite changes

$(\Delta G)_{T,P} < 0$

- That is, all spontaneous processes taking place at content temperature and Pressure are accompanied by a decrease in free energy and for a system in equilibrium the free energy must be minimum.

- For Spontaneous process the free energy decreases and the spontaneous processes have tendency to attain the stable of equilibrium.

- Once equilibrium has been attained under a given set of conditions, the properties of system will not change any more with time.

- Any quantity which is decreasing must attain its minimum value beyond which it can not change with time. So at equilibrium the free energy must be minimum.

Property	Sign	Nature of the Process
$(\Delta G)T,P$	-Ve	Spontaneous
Or	zero	Equilibrium
$(\Delta A)T,V$	+Ve	Spontaneous in reverse direction

Why is reversible work done is greater than irreversible work.

Isothermal reversible work of expansion is always greater than that of irreversible expansion of an ideal gas.

Reversible work of expansion $Wrev = nRT \ln \dfrac{P1}{P2}$

On adding and subtracting one we get

$Wrev = nRT \ln 1 - 1 + \dfrac{P1}{P2}$

$= nRT \left[1 - \left(1 - \dfrac{P1}{P2}\right)\right]$

$[\ln (1-x) = -x - 1/2\ x^2] = -x\ ]$ for small changes

$$W_{rev} = -\ nRT\ [\frac{P1}{P2} - 1]\text{----------}1$$

Irreversible work for expansion

$$W_{irv} = nRT\ [1 - \frac{P2}{P1}]\text{-------------}2$$

Comparing equation 1 and 2, we get

$$W_{rev} - W_{irv} = nRT\ [\frac{P1}{P2} - 1]\text{-}\ nRT\ [1 - \frac{P2}{P1}]$$

$$= nRT\ [\frac{P1}{P2} - 2 + \frac{P2}{P1}]$$

$$W_{rev} - W_{irv} = nRT\ [\frac{P_1^2 - 2P1P2 + P_2^2}{P1P2}]$$

$$W_{rev} - W_{irv} = \frac{nRT}{P1P2}\ (P1 - P2)\text{----------}3$$

Since $(P1 - P2)^2$ are always a +ve quantity therefore RHS of equation 3 is +ve irrespective of the fact whether P1 is greater than or less than P2.

Thus LHS of the equation 3 should also be a +ve quantity and hance $(W_{rev} - W_{irv}) > 0$ and $W_{rev} > W_{irv}$ for isothermal expansion of an ideal gas.

Maxwell's relations

These are extensively used particularly for the systems in equilibrium.

Maxwell relation's -1

From first law of thermodynamics

dq = dE+ PdV--------------1

dE = dq – Pdv-------------2

Wks $dS = \frac{dq}{T}$

dq= T.dS ------------------3

Equation 2 dE = T.dS – PdV------4

At constant volume, dV=0

dE= T.dS or $\left(\frac{\partial E}{\partial S}\right)_V = T$ ---------5

At constant entropy dS=0

dE= - PdV   or $\left(\frac{\partial E}{\partial V}\right)_S = -P$ ---------6

Differentiating equation 5 w r t V at dS = 0 and equation 6 w r t S at dV= 0

Eqn. 5. $\frac{\partial^2 E}{\partial v \partial S} = \left(\frac{\partial T}{\partial V}\right)_S$ ------------------7

Eqn. 6. $\frac{\partial^2 E}{\partial v \partial S} = -\left(\frac{\partial P}{\partial S}\right)_V$ ---------------8

Compare equation 7 and 8

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

Maxwell relation's -2

H= E + PV ---------------1

Differentiating equation 1

dH = dE + PdV + VdP ---------2

W k t dS = $\dfrac{dq}{T}$

dq= T.dS ---------3

dH = dq + V dP

dH = T.dS + V.dP --------4

dP = 0 , dH = T.dS

$\left(\dfrac{\partial H}{\partial S}\right)_P = T$ -----------5

dS= 0

dH= V dP

$\left(\dfrac{\partial H}{\partial S}\right)_P = V$ ------------6

Differentiating equation 5 w r t P at dP = 0 and equation 6 w r t S at dS= 0

$\dfrac{\partial^2 H}{\partial S\,\partial P} = \left(\dfrac{\partial T}{\partial P}\right)_S$ -------------7

$\dfrac{\partial^2 H}{\partial P\partial S} = \left(\dfrac{\partial V}{\partial S}\right)_P$ ----------------8

Compare equation 7 and 8

$$\left(\dfrac{\partial T}{\partial P}\right)_S = \left(\dfrac{\partial V}{\partial S}\right)_P$$ ----------------B

Maxwell relation's -3

A= E- T.S -------------1

Differentiating equation 1

dA = dE – T dS – S.dT --------2

W k t   dS = $\dfrac{dq}{T}$ $\dfrac{dE+PdV}{T}$

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T.dS = dE + PdV ---------3

Equn. 2

dA = dE – dE – PdV – S.dT

dA = -PdV – S dT ---------4

dV=0

dA = - SdT

$\left(\dfrac{\partial A}{\partial T}\right)_V = - S$ --------5

dT=0

dA = - PdV

$\left(\dfrac{\partial A}{\partial V}\right)_T = - P$ ---------6

Differentiating equation 5 w r t T at dT= 0 and equation 6 w r t V at dV = 0

$Eqn.\,5 \quad \dfrac{\partial^2 A}{\partial T \, \partial V} = \left(\dfrac{\partial S}{\partial V}\right)_T$ ---------------7

$Eqn.\,6 \quad \dfrac{\partial^2 A}{\partial T \, \partial V} = -\left(\dfrac{\partial P}{\partial T}\right)_V$ ------------------8

Compare equation 7 and 8

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

Maxwell relation's -4

G = H – T.S --------1

G = E + P. V - T.S --------2

Differentiating equation 2

dG = dE + P dV + V dP – T.dS – S dT

W k t $dS = \dfrac{dq}{T}$ $\dfrac{dE+PdV}{T}$

TdS = dE + PdV ----------------3

dG = T dS + VdP –TdS – SdT

dG = VdP – S dT -------------4

dP =0

dG = -SdT

$\left(\dfrac{\partial G}{\partial T}\right)_P = - S$ ---------5

dT=0

dG=VdP

$\left(\dfrac{\partial G}{\partial P}\right)_T = V$ -------6

Differentiating equation 5 w r t P   at dP= 0 and equation 6 w r t T at dT = 0

$Eqn.\,5 \quad \dfrac{\partial^2 G}{\partial P\,\partial T} = -\left(\dfrac{\partial S}{\partial P}\right)_T$ ---------------7

$Eqn.\,6 \quad \dfrac{\partial^2 G}{\partial P\,\partial T} = \left(\dfrac{\partial V}{\partial T}\right)_P$ ----------------8

Compare equation 7 and 8

$$\left(\dfrac{\partial V}{\partial T}\right)_P = -\left(\dfrac{\partial S}{\partial P}\right)_T \text{---------------D}$$

Application of Maxwell's Relations

The Four Maxwell relations have a very wide range of applications . They apply to all kind of substances (solids, liquids, gases)under all type of conditions of Pressure, volume and temperature. Before Discussing applications

1. Cooling Produced By Adiabatic Expansion of Any Substance

In adiabatic process entropy S remains constant. Therefore by considering

 the Thermodynamic relation

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

We can prove

$$\Delta T = \frac{-Tp\beta}{mC_v}$$

Most of the substances expand on heating , they have +ve beta value. ΔT Will be –ve

i.e all the substances will cool down. A few substances like rubber have –ve beta value.

They will get heat up..

 2. Adiabatic Compression of A Substance

 By considering the Thermodynamic relation

$$\left(\frac{\partial T}{\partial p}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_p$$

We can prove

$$\Delta T = \frac{TV\alpha}{C_p}$$

Above result shows that if α is +ve, then adiabatic increase in pressure

causes the temprature to rise.

Similarily using other maxwell's equations we can explain the stretching

of wires and thin films

3. Change of internal energy with Volume,

Using the third Maxwell's relation

$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial P}{\partial T}\right)_v$$

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$$\left(\frac{\partial u}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right) - P$$

$$C_V = T\left(\frac{\partial s}{\partial T}\right)_v \quad \text{or} \quad \left(\frac{\partial s}{\partial T}\right)_v = \frac{C_V}{T}$$

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

4. $C_p - C_v = R$ for ideal gases.

Other relations for the specific heats are given below.

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

$$C_p - C_v = \frac{vT\beta^2}{\alpha}$$

where β is the *volume expansivity* and α is the *isothermal compressibility,* defined as

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P \quad \text{and} \quad \alpha = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

$$v = \frac{RT}{P}$$

$$\beta = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P = \frac{1}{v}\left(\frac{R}{P}\right) = \frac{1}{T}$$

$$\alpha = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T = -\frac{1}{v}\left(-\frac{RT}{P^2}\right) = \frac{1}{P}$$

$$C_p - C_v = \frac{vT\beta^2}{\alpha} = \frac{vT\left(\frac{1}{T}\right)^2}{\frac{1}{P}} = \frac{vP}{T}$$

$$= R$$

The difference $C_p - C_v$ is equal to R for ideal gases and to zero for incompressible substances ($v =$ constant).

5. Variation of C_v with specific volume.

$$\left(\frac{\partial C_v}{\partial v}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_v$$

5. Variation of C_v of an ideal gas does not depend upon specific volume.

For an ideal gas

$$P = \frac{RT}{v}$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v}$$

$$\left(\frac{\partial u}{\partial v}\right)_T = T\frac{R}{v} - P = P - P = 0$$

$$P = \frac{RT}{v}$$

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{R}{v}$$

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_v = 0$$

$$\left(\frac{\partial C_v}{\partial v}\right)_T = 0$$

Therefore, the specific heat at constant volume of an ideal gas is independent of specific volume.

For Vander Waal's gas also it is independent of volume.

6. Change of state and clapeyron's equation

In ordinary phase transition of matter(solid phase to liquid phase, liquid to vapour, and solid to vapour) take place under constant temperature and pressure. During the transition a certain amount of heat, known as latent heat must be supplied to the substance for a change of phase.

During this change temperature remains constant.

Therefore using Maxwell relation

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

using $\Delta U = L$, the latent heat, We have

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{L}{T(V_f - V_i)}$$

This equation is known as Clausius-Clapeyron's latent heat Equation.

Partial Molar properties

Some thermodynamic properties like entropy, enthalpy, internal energy, etc., are known as extensive properties because their values change by varying mass of the system. In many thermodynamic equations, the change of state was due to variation of temperature and pressure only. Accordingly, it was assumed that in the case of a closed system there is no change in mass of the system, while in the case of an open system containing two or more components, the number of moles of various components can also be changed. In such case, the extensive property (X) must be function of number of moles of various components of the system, in addition to temperature and pressure of the system.

Expression of Partial molar quantity Suppose the temperature of the system be T and pressure be P and n1, n2,n3 .... j be the corresponding number of moles of the components 1, 2, 3, ….., j. Thus accordingly the property X must be the function of temperature, pressure and the number of moles of the various components of the system, i.e.,

X= f(T,P,n$_1$,n$_2$,n$_3$,…..n$_j$)-----------------1

 The total number of moles N = Thus change in property dX when the temperature, pressure and number of moles change will be: dX= $\left(\frac{\partial X}{\partial T}\right)_{P,N}$ dT + $\left(\frac{\partial X}{\partial P}\right)_{T,N}$ dP + $\left(\frac{\partial X}{\partial n1}\right)_{T,N,n2...nj}$ dn1 + $\left(\frac{\partial X}{\partial n2}\right)_{T,P,n1,n3...nj}$ dn2-----------------2

This quantity $\left(\frac{\partial X}{\partial n1}\right)_{T,N,n2...nj}$ dn$_1$ is called the partial molar property of the ith component. This is also represented as $\bar{X}i$. Thus partial molar property may be defined as a thermodynamic quantity, which shows that an extensive property of a solution or mixture changes with the change in the molar composition of the solution, while keeping the temperature and pressure

constant. It is a partial derivative of the extensive property with respect to the amount of the component of interest. Each extensive property of a mixture has its corresponding partial molar property. Thus for any component (say ith) component of a system:

Thus, for the ith component in a system

Partial molar internal energy $= \left(\frac{\partial U}{\partial n_i}\right)_{T,\,P,\,n_1,n_2,n_3\ldots} = \bar{U}_i$

Partial molar enthalpy $= \left(\frac{\partial H}{\partial n_i}\right)_{T,\,P,\,n_1,n_2,n_3\ldots} = \bar{H}_i$

Partial molar entropy $= \left(\frac{\partial S}{\partial n_i}\right)_{T,\,P,\,n_1,n_2,n_3\ldots} = \bar{S}_i$

Partial molar volume $= \left(\frac{\partial V}{\partial n_i}\right)_{T,\,P,\,n_1,n_2,n_3\ldots} = \bar{V}_i$ ------------------------3

Physical significance of Partial molar quantity The quantity X_i represents the actual value of X per mole of the ith component of the system.

This value may be same or different from the actual molar value X^* in the pure state.

These two values i.e. partial molar value and actual molar value are same in the case of ideal systems.

While in the case of non-ideal systems, these two values are different because of the interactions between the constituents, i.e., actual molar value get modified to partial molar value.

This partial molar value may not be same throughout the whole solution since the extent of interactions vary according to the amount of the constituents in the system.

Hence the partial molar value is dependent on the composition of the system.

Therefore, the partial molar quantities are meant for the individual components of the system, but their values are not only dependent on the nature of the particular component in consideration but also on the nature and amounts of the other components of the system.

Partial molar volume

The partial molar volume of a substance (say ith component) in a mixture is the change in volume per mole of substance 'i' added to a large volume of the mixture. In the case of ideal solution, the partial molar volume of the ith component will be equal to its molar volume in the pure state, whereas in the case of non-ideal solution the partial molar volume is the molar volume actually occupied by the substance in a solution of known composition. The partial molar volume of constituents of the mixture changes with the composition. As the partial molar volume is the actual molar volume of the component present in the solution of known composition therefore the total volume of solution will be given as:

$$V_{total} = n_1 V_{1,} + n_2 V_{2,}\text{-----------------------}4$$

Determination of Partial Molar Volumes (For two component system) The values of partial molar volumes of the components of the solution can be determined by various methods. A direct method to measure $V_{1,pm}$ (partial molar volume of component 1) is to measure the volume of the solutions which is formed by adding different amount of component 1 in a definite amount of component 2. Then a graph is plotted between volume of solution and amount of component 1. At the given composition of the solution, the slope of the line at that composition gives partial molar volume of the component 1. But better method for determining the partial molar volumes is the intercept method.

Determination of partial molar volume by Intercept method

Assuming $V_{m,mix}$ be the volume of mixture consisting of total of one mole of the two components.

Thus, we can write it as $V_{m.mix} = \dfrac{V}{n_A + n_B}$

In the above expression, V stands for the volume of the mixture consisting the amounts n_1 and n_2 of the corresponding components 1 and 2. Under constant temperature and pressure the partial molar volume can be written as:

$$V_{1,pm} = \left(\frac{\partial V}{\partial n_1}\right)_{n_2} = \left(\frac{\partial (n_1 + n_2)\ V_{m,mix}}{\partial n_1}\right)_{n_2}\text{--------------}1$$

After undergoing the differentiation, the expression becomes:

$$= V_{m,mix} + (n_1 + n_2)\left(\frac{\partial V_{m,mix}}{\partial n_1}\right)_{n_2}\text{--------------------}2$$

Since the total mole fraction of the system is equal to 1, i.e., $x_1 + x_2 = 1$, Thus the total molar volume $V_{m,mix}$ at specified temperature and pressure will be the function of only one of the mole fraction terms.

$V_{m,mix} = f(x_2)$

Taking differential of the above expression:

$dV_{m,mix} = \left(\frac{dV_{m,mix}}{dx_2}\right) dx_2$ -------------3

Now dividing the equation by dn_1 and taking n_2 be constant, we get

$\left(\frac{\partial V_{m,mix}}{\partial n_1}\right)_{n_2} = \left(\frac{dV_{m,mix}}{dx_2}\right)\left(\frac{\partial x_2}{\partial n_1}\right)_{n_2}$ -----------4

Since the mole fraction is given by

$x_2 = \frac{n_2}{n_1+n_2}$ ----------------5

Thus for expression, $\left(\frac{\partial x_2}{\partial n_1}\right)_{n_2}$ we can write

$\left(\frac{\partial x_2}{\partial n_1}\right)_{n_2} = -\frac{n_2}{(n_1+n_2)^2}$ ------------6

Substituting equation 5 in 6 we get:

$\left(\frac{\partial x_2}{\partial n_1}\right)_{n_2} = -\frac{x_2}{(n_1+n_2)}$ -------------7

Substituting equation 7 in equation 4 we get:

$\left(\frac{\partial V_{m,mix}}{\partial n_1}\right)_{n_2} = \left(\frac{dV_{m,mix}}{dx_2}\right)\left(-\frac{x_2}{(n_1+n_2)}\right)$ ------------8

Putting this expression in equation (2), we get:

$V_{1,p,m} = V_{m,mix} - x_2\left(\frac{dV_{m,mix}}{dx_2}\right)$ ----------------9

Or

$V_{m,mix} = V_{1,p,m} + x_2\left(\frac{dV_{m,mix}}{dx_2}\right)$ ----------------10

Similarly for second component, the partial molar volume will be given by:

$V_{m,mix} = V_{2,p,m} + x_1\left(\frac{dV_{m,mix}}{dx_1}\right)$ --------11

The above equations represent tangent line drawn to the plot of $V_{m,mix}$ versus x_2 (taking equation 10) with the intercept equal to $V_{1,pm}$ and accordingly the slope of the line is $\left(\frac{dV_{m,mix}}{dx_2}\right)$ Similarly the plot is drawn between $V_{m,mix}$ and x_1 in which the intercept becomes $V_{2,pm}$ and slope is $\left(\frac{dV_{m,mix}}{dx_1}\right)$ Both the equations given above represent a single plot because $x_1 + x_2 = 1$.
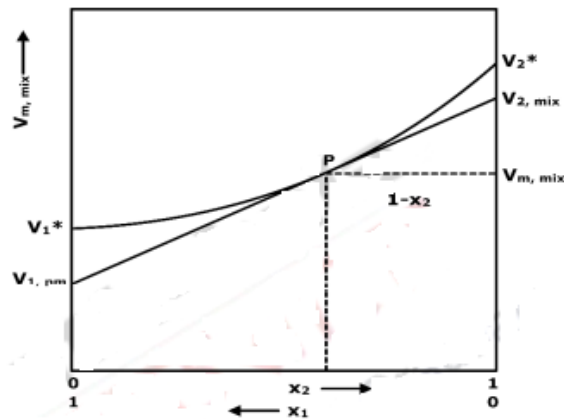
This plot is shown in the figure given below

Figure: The method of intercepts to determine the partial molar volumes of components of a binary solution

In Figure: Intercepts are: $V_{1,pm}$ at $x_2 = 0$ (or $x_1 = 1$)

$$V_{2,pm} \text{ at } x_2 = 1 \text{ (or } x_1 = 0)$$

Equation 10 and 11 are valid for any extensive property Y (V,G, U,S,A,H) of the mixture.

Thus generalized equation is can be written as

$$Y_{m,mix} = Y_{1,p,m} + x_2 \left(\frac{dY_{m,mix}}{dx_2} \right) \text{----------------}12$$

$$Y_{m,mix} = Y_{2,p,m} + x_1 \left(\frac{dY_{m,mix}}{dx_1} \right) \text{----------------}13$$

1. Change from ΔH° and ΔS° Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the vaporization of water at room temperature (298 K). What does the computed value for ΔG° say about the spontaneity of this process?

Solution

The process of interest is the following:

$$H_2O(l) \longrightarrow H_2O(g)$$

The standard change in free energy may be calculated using the following equation:

$$\Delta G^\circ_{298} = \Delta H^\circ - T\Delta S^\circ$$

From Appendix G, here is the data:

Substance	ΔH°_f (kJ/mol)	S°_{298} (J/K·mol)
$H_2O(l)$	−286.83	70.0
$H_2O(g)$	−241.82	188.8

Combining at 298 K:

$$\Delta H^\circ = \Delta H^\circ_{298} = \Delta H^\circ_f(H_2O(g)) - \Delta H^\circ_f(H_2O(l))$$
$$= [-241.82 \text{ kJ} - (-285.83)] \text{ kJ/mol} = 44.01 \text{ kJ/mol}$$

$$\Delta S^\circ = \Delta S^\circ_{298} = S^\circ_{298}(H_2O(g)) - S^\circ_{298}(H_2O(l))$$
$$= 188.8 \text{ J/mol} \cdot K - 70.0 \text{ J/K} = 118.8 \text{ J/mol} \cdot K$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

Converting everything into kJ and combining at 298 K:

$$\Delta G^\circ_{298} = \Delta H^\circ - T\Delta S^\circ$$
$$= 44.01 \text{ kJ/mol} - (298 \text{ K} \times 118.8 \text{ J/mol} \cdot K) \times \frac{1 \text{ kJ}}{1000 \text{ J}}$$
$$44.01 \text{ kJ/mol} - 35.4 \text{ kJ/mol} = 8.6 \text{ kJ/mol}$$

At 298 K (25 °C) $\Delta G^\circ_{298} > 0$, and so boiling is nonspontaneous (not spontaneous).

Problems on free energy

Use standard enthalpy and entropy data from Appendix G to calculate the standard free energy change for the reaction shown here (298 K). What does the computed value for ΔG° say about the spontaneity of this process?

$$C_2H_6(g) \longrightarrow H_2(g) + C_2H_4(g)$$
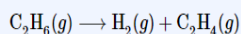
Answer:

2. $\Delta G^\circ_{298} = 102.0 \text{ kJ/mol}$; the reaction is nonspontaneous (not spontaneous) at 25 °C.
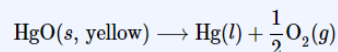
Free energy changes may also use the standard free energy of formation (ΔG°f)(ΔGf°), for each of the reactants and products involved in the reaction. The standard free energy of formation is the free energy change that accompanies the formation of one mole of a substance from its elements in their standard states. Similar to the standard enthalpies of formation, (ΔG°f)(ΔGf°) is by definition zero for elemental substances under standard state conditions. The approach to computing the free energy change for a reaction using this approach is the same as that demonstrated previously for enthalpy and entropy changes. For the reaction.

$$mA + nB \longrightarrow xC + yD,$$

the standard free energy change at room temperature may be calculated as

$$\Delta G^\circ_{298} = \Delta G^\circ = \sum \nu \Delta G^\circ_{298}(\text{products}) - \sum \nu \Delta G^\circ_{298}(\text{reactants})$$
$$= [x\Delta G^\circ_f(C) + y\Delta G^\circ_f(D)] - [m\Delta G^\circ_f(A) + n\Delta G^\circ_f(B)].$$

Consider the decomposition of yellow mercury(II) oxide.

$$HgO(s, \text{yellow}) \longrightarrow Hg(l) + \frac{1}{2}O_2(g)$$

Calculate the standard free energy change at room temperature, ΔG°_{298}, using (a) standard free energies of formation and (b) standard enthalpies of formation and standard entropies. Do the results indicate the reaction to be spontaneous or nonspontaneous under standard conditions?

Solution

The required data are available in Appendix G and are shown here.

Compound	ΔG°_f (kJ/mol)	ΔH°_f (kJ/mol)	S°_{298} (J/K·mol)
HgO (s, yellow)	−58.43	−90.46	71.13
Hg(l)	0	0	75.9
O₂(g)	0	0	205.2

3.

(a) Using free energies of formation:

$$\Delta G^\circ_{298} = \sum \nu G S^\circ_{298}(\text{products}) - \sum \nu \Delta G^\circ_{298}(\text{reactants})$$

$$= \left[1\Delta G^\circ_{298} Hg(l) + \frac{1}{2}\Delta G^\circ_{298} O_2(g) \right] - 1\Delta G^\circ_{298} HgO(s, \text{yellow})$$

$$= \left[1 \text{ mol}(0 \text{ kJ/mol}) + \frac{1}{2}\text{mol}(0 \text{ kJ/mol}) \right] - 1 \text{ mol}(-58.43 \text{ kJ/mol}) = 58.43 \text{ kJ/mol}$$

(b) Using enthalpies and entropies of formation:

$$\Delta H^\circ_{298} = \sum \nu \Delta H^\circ_{298}(\text{products}) - \sum \nu \Delta H^\circ_{298}(\text{reactants})$$

$$= \left[1\Delta H^\circ_{298} Hg(l) + \frac{1}{2}\Delta H^\circ_{298} O_2(g) \right] - 1\Delta H^\circ_{298} HgO(s, \text{yellow})$$

$$= [1 \text{ mol}(0 \text{ kJ/mol}) + \frac{1}{2}\text{mol}(0 \text{ kJ/mol})] - 1 \text{ mol}(-90.46 \text{ kJ/mol}) = 90.46 \text{ kJ/mol}$$

$$\Delta S^\circ_{298} = \sum \nu \Delta S^\circ_{298}(\text{products}) - \sum \nu \Delta S^\circ_{298}(\text{reactants})$$

$$= \left[1\Delta S^\circ_{298} Hg(l) + \frac{1}{2}\Delta S^\circ_{298} O_2(g) \right] - 1\Delta S^\circ_{298} HgO(s, \text{yellow})$$

$$= \left[1 \text{ mol}(75.9 \text{ J/mol K}) + \frac{1}{2}\text{mol}(205.2 \text{ J/mol K}) \right] - 1 \text{ mol}(71.13 \text{ J/mol K}) = 107.4 \text{ J/mol K}$$

Chemical Potential:

The partial molar gibbs free energy has been given a specific symbol μ because of its univerasality in dealing with various aspects of thermodynamics studies. Its signifecance is discussed here. For a multicomponent system, free energy is a function of T,P and number of moles (n_i) of various specis.

Thus, $G = f(T, P, n_1, n_2, \dots n_i)$

And $dG = \left(\dfrac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT + \left(\dfrac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP + \left(\dfrac{\partial G}{\partial n_1}\right)_{T,P,n_2} dn_1 + \cdots$

$$= \left(\dfrac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT + \left(\dfrac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP + \overline{G_1}\ dn_1 + \overline{G_2}\ dn_2 + \dots\dots \text{-----(1)}$$

Where

$$\overline{G_1} = \left(\dfrac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \mu_{i,\ j \neq i} \quad \text{--------(2)}$$

μ_i = Chemical potential of the component i in the system and is defined as the change in the Gibbs free energy with the change in the number of moles of component i when T and P and the moles of other components are kept constant.

It is intensive property and is a meassure of escaping tendency.

For a closed system $dn_1 = 0, dn_2 = 0$ and equation (1) gives

$$(dG)_N = \left(\dfrac{\partial G}{\partial T}\right)_{P,n_i} dT + \left(\dfrac{\partial G}{\partial P}\right)_{T,n_i} dP \text{----------(3)}$$

But for a closed system

dG= -SdT + VdP -----------(4)

Comparing the coefficient in the equation (3) and (4) we get,

$$\left(\dfrac{\partial G}{\partial T}\right)_P = -S, \left(\dfrac{\partial G}{\partial P}\right)_T = V \text{----------(5)}$$

From the equation (1),(2) and (5) we have

dG = -S dT + V dP + $\mu_1\ dn_1 + \mu_2 dn_2 + \cdots$

$\qquad$ = -SdT + Vdp+ $\sum_i \mu_i dn_i$ ---------(6)

For constant T and P; dT=0 and dP=0 and

$dG = \sum_i \mu_i dn_i$

$\quad = \mu_1 dn_1 + \mu_2 dn_2 + \ldots \quad \text{-------(7)}$

Equation (7) can be integrated for a constant composition system to give

$G = \mu_1 n_1 + \mu_2 n_2 + \text{----------} = \sum_i \mu_i dn_i \quad \text{---------(8)}$

(**Chemical Potential**)

The total differencial of G is given by

$dG = \mu_1 dn_1 + n_1 d\mu_1 + n_2 d\mu_2 + \mu_2 dn_2 \text{-----------(9)}$

Comparing equn. (6) and (9) we get

$-S\, dT + VdP + \sum_i \mu_i dn_i = \mu_1 dn_1 + n_1 d\mu_1 + n_2 d\mu_2 + \mu_2 dn_2$

$\qquad\qquad\qquad = \mu_1 dn_1 + \mu_2 dn_2 + n_1 d\mu_1 + n_2 d\mu_2$

$-S\, dT + VdP + \sum_i \mu_i dn_i = \sum_i \mu_i dn_i + \sum_i n_i d\mu_i$

Terms getting cancel and we get

$-S\, dT + VdP = \sum_i n_i d\mu_i$

Or $\quad -S\, dT + VdP - \sum_i n_i d\mu_i = 0 \text{--------- (10)}$

Equation (10) is the Gibbs- Duhem equation,

For an isothermal and isobaric process eqn. (10) reduces to

$\sum_i n_i d\mu_i = 0$

Variation of temperature on chemical potential

Chemical potential of i th component of a system is defined as

$\mu_i = \left(\dfrac{\partial G}{\partial n_i}\right)_{T,P,n_j} \text{--------(1)}$

Differenciating equation(1) wrt T at constant P and composition we get

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

Since G is a state function

$$\frac{\partial^2 G}{\partial T \partial n_i} = \frac{\partial^2 G}{\partial n_i \partial T}$$

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

$$= -\frac{\partial}{\partial n_i}(S)_{T,P,n_j} = -\bar{S_i} \text{--------- (2)}$$

Where $\bar{S_i} = \left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_j}$ = Partial molar entropy.

From equation (2) it is clear that the chemical potential will decrease with increase temperature as entropy is always a positive quantity. However the rate of change of chemical potential with temperature is different for the gases ,liquids and solids as,

$$S^g > S^l > S^s.$$

Variation of Pressure on chemical potential ;

Chemical potential of i th component of a system is defined as

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} \text{--------(1)}$$

Differenciating equation(1) wrt P at constant T and composition we get

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

Since G is a state function

$$\frac{\partial^2 G}{\partial P \partial n_i} = \frac{\partial^2 G}{\partial n_i \partial P}$$

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

$$= \left(\frac{\partial V}{\partial n_i}\right)_{T,P,n_j} = \overline{V_i}$$

$$\frac{d\mu_i}{dP} = \overline{V_i}$$

$$d\mu_i = \overline{V_i}\, dP \text{ ---------- (2)}$$

Where $\overline{V_i}$ = Partial molar volume of ith component . Equation (2) can be integrated for suitable limits ,

$$\int d\mu_i = \int \overline{V_i}\, dP \text{ ------------(3)}$$

Equation (3) can be used to calculate the chemical potential of the gases, liquids and solids , provide we know the pressure dependence of volume.

The Duhem-Margules Equation :

For a system consisting of a liquid solution of two components equilibrium with their vapors, At constant temperature and pressure, the condition for an infinitesimal change of compoition is given by the Gibbs –Duhem equation in the form;

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \text{ -----------(1)}$$

Where $n_1\ and\ n_2$ are the numbers of moles of the constituents 1 and 2 present in the solution and $\mu_1\ and\ \mu_2$ are their partial molar free energies or chemical potentials. If equation (1) is divided by n_1+n_2 the result is

$$\frac{n_1}{n_1+n_2} d\mu_1 + \frac{n_2}{n_1+n_2} d\mu_2 = 0$$

$$N_1 d\mu_1 + N_2 d\mu_2 = 0 \text{ ------------(2)}$$

Where $N_1\ and\ N_2$ are the mole fractions of the respective components.

The chemical potential of any constituent of solution depends on the temperature , (total) pressure and composition of the solution, if the temperature and pressure are maintained constant, however , the chemical potential is determined by the composition only .It is then possible , therefore , to write for an infinitesimal change of composition,

$$d\mu_i = \left(\frac{\partial \mu_i}{\partial N_i}\right)_{T,P} dN_i$$

and upon substitution in (2) it follows that

$$N_1 \left(\frac{\partial \mu_1}{\partial N_1}\right)_{T,P} dN_1 + N_2 \left(\frac{\partial \mu_2}{\partial N_2}\right)_{T,P} dN_2 = 0 \quad \text{----------------(3)}$$

$$\left(\frac{\partial \mu_1}{\partial \ln N_1}\right)_{T,P} dN_1 + \left(\frac{\partial \mu_2}{\partial \ln N_2}\right)_{T,P} dN_2 = 0 \quad \text{----------------(4)}$$

$$\left[\because \left(\frac{\partial \mu_1}{\frac{1}{N_1}\partial N_1}\right)_{T,P} dN_1 + \left(\frac{\partial \mu_2}{\frac{1}{N_2}\partial N_2}\right)_{T,P} dN_2 \right]$$

Since the sum of the two mole fractions is equal to unity ,i.e., $N_1 + N_2 = 1$, it is seen that

$$dN_1 + dN_2 = 0 \quad or \quad dN_2 = -dN_1$$

So that equation (4) can be written as

$$\left(\frac{\partial \mu_1}{\partial \ln N_1}\right)_{T,P} - \left(\frac{\partial \mu_2}{\partial \ln N_2}\right)_{T,P} = 0$$

Giving a useful form of the Gibbs-Duhem equation . we know that the chemical potential of any constituent of a liquid mixture is represented by

$$\mu_i = RTd \ln f_i \quad \text{------------------(6)}$$

Using (6) in (5) we get

$$\left(\frac{RTd \ln f_1}{\partial \ln N_1}\right)_{T,P} - \left(\frac{RTd \ln f_2}{\partial \ln N_2}\right)_{T,P} = 0$$

Dividing throughout the equation by RT we get

$$\left(\frac{d \ln f_1}{\partial \ln N_1}\right)_{T,P} - \left(\frac{d \ln f_2}{\partial \ln N_2}\right)_{T,P} = 0$$

$$\left(\frac{d \ln f_1}{\partial \ln N_1}\right)_{T,P} = \left(\frac{d \ln f_2}{\partial \ln N_2}\right)_{T,P} \text{------------(7)}$$

This is the precise form of what is known as the Duhem-morgules equation.

It is frequently encountered and employed in a less exact form which is based on the approximation that the vapor behaves as an exact gas. In this event the fugacity of the each component in the vapor may be replaced by itds respective partial (vapor) pressure , so that equation (7) becomes

$$\left(\frac{d \ln p_1}{\partial \ln N_1}\right)_{T,P} = \left(\frac{d \ln p_2}{\partial \ln N_2}\right)_{T,P} \text{------------(8)}$$

Where p_1 and p_2 are the partial vapor pressures of the two constituents in equilibrium with the liquid containing the mole fractions $N_1 \ and \ N_2$ respectively of these constituents.

Applications of Duhem- Morgules equation.

It is important to note that equation (8) is applicable to any liquid solution of two constituents, irrespective of whether the solution (or vapor) is ideal or not.

In the derivation of this equation no assumptions or postulate was made concerning the properties of the solution. The results are based only on thermodynamic considerations ,and hence they are of complitely general applicability.

The form given in equation (8) is also independent of the ideality or otherwise of the solution, but it involves supposition that the vapor in equilibrium with it behaves ideally.