Thermodynamics: Classical to Statistical
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Lecture - 06
Introduction to chemical potential

In the last class we discussed about a few relationships and from these relationship we get some new relationship like,

$$dU = TdS - PdV \quad \Rightarrow \quad (\partial V/\partial S)_P = T \text{ and } (\partial U/\partial V) = -P$$

$$dH = TdS + VdP \quad \Rightarrow \quad (\partial H/\partial S)_P = T \text{ and } (\partial H/\partial P)_S = V$$

$$dA = -PdV - SdT \quad \Rightarrow (\partial A/\partial V)_T = -P \text{ and } (\partial A/\partial T)_V = -S$$

$$dG = VdP - SdT \quad \Rightarrow (\partial G/\partial P)_T = V \text{ and } (\partial G/\partial T)_P = -S$$

So, these are the relationships we have we have got so far.

$$(\partial U/\partial S)_V = T \qquad\qquad (\partial U/\partial V)_S = -P$$

$$\Rightarrow \partial^2 U/\partial S\partial V = (\partial T/\partial V)_S \qquad\qquad \Rightarrow \partial^2 U/\partial S\partial V = -(\partial P/\partial S)_V$$

Since U is a state function ⇒dU ⇒exact differencial

$$\left.\begin{array}{l} (\partial T/\partial V)_S = -(\partial P/\partial S)_v \\ \text{Similarly} \\ (\partial T/\partial P)_S = (\partial P/\partial S)_p \\ (\partial S/\partial V)_T = (\partial P/\partial S)_v \end{array}\right\} \text{Maxwell's relations}$$

$$(\partial S/\partial P)_T = -(\partial P/\partial S)_p$$

So, these four relations or expressions are known as Maxwell's relations.

We can have another set of Maxwell's relations

$$(\partial U/\partial S)_V = (\partial H/\partial S)_P$$

$$(\partial U/\partial V)_S = - (\partial A/\partial V)_T$$

$$(\partial H/\partial P)_S = (\partial G/\partial P)_T$$

$$(\partial A/\partial T)_V = (\partial G/\partial T)_P$$

Show that for ideal gas $(\partial U/\partial V)_T = 0$

Soln: We know $dU = TdS - PdV$ . . . . (1)

Again , $S = S(T, V)$

$\Rightarrow dS = (\partial S/\partial T)_V dT + (\partial S/\partial V)_T dV$

Substracting the value of dS in equation (1)

$dU = T(\partial S/\partial T)_V dT + T(\partial S/\partial V)_T dV - PdV$

$dU = T(\partial S/\partial T)_V dT + [T(\partial S/\partial V)_T - P]$ . . . (2)

Again , $U \Rightarrow U(T, V)$

$dU = (\partial U/\partial T)_V dT + (\partial U/\partial V)_T dV$ . . . . (3)

equating the co-efficients of dV in equation (2) and (3)

$T(\partial S/\partial V)_T - P = (\partial U/\partial V)_T$

$\Rightarrow T(\partial P/\partial T)_V - P = (\partial U/\partial V)_T$

Fotr ideal gas $P = (nRT)/V$

$(\partial P/\partial T)_V = nR/V$

$-P = (\partial U/\partial V)_T$

$\Rightarrow \boldsymbol{(\partial U/\partial V)_T = 0}$

show that for ideal gas $(\partial U/\partial P)_T = 0$

Soln: $H = U + PV = U + nRT$

$\Rightarrow U = H - nRT$

$\Rightarrow (\partial U/\partial P)_T = (\partial H/\partial P)_T - (\partial nRT/\partial P)_T$

We know $dH = TdS + VdP$

$\Rightarrow (\partial H/\partial P)_T = T(\partial S/\partial P)_T + V$

$\Rightarrow (\partial H/\partial P)_T = V - T(\partial V/\partial T)_P$

For Ideai gas ,

$V = nRT/P$

$\Rightarrow (\partial V/\partial T)_P = nR/P$

$\Rightarrow (\partial V/\partial T)_T = (\partial H/\partial P)_T - (\partial nRT/\partial P)_T$

$\Rightarrow (\partial H/\partial P)_T = 0$

We know ,$(\partial G/\partial P)_T = V$

$\Rightarrow dG = VdP$ at constant T

For ideal gas , aav = nRT/P

$\int_{G1}^{G2} dG = \int_{P1}^{P2} (nRT/P)\, dP$

$\Rightarrow G_2(T,P_2) - G_1(T,P_1) = nRT \ln P_2/P_1$

$\Rightarrow G_2(T,P_{2/})/n - G_1(T,P_1)/n = RT \ln P_2/P_1$

$\bar{G}_2(T,P_2) - \bar{G}_1(T,P_1) = RT \ln P_2/P_1$

Where $\bar{G}_2$ and $\bar{G}_1$ are molar Gibbs free energy

$\mu_2 (T,P_2) - \mu_1(T,P_1) = RT \ln P_2/P_1$

where μ refers to chemical potential

If P_1 = 1 atm and P_2 = P atm

$\mu_2 = \mu(T,P)$, $\mu_1 = \mu^0 (T)$, μ^0 standard chemical potential

$\mu(T,P) = \mu^0 (T) + RT \ln P$

So, what is the definition of standard state then? Standard state means pressure is 1 atmospheric pressure and temperature can be anything, we need to define temperature.

Gibbs –Helmhotz Equation

We know , G = H- TS

G/T= H/T –S

$[\partial(G/T)/\partial T]_P = - H/T_2 + 1/ T(\partial H/\partial T)_P - (\partial S/\partial T)_P$

Now , $1/T(\partial H/\partial T)_P = (\partial S/\partial T)_P$

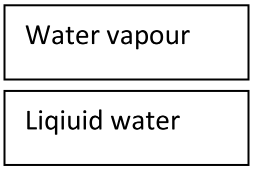
$\left(\frac{\partial(G/T)/}{\partial T}\right)_P = -\ H/T^2$ …..Gibbs Helmotz equation

$\left(\frac{\partial(\Delta G/T)/}{\partial T}\right)_P = -\ \Delta H/T^2$ …..another form of Gibbs Helmotz equation

So, this is also another form of Gibbs-Helmholtz equation.

<u>The chemical potential of a pure substance in tow phase in equilibrium are equal</u>

Let us consider a system of two phase of a pure substance in equilibrium with each other at constant T and P (Figure 1)



At constant T and P

Figure 1

Suppose G^l and G^v represent Gibbs free energy in liquid and vapour phase respectively

Next we will discuss one interesting thing. The chemical potential of a pure substance in 2 phases in equilibrium are equal. We know the statement, today we are going to prove it. Let us consider a system of 2 phases of a pure substance in equilibrium with each other.

The total Gibbs free energy of the system,

$G = G^l + G^v$

$\Rightarrow dG = (\partial G^l/\partial n^l)_{P,T}\, dnl + (\partial Gv/\partial n^v)_{P,T}\, dn^v$……(1)

Where ,$dn^l \Rightarrow$ change in noumber of moles

$dn^v \Rightarrow$ change in number of moles in the upper state

So, liquid and vapour they are in equilibrium with each other. The sum of the molecules in the liquid state goes to vapour state.

Similarly, some vapour molecules comes back to the liquid state. dn^v represents change in number of moles in the vapour state. As I stated just now that some of the molecules in the liquid state go into the vapour state and some of the molecules in the vapour state come to liquid state. And since the system is in equilibrium, we can write or it is quite obvious that, $dn^l = -dn^v$, because the system is in equilibrium.

$dG = [(\partial G^l/\partial n)_{P,T} - = [(\partial G^v/\partial n)_{P,T}]dn^l$

now $(\partial G^l/\partial n^l)_{P,T} = \mu^l$

and $(\partial G^l/\partial n^l)_{P,T} = \mu^v$

$dG = [\mu_l - \mu_v]dn^l$

since at equilibrium $dG_{T,P} = 0$

$[\mu^l - \mu^v]dn^l = 0$

Since ,$dn^l \neq 0$

Chemical potential in liquid state=chemical potential in vapour phase

Now in other words chemical potential in liquid state equals to chemical potential in vapour state.

$dG = [\mu^l - \mu^v]dn^l$

If the two states are not in equilibrium with each other, a spontenious transfer matter from one phase to the other will occur in the direction such that dGT,P<0

if dnl is positive, then in order to make $dG_{T,P}$ negative, $\mu^l < \mu^v$

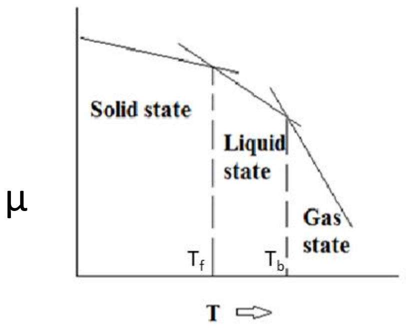
So, when chemical potential of liquid state is lower than the chemical potential of the vapour state then few of the vapour molecules will condense to the liquid state.

on the other hand , if dnl is negative ⇒$dG_{T,P}$ negative ,$\mu^l > \mu^v$

So, chemical potential of liquid state is greater than the chemical potential of the vapour state then some of the molecules in the liquid state will go to the vapour state.

Temareture dependence of chemical potential

$(\partial\mu/\partial T)P = -\bar{S} = -\overline{Sm}$ ⇒ molar entropy



$(\partial\mu/\partial T)_P = -S$

$\Rightarrow[(\partial G/n)/\partial T\ ]_P = -S/n$

$(\partial\mu/\partial T)_P = -\bar{S}$

Absolute entropy

$$\overline{Sg} > \overline{Sl} > \bar{S}s$$

Figure 2

Next we will discuss temperature dependence of chemical potential (Figure 2). We get like this. This is known as melting temperature or freezing temperature T_f. This is boiling temperature or T_b. This is freezing temperature, T_f. So, here solid stable, here liquid stable and here gas stable. Why we get different slopes? We get different slopes because absolute entropy for gaseous state is greater than that of liquid state greater than that of solid state. Since, we get different slopes and then the steepest slope we observe for gaseous state. Now, what would happen if we consider pressure is changed or pressure is being changed? So, we will consider now basically consider the dependence of boiling and freezing point. We know if we change the pressure boiling point and freezing point changes. Both of them change. So, how do they change let us see.

Pressure dependence Boiling and Frezing point

We know, $(\partial\mu/\partial P)_T = \bar{V}$ = Vm ⇒molar volume

Now in general, $\overline{Vg} >> \overline{Vl} >> \overline{Vs}$

$(\partial G/\partial P)_T = V$

$\Rightarrow (\partial G/n)/\partial P = V/n$

$\Rightarrow (\partial\mu/\partial P)_T = \bar{V}$

This is reverse in case of water that molar volume of ice is lower than the molar volume of liquid water. But in general for most of the matter molar volume of gaseous state is much much higher than the molar volume of liquid which is higher than the molar volume of solid state. Now, we consider all of them are positive quantities. Now, if we plot like this; this is very important plot. So, here we have low pressure, here high pressure. At a fixed temperature here, if we increase pressure μ increases. Consider this point is freezing temperature at a particular pressure. If we increase pressure we get freezing point at high temperature value. Now, what about here? If that is the case, if we increase the pressure or the plot of μ versus T (Figure 3) will give you positive slope. At fixed temperature if we fix the temperature and if we change the pressure the chemical potential will increase. Since molar volume of vapour state is much higher than solid state, we get this,

$$\Delta T_f\,(= T`_f - T_f) < \Delta T_b\,(= T`_b - T_b)$$

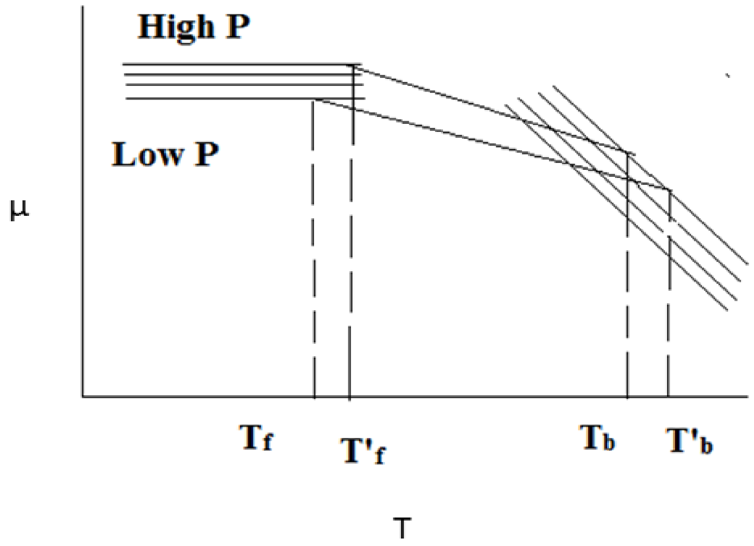


Figure 3