Thermodynamics of Fluid Phase Equilibria

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Lecture – 14
Legendre Transformation and free energy

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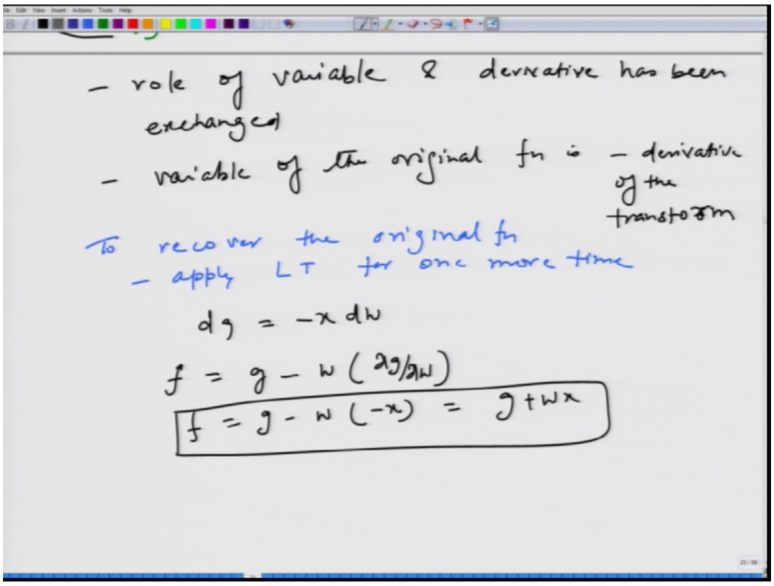

- role of variable & derivative has been exchanged
- variable of the original fn is − derivative of the transform

To recover the original fn
- apply LT for one more time

$$dg = -x\,dw$$

$$f = g - w\,(\partial g/\partial w)$$

$$\boxed{f = g - w(-x) = g + wx}$$

Welcome back. In the last class, we went through Legendre transformation in order to change the variable and such that we retain the information of the properties. So, what we are going to do is we are going to apply a Legendre transformation thermodynamic functions ok.

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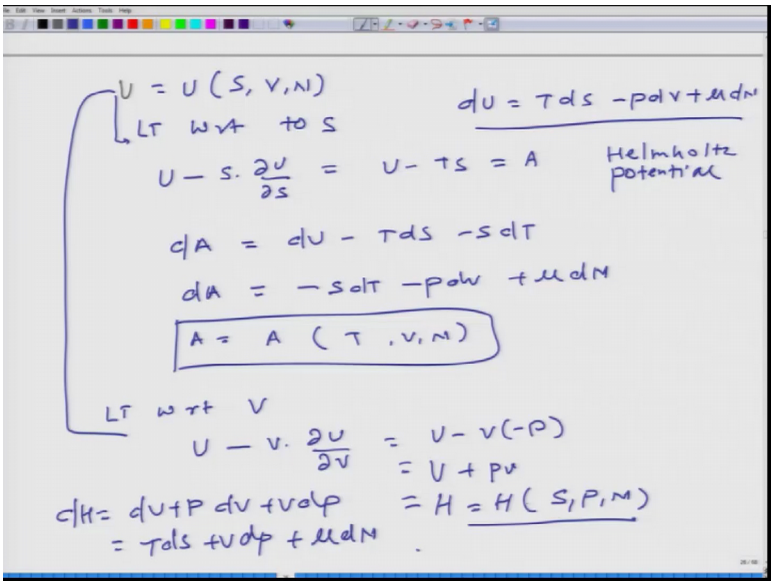

$U = U(S, V, N)$

LT wrt to S

$dU = TdS - pdV + \mu dN$

$U - S \cdot \frac{\partial U}{\partial S} = U - TS = A$ Helmholtz potential

$dA = dU - TdS - SdT$

$dA = -SdT - PdV + \mu dN$

$\boxed{A = A(T, V, N)}$

LT wrt V

$U - V \cdot \frac{\partial U}{\partial V} = U - V(-P)$

$= U + PV$

$= H = H(S, P, N)$

$dH = dU + PdV + VdP$

$= TdS + VdP + \mu dN$

So, I will just start with U as a function of U, S, V, N, and what we are interested is will apply Legendre transformation with respect to S so; that means, we can get a function U minus S times derivative of U with respect to S keeping all other things constant now knowing that from the differential or the derivative relation of U is TdS minus Pdv plus mu dN for pure system.

So, from here, we can see that partial derivative of U with respect to S is nothing, but T. So, this is equivalent to U minus TS. So, now, we can define this as another function which we call it a all right now a is nothing, but we say this as Helmholtz potential or function if we take a derivative or relation of this is going to be da is equal to du minus TdS minus SdT, ok, we can plug in this expression of du here and we can show this as minus SdT minus Pdv plus mu dN and this is nothing, but a function of V N and T ok. So, we have converted S variable to TvN by taking the first taking the Legendre transformation with respect to S. So, for this function TvN is a natural variable similarly we can also do Legendre transformation of this with respect to V and in that case U is going to be U minus V times the derivative of U with respect to V.

And from this expression we know that del U by del V is nothing, but minus p ok. So, that is U plus PV and this is nothing, but. So, this is this turns out to be U plus PV and this is nothing, but our enthalpy which is a function of S P N, ok, you can see this by getting in a derivative relation, this is going to be dH is du plus P dv plus vdp you make use of the expression of U and thus you can get TdS plus vdp plus mu dN and thus this is a function of S P M which is a natural variable for enthalpy.

We can also try to do successive transformation of U successive transformation of U Legendre transformation of U with respect to S and V ok.

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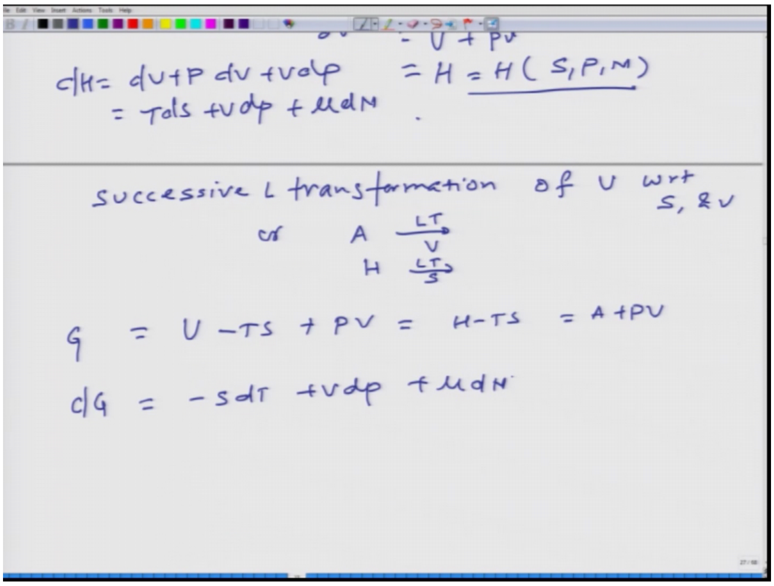

$= U + PV$

$dH = dU + P\,dV + V\,dP = H = \underline{H(S, P, M)}$

$= T\,dS + V\,dP + \mu\,dN$

successive L transformation of U wrt S, & V

or $A \xrightarrow[V]{LT}$

$H \xrightarrow[S]{LT}$

$G = U - TS + PV = H - TS = A + PV$

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

So, either we do successive Legendre transformation of U with respect to S and V or if we do single of the Legendre transformation with respect to V or single transformation of H with respect to S we get the following expression U minus TS with respect to S minus U minus TS plus PV ok. So, this is the first trans transformation this is the second transformation oh this would be your A A transformation with respect to V or you can consider U plus PV and take this edge edge transformation with respect to S will lead to the same expression and this we call it G; the same as a plus PV or H minus TS all right.

So, you can get a derivative relation as a minus SdT plus vdp plus mu dN ok. So, this is how we derive the thermodynamic functions of in order to get potential functions which depends on different natural variables. So, what we have done is we have taken internal energy which is a function of su A H svn and converted in 2 different functions which depends on different variables which are more important or relevant for experimental conditions.

So, let me make use of Euler integration to come up with another expression. So, I will start here with du.

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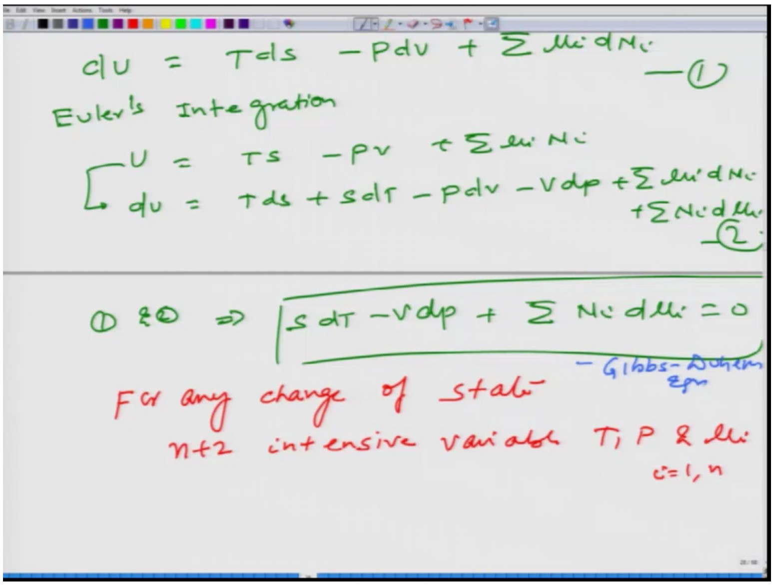

$$dU = Tds - Pdv + \sum \mu_i dN_i \quad — ①$$

Euler's Integration

$$U = TS - PV + \sum \mu_i N_i$$

$$du = Tds + SdT - Pdv - Vdp + \sum \mu_i dN_i + \sum N_i d\mu_i \quad — ②$$

$$① \& ② \Rightarrow \boxed{SdT - Vdp + \sum N_i d\mu_i = 0} \quad \text{— Gibbs-Duhem Eqn}$$

For any change of state

n+2 intensive variable T, P & μ_i

$i = 1, n$

As TdS minus Pdv plus summation mu i d Ni for multi component mixture and using if either integration, we can come up with this expression us TS minus PV plus summation mu i N i, ok. Now here if you take a derivative. So, this is an du TdS plus SdT minus Pdv minus vdp plus summation mu i d N i plus N I d mu i. Now using this expression. So, this is let us say 1, this is 2 and using this 2 expression, you can derive the following which means 1 and 2 will SdT minus vdp plus summation N i d mu i should be 0 because both this expression holds and thus this relation should exist, this leads to an extremely important conclusion which is that for any change of state having N plus 2 intensive variable TP and mu i where i is equal to 1 to N where N is number of components, it tells you this expression which is also called Gibbs Duhem equation or relation.

So, it tells you this that that N plus 2 intensive variable cannot be independent.

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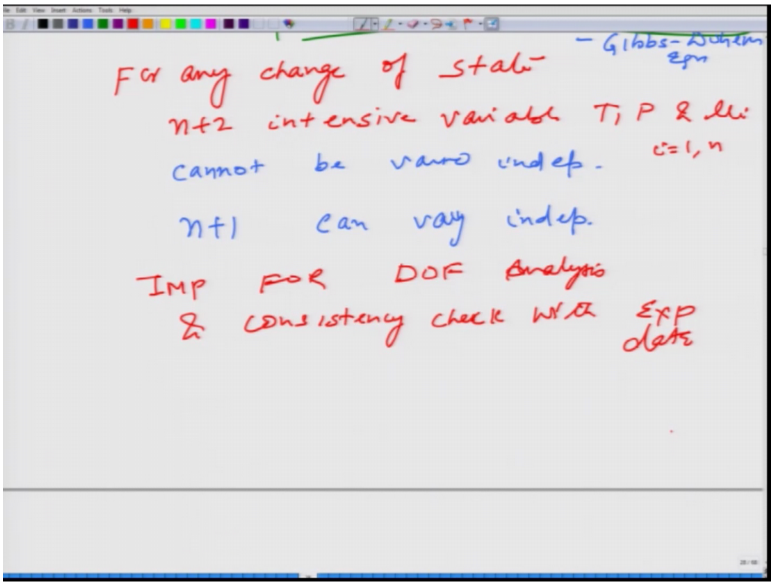

– Gibbs-Duhem eqn

For any change of state

$n+2$ intensive variable T, P & μ_i $i=1,n$

cannot be varied indep.

$n+1$ can vary indep.

IMP FOR DOF Analysis

& consistency check with Exp data

So, this cannot be varied cannot vary independently ok, it also tells you that since this is a constraint which is being put it tells you that n plus 1 only, n plus 1 variables are independent can vary independently ok. Now, this expression is important for degree of freedom analysis and consistency check with experimental data ok.

So, having derived this expression which is which are thermodynamic functions let me just summarize these auxiliary functions corresponding a definition and as well as the derivative and natural variables ok. So, you have this enthalpy.

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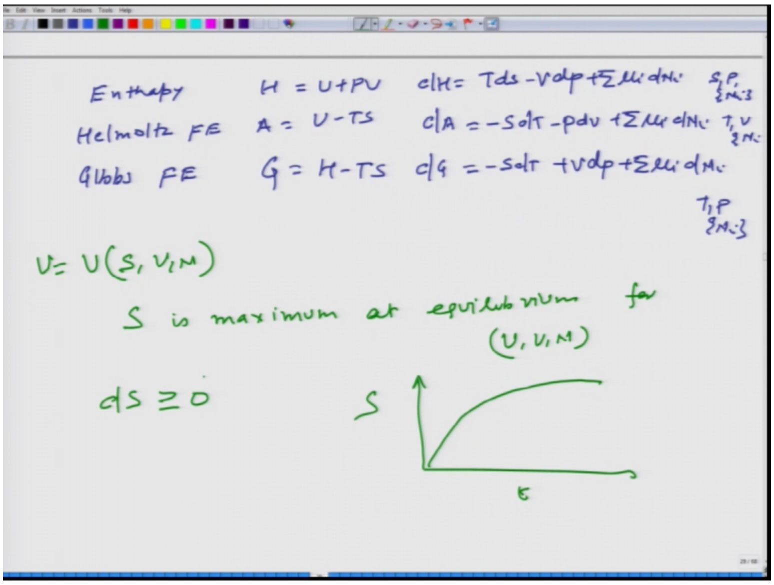

Enthapy $H = U + PV$ $dH = TdS - Vdp + \sum \mu_i dN_i$ $S, P, \{N_i\}$

Helmholtz FE $A = U - TS$ $dA = -SdT - pdV + \sum \mu_i dN_i$ $T, V, \{N_i\}$

Gibbs FE $G = H - TS$ $dG = -SdT + Vdp + \sum \mu_i dN_i$ $T, P, \{N_i\}$

$U = U(S, V, N)$

S is maximum at equilibrium for (U, V, N)

$dS \geq 0$

Helmoltz free energy and Gibbs free are U plus PV is U minus TS and G is H minus TS and the corresponding derivatives are dH is TdS minus vdp the summation mu i d Ni the what are the natural variables here S P and i ok.

Similarly, for dA is minus SdT minus Pdv plus summation mu i d Ni the natural variables are TV and Ni for G of del dG is minus SdT plus vdp the summation mu i dNi and natural variables here is TP Ni ok. This for thermodynamic functions which we have derived plays important role in many applications one thing we should understand that these functions plays this direct role in equilibrium or conditions for a given for their own natural variables for that matter let us assume that if you are talking about Helmholtz free energy A, it means that a is going to be minimum at equilibrium for a given a temperature volume and amount of the substance ok. Similarly, Gibbs free energy also plays an important role for condition temperature pressure and amount of substance when it is kept constant G is going to be minimum.

Let me just go through this briefly this importance of this thermodynamic function and its role in analysing the equilibrium for specific set of variables which are kept constant. So, if we let us go back to the to the case of S V N for such a variable fundamental equation or natural U is a fundamental thermodynamic function for natural variable S V N the consequence of second law is that that S is maximum at equilibrium for given U V N ok. Now in other word, S as a function of time, it continuously increases until it reaches a equilibrium values ok.

So, second law tells you that del S is going to be greater than equal to 0 ok. So, this also implies that U is going to be minimum for given S V N ok. So, let me just try to explain.

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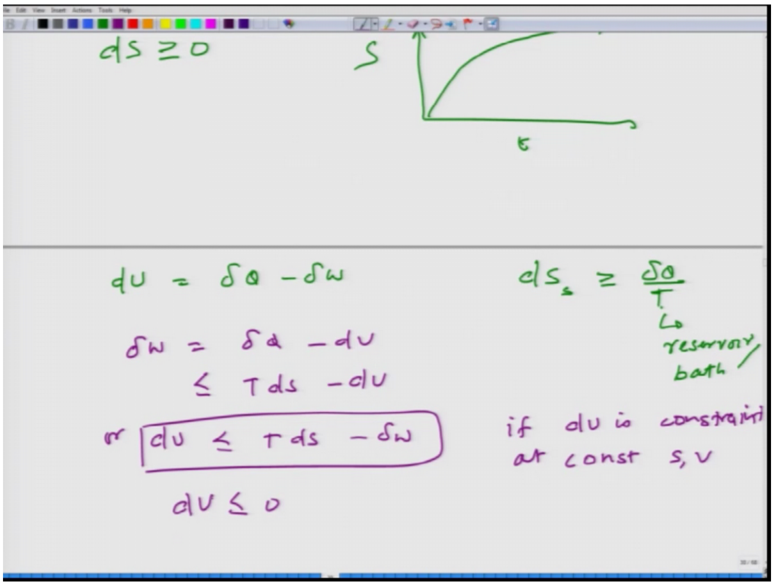

$dS \geq 0$

$dU = \delta Q - \delta W$

$\delta W = \delta Q - dU$

$\leq T dS - dU$

or $\boxed{dU \leq T dS - \delta W}$

$dU \leq 0$

$dS_s \geq \frac{\delta Q}{T}$ ↳ reservoir/bath

if dU is constraint at const S, V

So, we can consider the first law and we know that change in the entropy of the system is greater than or equal to del Q by T where T is basically nothing, but the temperature of the reservoir the bath ok. So, this is for reservoir or bath ok. So, I can rewrite this expression as the w is equal to del Q minus du which is nothing, but TdS minus U or I can write du less than TdS minus w ok. So, now, if do you is constraint if du is constraint at constant S and V, this implies that du is going to be less than equal to 0 ok.

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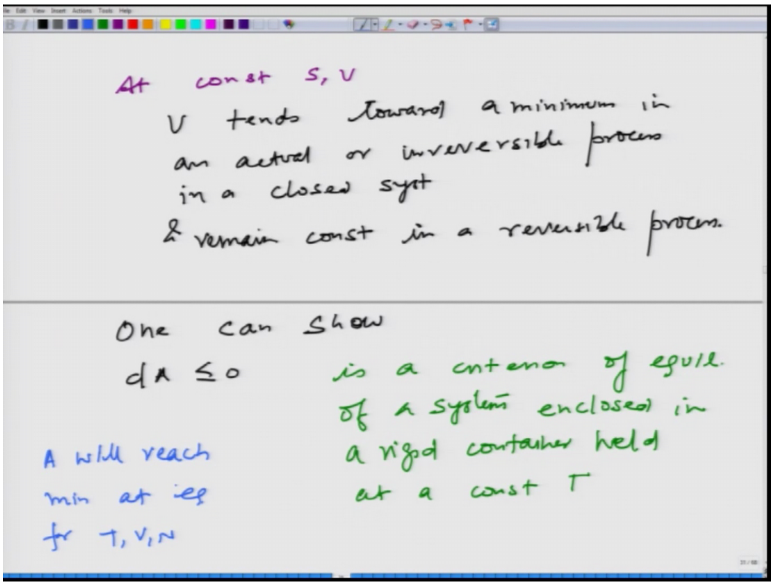

At const S, V

U tends toward a minimum in an actual or irreversible process in a closed syst

& remain const in a reversible process.

One can show

$dA \leq 0$ is a criterion of equil. of a system enclosed in a rigid container held at a const T

A will reach min at eq for T, V, N

So, what it says that at constant entropy and volume U tends towards minimum in an actual or irreversible process in a closed system and it remains constant in a reversible process.

So, in other word it provides this expression provides a criteria for equilibrium; that means, du less than equal to 0 or U tending towards minimum in a closed system provides an criteria for equilibrium system we can we can make use of this analysis also and extend it to the different free energies. So, I will take an example. So, instead of deriving it I will just make a statement here that similarly we can try to show, one can show that one can show that da is less than equal to 0 is a criteria is a criterion of equilibrium of a system enclosed in a rigid container held at a constant T it basically means S T V N is basically the variables which is kept constant that is what we are saying is basically a will reach minimum at equilibrium for a given TVN ok.

Now, similarly, you can show also that G the Gibbs free energy will each a minimum for a given T P N.

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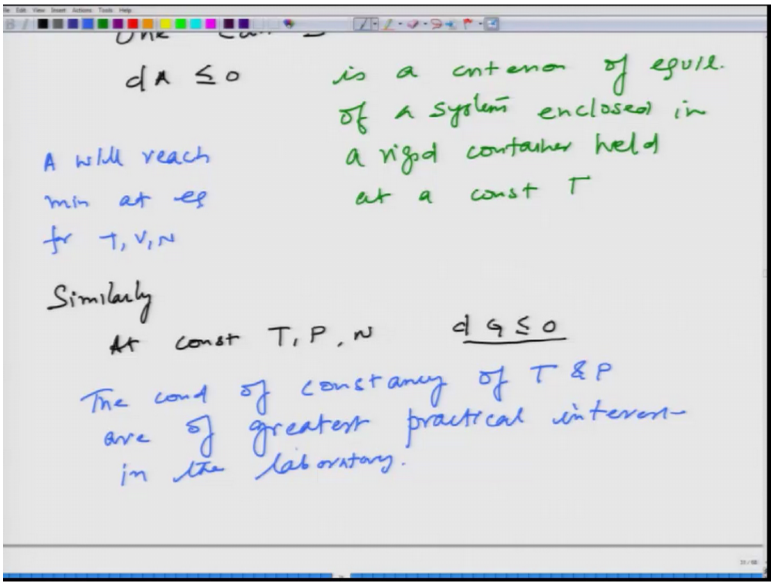

$dA \leq 0$ is a criterion of equil. of a system enclosed in a rigid container held at a const T

A will reach min at eq for T, V, N

Similarly

At const T, P, N $\underline{dG \leq 0}$

The cond of constancy of T & P are of greatest practical interest in the laboratory.

So, similarly now this particular condition of constant temperature and pressure of greatest importance to practical conditions because this is what you maintain in laboratory and there is this day dG greater than dG less than equal to 0 or the condition for equilibrium plays an important role in phase equilibria and reaction equilibrium analysis ok.

Now, in addition to a 2 G ai also plays an important role because you can also maintain temperature volume and N constant in a in a closed rigid container. So, let me just give a little bit flavour of this and understanding of this free energy.

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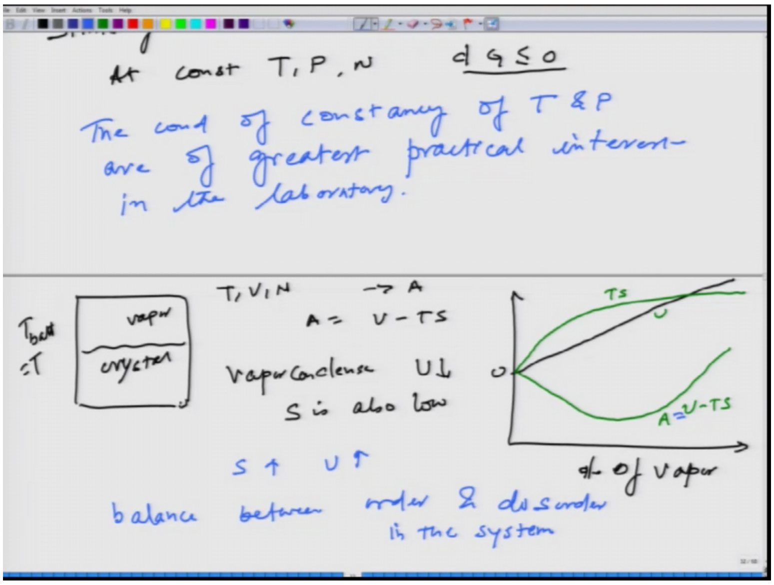

At const T, P, N $\underline{dG \leq 0}$

The cond of constancy of T & P are of greatest practical interest in the laboratory.

T, V, N → A

A = U − TS

vapor condense U↓

S is also low

S ↑ U ↑

balance between order & disorder in the system

So, if you consider for example, a case where you have a rigid container where you have maintained the bath at T and there is a vapour which is you can get kind of condensed and crystal can be formed ok. Now, in this case, of course, the volume is fixed temperature is fixed the world amount is fixed. So, basically this is TV and the natural thermodynamic function the potential is A. So, A can be A is nothing, but U minus TS all right.

Now, if we make use of some statistical methods and evaluate this U and TS in some way it turns out that it will look like the following. So, let us say this is 0 and this is your percentage of vapour ok. So, as the amount of vapour increases what we see is that U keeps increasing whereas, TS increases, but at certain point U is more than TS and effectively the a shows a minimum. So, in other word a is minimum for a specific value or specific composition of vapour and crystal ok.

So, we can understand this little bit more by considering that there are attractive forces between the molecules which tends to make the vapour or condensed. So, vapour condenses you tend to decrease and if U is minimum S is also low its becoming more ordered on the other hand if there is a heat being found from the bath S increases. So, does U ok. So, there is a certain balance between the order and disorder in order to minimize A ok. So, the balance between order and disorder in the system leads to a minimum value of A in an isolated system.

Of course, S would have been maximum and U would have been minimum, but considering that in this particular case you have fixed the temperature volume what it leads that there is a competition between U and TS which we essentially means order and disorder and thus there is a minimum for a specific value of the vapour ok. So, this is how we try to analyse or make use of the free energy which has plays a significant role in understanding the equilibrium behaviour of the system.

So, with this, I will stop, we will continue this exercise in the next lecture.