Thermodynamics of Fluid Phase Equilibria
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Lecture – 10
Thermodynamic Calculus-1

Welcome back in today's lecture, we will we will be covering thermodynamics Calculus.

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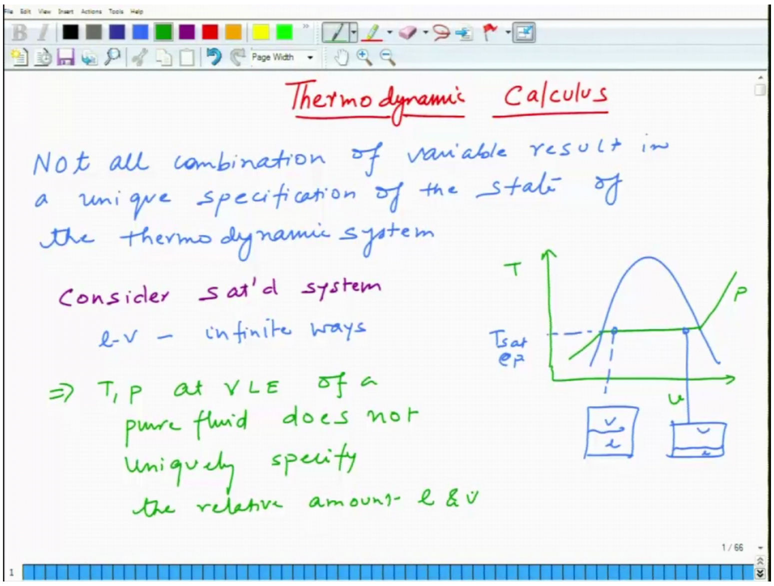

Thermodynamic Calculus

Not all combination of variable result in a unique specification of the state of the thermodynamic system

Consider sat'd system

l-v – infinite ways

⇒ T, P at VLE of a pure fluid does not uniquely specify the relative amount l & v

So, not all combination of variable results in a unique specification of the state of the thermodynamic system, this is something which we can understand by considering a simple saturated system. So, let us just consider saturated system now what I am going to do is I am going to just plot T V diagram and this is my saturated vapor liquid a region.

I am going to consider isobar which is at certain pressure now once we specify let us say this pressure p then the t sat is fixed at p it tells you that within this region is going to be 2 phase system, but the possibilities of liquid vapor system along this line will be infinite ok.

In other word there is infinite ways to arrange liquid and vapor in this range or in this within this saturated two phase region ok. So, for example, here there will be certain amount of vapor which will be much less and here there will be more amount of the vapor, but fixing temperature and pressure do not quantify the amount of the vapor liquid which are present in a given system.

So; that means, this this information is not sufficient to specify unique information or unique values of the vapor liquid in the system. So, this implies that temperature and pressure at VLE of a pure fluid does not uniquely specify the relative amount of liquid and vapor.

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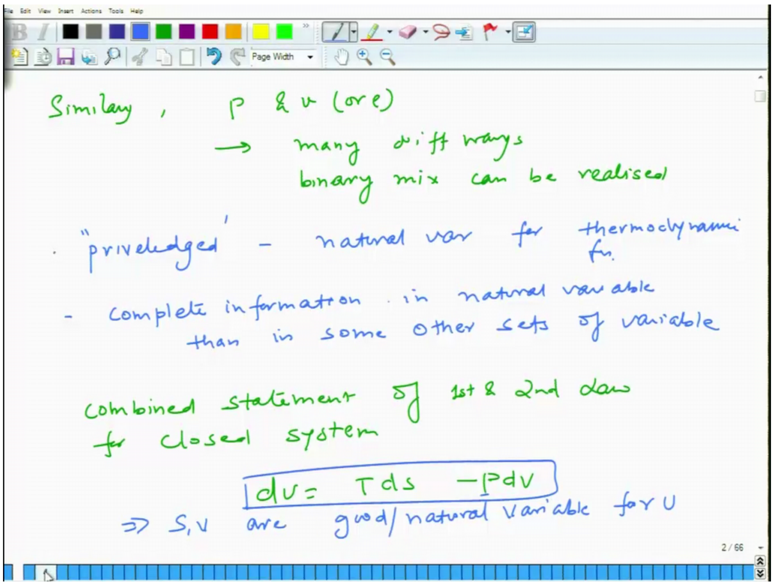

Similary , P & v (or e)

→ many diff ways
binary mix can be realised

· "priveledged" – natural var for thermodynamic fn.

- complete information · in natural variable than in some other sets of variable

combined statement of 1st & 2nd law
for closed system

$$\boxed{dU = Tds - Pdv}$$

$\Rightarrow$ S, V are good/natural variable for U

Now, similarly if you consider binary mixture, then at a given pressure and specific volume or density the system can be realized in many different ways binary mixture.

Now, in addition to the issue of the uniqueness of the system or thermodynamic state certain privileged variables which are a set of variables that are natural for specific properties. So, for a given thermodynamic function there are certain privileged variables which are nothing, but natural variables for thermodynamic function and thermodynamic function expressed in the natural variable contain more information as opposed to expressing other sets of variable ok.

So, this complete information in natural variables then in some other sets of variables. Now, in order to understand this. So, let us just consider simple first law and second law we have combined it let us consider a simple set of equations here.

So, if we consider for the closed system. So, if we combined statement first and second law for closed system. So, we are going to consider equilibrium condition. So, in that case you have nothing, but d u as t d s minus p d v ok. So, if you look at this equation it is very clear that s and v is natural variable for function u or that is good enough to express this changes in u.

So, this implies s and v are good or natural variable for describing, for describing u for a closed system.

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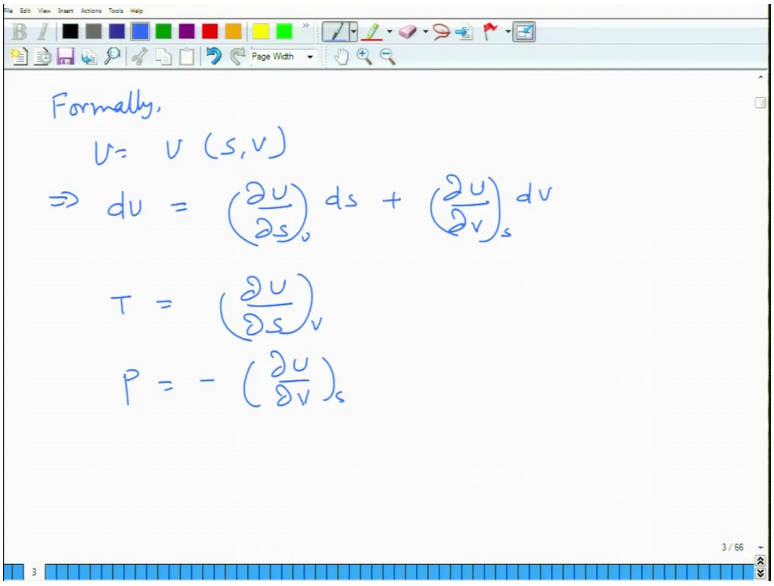

Formally,

$$U = U(s,v)$$

$$\Rightarrow dU = \left(\frac{\partial U}{\partial s}\right)_v ds + \left(\frac{\partial U}{\partial v}\right)_s dv$$

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

$$P = -\left(\frac{\partial U}{\partial v}\right)_s$$

Now formally I can write u as function of u, s n v this implies the derivative differentiation of u s can be written as del u by del s as a function of d s plus del u by del v constants as a function and multiplied by d v.

Now, if you compare this equation with our first law equation then you can relate this partial derivatives ok, in terms of intensive variables T is nothing, but d u by d s is constant v similarly if you compare p here p is p is nothing, but minus of del u by del v at constant s.

Now, it is very clear that this particular expression do not capture how much for example, liquid and vapor amount will be present in a given system for a saturated system. So, we need to provide little more information that is to obtain the full expression for u as a function also of the amount of material in the system in addition to entropy and volume we need to augment this equation ok.

We need to augment this equation in order to have another set of variables which represent the amount of material present or which affects the u. So, in order to augment this equation let me defined a variable.

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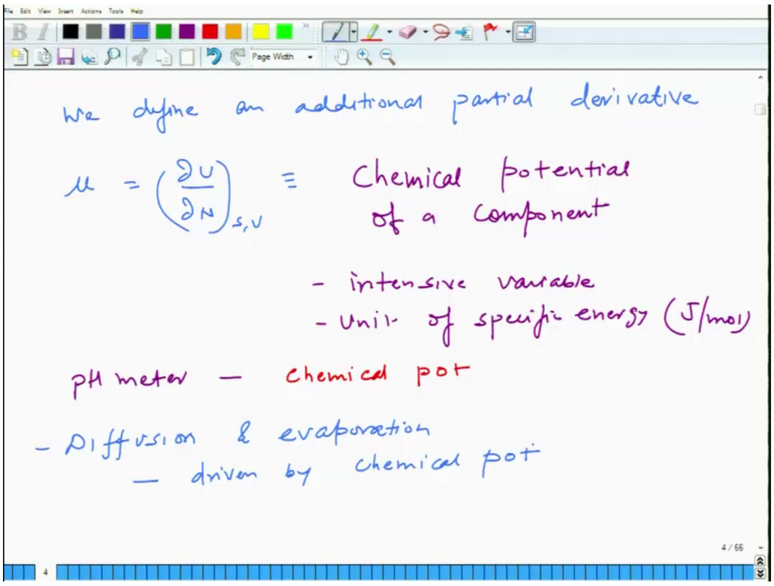

we define an additional partial derivative

$\mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}$ ≡ Chemical potential of a component

- intensive variable
- Unit of specific energy (J/mol)

pH meter — chemical pot

- Diffusion & evaporation
  - driven by chemical pot

So, for this purpose we define an addition an additional partial derivative and. So, this is again for one component, for one component we defined del u by del n where n is number of moles at constant s v and this is nothing, but chemical potential of a component.

Now, this is a intensive variable it has a unit of specific energy such as jay joules per mole. Now, this chemical potential which represent the changes in the internal energy with the change in the amount of the material present for few system in order to understand physical meaning of it we have to take certain example.

But it is more or less is quite obscure, but let us take some example for example, p h meter. So, what does ph meter do it actually measures nothing, but a chemical potential not the concentration this chemical potential.

Now, similarly you can also consider examples of diffusion and evaporation, now what are that this particular phenomena are driven by is it by concentration or is it by chemical potential ok.

So, without deriving these concepts I am just making the statement that this is basically driven by chemical potential difference we can take an example which possibly you can relate particularly here in India on a hot and humid summer day.

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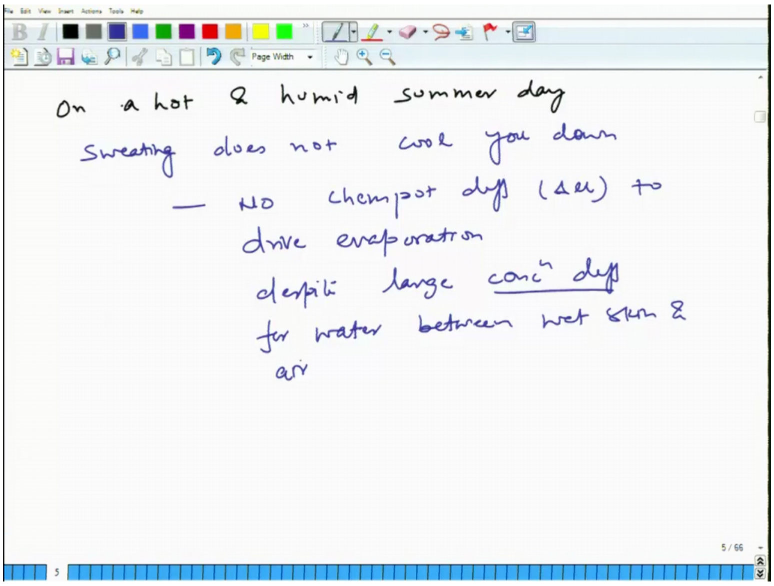

On a hot & humid summer day

Sweating does not cool you down

— NO chempot diff ($\Delta\mu$) to drive evaporation

despite large <u>conc^n diff</u> for water between wet skin & air

Many times you feel that sweating does not cool you down your sweating, but it is not cooling you down and the reason behind is that there is no chemical potential difference to drive the evaporation of the water on a skin to the air.

So, on a hot and humid summer day many times, you see sweating does not cool you down because there is no chemical potential difference to drive evaporation. Now, this is despite the fact that there is a large concentration difference for water between the wet skin and air and thus, it is not just concentration difference which is responsible for evaporation, but it is basically a chemical potential difference and thus chemical potential plays a significant role or fundamental role in thermodynamic such as a similar to temperature and pressure ok. So, let me now complete the differential relation of u now for complete information you have s v as well as n.

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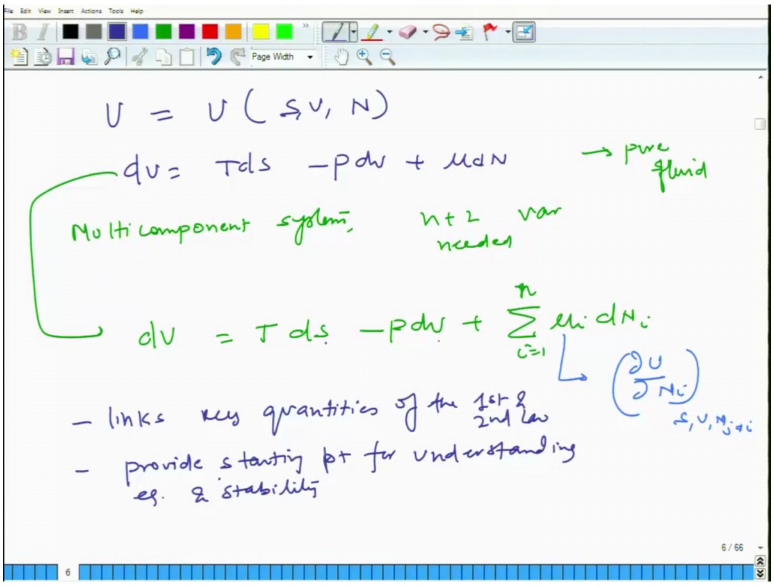

$$U = U(S, V, N)$$

$$dU = TdS - PdV + \mu dN$$ → pure fluid

Multicomponent system: n+2 var needed

$$dU = TdS - PdV + \sum_{i=1}^{n} \mu_i dN_i$$

$$\hookrightarrow \left(\frac{\partial U}{\partial N_i}\right)_{S, V, N_{j \neq i}}$$

- links key quantities of the 1st & 2nd law
- provide starting pt for understanding eq. & stability

So, the differential relation is t d s minus p d v plus mu d n ok. So, this is for pure system pure fluid more generally for your; for multi component system you need n plus 2. So, if n component you need n plus 2 variables to characterize the state to characterized the state of the system.

In that case your expression, the fundamental equation can be written as t u is equal to t d s minus p d v plus summation mu I d N i i is equal to 1 2 or number of components ok.

So, this is your expression, now this equation where mu i is nothing, but the partial derivative of u with respect to N i at constant s v and n j not equal to i. Now, this particular equation which is a fundamental equation is plays a significant role in thermodynamics it is a link, it links key quantities of the first and second law provide starting point for understanding equilibrium and stability and this also provides a starting point for deriving thermodynamic relation.

Once should note here that s v and n these are extensive quantities whereas, t p and mu which are conjugate variables of this extensive properties are which are also the first derivatives of this extensive properties are intensive variables ok.

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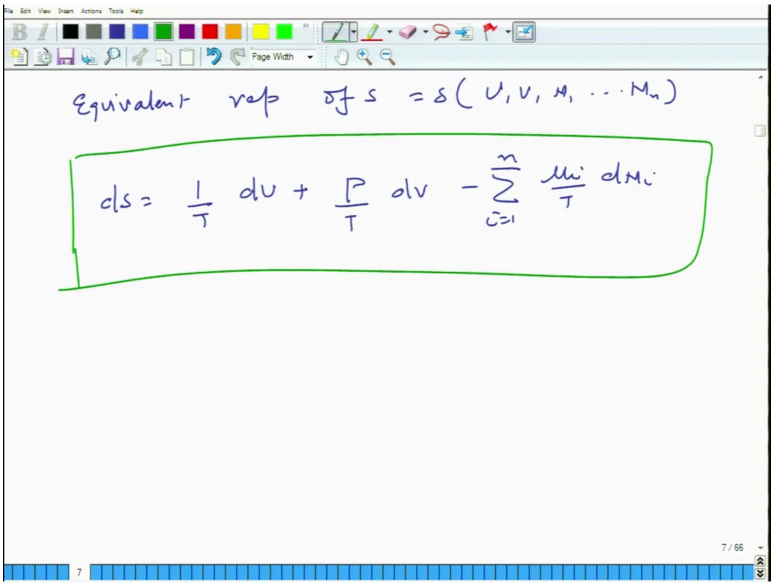

Equivalent rep of s $= s(U, V, N_1, \dots N_n)$

$$\boxed{ds = \frac{1}{T}\,dU + \frac{P}{T}\,dV - \sum_{i=1}^{n} \frac{\mu_i}{T}\,dN_i}$$

So, we can also rearrange this in order to get an equivalent representation of entropy as a function of u v n for n number of component and we can rearrange this expression here in this form ok. So, this is what we have derived.

So, I will stop here and we will continue in the next lecture multivariable calculus ok.