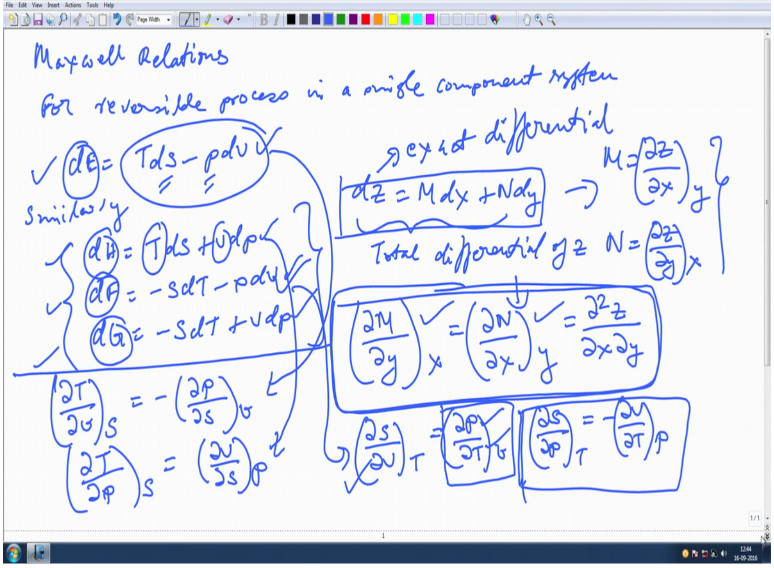
Heat Transfer And Combustion in Multiphase Systems
Prof. Saptarshi Basu
Department of Mechanical Engineering
Indian Institute of Science-Bangalore

Lecture 03
Thermodynamics of Interface-I

So, welcome to lecture 3 essentially. So, the last time what we did was that we started the thermodynamics of the multiphase system and we considered that what is the stability and the equilibrium criteria. We went through the Gibb's phase rule and we identified some related parameters that the degree of freedom of a system. This time we are going to go into a little bit further

(Refer Slide Time: 00:48)



Maxwell Relations

For reversible process in a single component system

$$dE = Tds - pdv$$

Similarly

$$dH = Tds + vdp$$
$$dF = -SdT - pdv$$
$$dG = -SdT + vdp$$

exact differential

$$dz = Mdx + Ndy$$

Total differential of z

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

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x \partial y}$$

$$\left(\frac{\partial T}{\partial v}\right)_S = -\left(\frac{\partial p}{\partial s}\right)_v$$
$$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial v}{\partial s}\right)_p$$
$$\left(\frac{\partial s}{\partial v}\right)_T = \left(\frac{\partial p}{\partial T}\right)_v \qquad \left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p$$

And so, first we will start with Maxwell equation or the Maxwell relations okay. Now for reversible process in a single component we are still in the single component we have not gone into the multiphase multi component part as of now. For a single component system the internal energy change is given by Tds - Pdv, this we already did.

Similarly there are varieties of other forms by which we can write essentially the same expression. Same represent the same thing essentially Tds + Vdp this is written in terms of the enthalpy. Similarly you can write it in terms of the Helmholtz free energy - Pdv and the Gibbs free energy as well.

So, - SdT + Vdp, so, these are the equivalent forms okay. Now if you look at all these forms they all have a generalized format which is given as this okay. So, this is basically what we call the total differential of z right okay. Now if you write it like this see all the forms exactly has that particular format. So, if we write it properly the M okay can be written as dz by dx.

And then constant y, N is given as dz by dy at a given x right. Remember that dz is an exact differential okay. So, from this particular expression this is the way that we can write. So, in general from this what we can say is that the partial of M with respect to y at a constant x and the partial of N with respect to x at a constant y they must be the same and they are both equal to this okay.

Now using this format okay we can basically cast all the equations and we can derive some handy relationships which are basically called the Maxwell relation is equal to for example - dp by ds at constant v. So, you can see we have four fundamental equation and we have this relationship that we can write okay.

So, each of this is like as z this, this, this, these are like dz's okay. So, just by using that combination okay we can write say for example the first one that we have written okay dT by dV at constant s because this is that a this is ds, if you see this particular relationship and this is dp by ds at constant v.

So, from this expression we can write this okay. So, that is the first Maxwell relations okay similarly you can write it as dP by dT by dP at constant S is equal to dv by ds at constant P okay. So, that is the second relation that you can get out of this okay. So, you just have to assume that this is your M this is your N and then you have to correspondingly apply this particular form okay.

So, then you will get these relationships similarly from the last two equations we can get ds by dv at constant T is equal to dP by dT at constant V and the last form so that is the that comes from this equation now this particular form and the last form is dS by dP at constant T is equal to - dV by dT at constant P. So, these are the four Maxwell's relations that you can that we can derive.

Out of the four fundamental equations okay and for reversible process obviously and using this kind of a total differential form okay. So, the Maxwell equations is particularly useful okay because if you want to develop the relationship between quantities. There are certain quantities for example which you cannot even measure okay. So, to cast that particular quantity in terms of something else is very, very important.

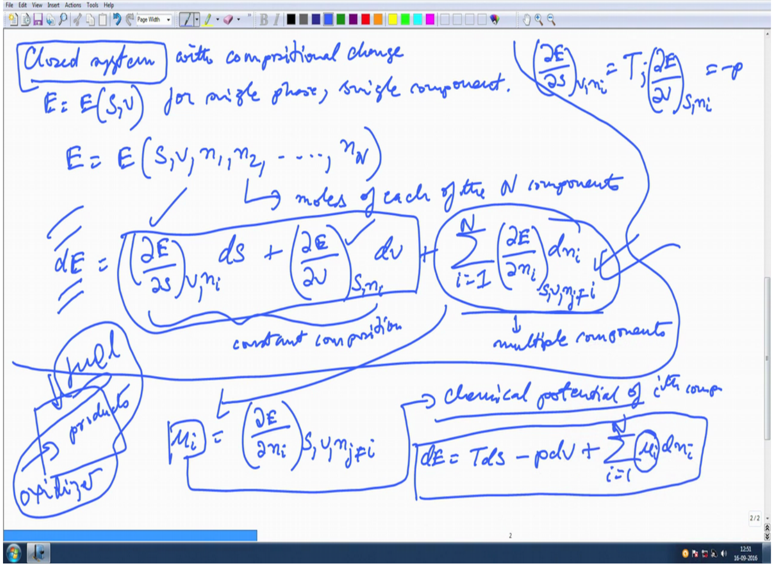
For example entropy is something that you may not be able to measure right take this particular relationship. But you may be interested in knowing the variation of entropy with volume right at a constant temperature. But if you can cast it in terms of pressure and temperature differential right which is there on the right hand side both of these two terms are actually measurable okay.

So, you can get a variation of entropy say with volume at constant temperature by measuring something else okay. So, that is the part that is a vital importance over here right okay. At the same time, so, similar such expressions if you want to get the variation of entropy with pressure say for example you just measure the change of volume with respect to temperature at a constant P okay.

Similar things are available in all other cases some are experiment for example some quantities you can measure experimentally some quantities you may not be able to measure experimentally but you may be interested in knowing the variation of those quantities. So, this is the platform which actually gives you something similar to that okay.

So, that is the first thing that we have done over here so the Maxwell's relationships are therefore very important and it will come in handy as we move on into the later parts of these courses okay.

(Refer Slide Time: 07:48)



Closed system with compositional change

$E = E(S, V)$ for single phase, single component.

$\left(\frac{\partial E}{\partial S}\right)_{V, n_i} = T$; $\left(\frac{\partial E}{\partial V}\right)_{S, n_i} = -p$

$E = E(S, V, n_1, n_2, \ldots, n_N)$

↳ moles of each of the N components

$$dE = \underbrace{\left(\frac{\partial E}{\partial S}\right)_{V, n_i} dS + \left(\frac{\partial E}{\partial V}\right)_{S, n_i} dV}_{\text{constant composition}} + \underbrace{\sum_{i=1}^{N} \left(\frac{\partial E}{\partial n_i}\right)_{S, V, n_{j \neq i}} dn_i}_{\text{multiple components}}$$

fuel → products

oxidizer

$$\boxed{\mu_i} = \left(\frac{\partial E}{\partial n_i}\right)_{S, V, n_{j \neq i}}$$

→ chemical potential of i^{th} comp

$$\boxed{dE = TdS - pdV + \sum_{i=1}^{N} \mu_i \, dn_i}$$

Now let us start bringing, now the compositional changes in the system so far we have done like single phase single component, we have done that when you have multiphases how many degrees of freedom do you require. Now let us see a multi-component framework as well. So, let us start with a closed system okay with compositional change okay.

So, the closed system with compositional change now normally the internal energy will be a function of only two quantities right this is for single phase single component this we already know okay. But what happens when we actually have a compositional change over here. That means your energy now will be our function of s v, n1, n2 da da da up to nN okay.

Where these represent the number of moles of each of the N component understood. So, that thing now the internal energy is not just a function of two independent properties in this case entropy and volume. It is also a function of the different moles of the individual components that are present in the system okay.

So, and this is a closed system if you recall okay. Now if I do a total differential of this you can guess that this will be the first term correct. The second term will be as you can guess this is very standard s, ni at constant v right if differential with respect to v. And lastly now you have a summation 1 to N dE by dni, dni right.

This is for constant s constant v and n constant n where n is not equal to nj is not equal to ni okay. So, that is, this is for the constant composition part composition and this is the effect of multiple components okay. This is the effect of multiple components right okay. Now from our own knowledge of things we already know that this v, ni is equal to T right and similarly s, ni is equal to -P right.

So, these are, the this term and this term essentially right okay. So, these two terms we know the nature of this that is the variation of energy to internal energy with entropy for a constant volume and the constant number of moles or the fixed given configuration of the number of moles of the of the component is basically nothing but temperature whereas this particular term is nothing but the negative of the pressure.

So, what about this particular term right that is the most important part right. So, this particular part is nothing but something called a Mu i, this is basically called the chemical potential, the fancy name of this is the chemical potential. This is the chemical potential of the ith component essentially right.

So, that is the formation of all the chemical potentials okay. So, for a multi component system in general your dE is written as Tds - Pdv right plus summation i =1 to n Mu i dni that is what it right okay where Mu i is called the chemical potential of ith component correct. So, this part should be quite clear that what we have done is that only other thing that has come into the picture is this term Mu i or the chemical potential.

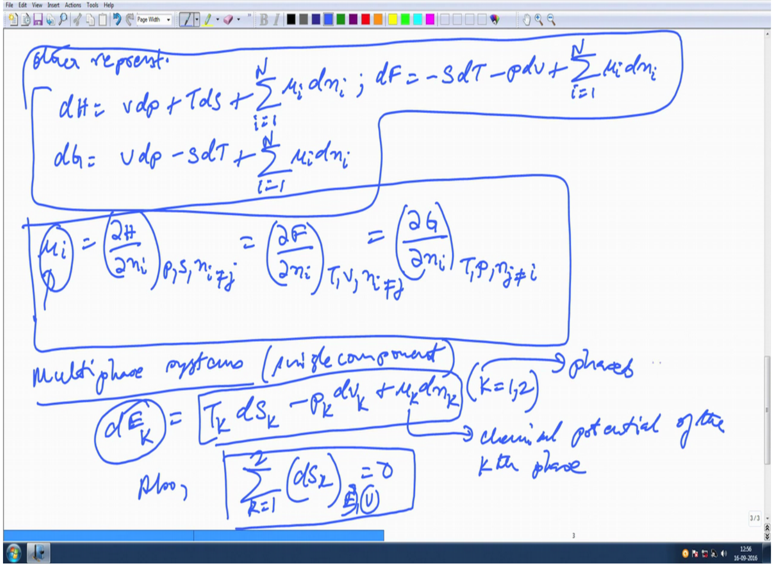
Why that has come that has come because the number of moles it is no longer a single component system that means it is not, for example if you deal with the with this room say for example room okay just the room, your bedroom, living room whatever right. Now that particular room what you will find is that it is composed of air right.

Now air normally though it is multi-component sometimes we take it as a single component system okay. But on the other hand if you take say a combustor right. A combustor in which you put fuel right you put oxidizer and at the end of the day in if it is a closed system okay. So, it is like a vessel you get; you burn this too and you get the products okay like CO2, CO and other things okay.

So, this is a perfect example of a multi-component system right because you have fuel okay, you have air, you have the oxidizer which is normally air. You have the products like water, CO2, CO, oxides of nitrogen etcetera or whatever okay. So, this is a perfect example of a multi-component system.

Not to analyze that particular problem you need to see that the change in internal energy of the system is not just given by the temperature and the pressure I mean the first two terms right. It is also given by the chemical potential and the number of available moles of each of the component okay. So, that is the expression that we kind of developed in terms of internal energy.

(Refer Slide Time: 15:04)



other represent.

$dH = vdp + Tds + \sum_{i=1}^{N} \mu_i dn_i$; $dF = -SdT - pdv + \sum_{i=1}^{N} \mu_i dn_i$

$dG = vdp - sdT + \sum_{i=1}^{N} \mu_i dn_i$

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{p,S,n_{i \neq j}} = \left(\frac{\partial F}{\partial n_i}\right)_{T,V,n_{i \neq j}} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j \neq i}}$$

Multiphase systems (single component)

$dE_K = T_K dS_K - P_K dV_K + \mu_K dn_K$ $(K = 1,2)$ → phases

→ chemical potential of the Kth phase

Also, $\boxed{\sum_{K=1}^{2} (dS_K)_{E,V} = 0}$

Now similarly there may be other representations also, so this is one representation. Other representations also in which you have say for example dH which is basically nothing but the enthalpy + Tds + summation again i = 1 to N Mu i dni okay. Then you have dF which is given as - sdT -Pdv + summation i =1 to N Mu i dni, dG on the other hand is written as Vdp - sdT + summation i = 1 to N Mu i dni okay.

So, these are the other equivalent representations that are actually possible okay. So, the Mu i therefore can be written in a variety of forms right. So, it can be written as dH dni for constant p constant s these are all equivalent representations right. This is also the same as dF dni, T,v, ni not equal to j right.

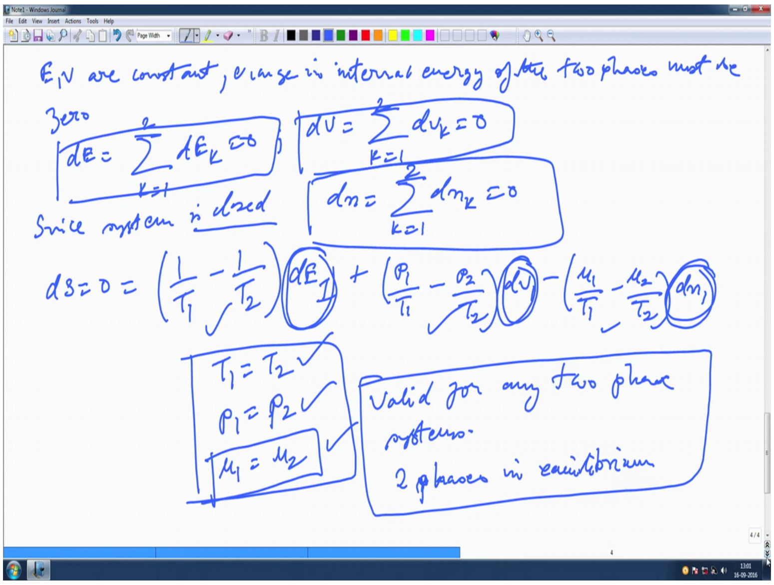
This is also equal to dG by dn dni okay for T,p nj not equal to i. So, all these are possible representations okay for the same thing essentially. So, all the chemical potential chemical potential is a term now that chemical potential can be represented in these varieties of ways right okay. Now, so, we have seen in a multi component system essentially the thing is still the same but except that we have this additional term which enters into the picture.

Now let us look at a multiphase system now okay. So, to do that first we, so multiphase happens in multiphase system and what is the similarity between that and a multi component system we will just look at it. In a multiphase system say it has a single component for simplicity a multiphase system as I told you in the first lecture it can be of multi component nature as well okay.

Now in a multiphase system we can write the same internal energy as Tk k = 1,2 where 1 and 2 are basically the two phases, k is basically the phase, it can be three phases also right now we have just chosen to just for the purpose of simplicity okay. So, for a multiphase system the internal energy change of the kth phase is actually given by this expression.

Where Mu k is basically the chemical potential of the kth phase that sounds awfully similar to the multi component system as well right, for the multi component system we have something very equivalent like this okay. Also just k = 1 to 2 you have dsk which is basically the change in entropy for constant energy and constant volume is equal to 0 correct.

So, the change in entropy for constant energy internal energy and constant volume is actually equal to 0 okay. So, since of the reason that the two phases E and V are since E and V are constant the change in internal energy of the two phases must also be equal to 0.
(Refer Slide Time: 19:51)



E, V are constant, change in internal energy of the two phases must be zero

$$\boxed{dE = \sum_{k=1}^{2} dE_k = 0}, \quad \boxed{dV = \sum_{k=1}^{2} dV_k = 0}$$

Since system is closed

$$\boxed{dn = \sum_{k=1}^{2} dn_k = 0}$$

$$dS = 0 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dn_1$$

$$\boxed{\begin{array}{l} T_1 = T_2 \checkmark \\ P_1 = P_2 \checkmark \\ \boxed{\mu_1 = \mu_2} \checkmark \end{array}}$$

Valid for any two phase systems.
2 phases in equilibrium

So, let us go to the next page and right that since E and V are constant right okay. The change in internal energy okay of the two phases it must be 0 as well okay. So, that would mean that dE is equal to sum total 1 to 2 dEk basically equal to 0 also dv which is easy to be equal to k = 1 to 2 dvk is also equal to 0 okay.

Since the system is closed because we are dealing with closed system is closed okay the dn which is basically nothing but summation of k = 1 to 2 dnk that is also equal to 0 that is the number of moles of each of the phases that is also equal to 0 right. So, no change in a number of moles the total moles resulting from the two phase changes right essentially that is what it means okay.

So, these are the three statements that you get and the last one I wrote it in the previous page okay. So, if you combine all of these things together so you combine that change in entropy is equal to 0, the change of internal energy is equal to 0, the change of volume is equal to 0 and the change of total number of moles is equal to 0.

If you combine all of them ds = 0 essentially this means 1 by T1, T1 1 and 2 are the two phases say for example as that we already mentioned dE1 + P1 byT1 - P2 by T2 dv1 - Mu1 by T1 - Mu 2 by T2 dn1 right correct. Now since this for equilibrium to exist between the two phases of a single component we can see that these are any variations of V in and all those things right.

So, the sum total of all these terms are actually equal to 0 correct but this variation can be anything right, dV1 E1 okay, dn1 right. So, that would mean in order for the sum total of these terms to be equal to 0 individually these terms should be equal to 0 as well right. So, from the first expression we get T1 = T2 right since T1 = T2.

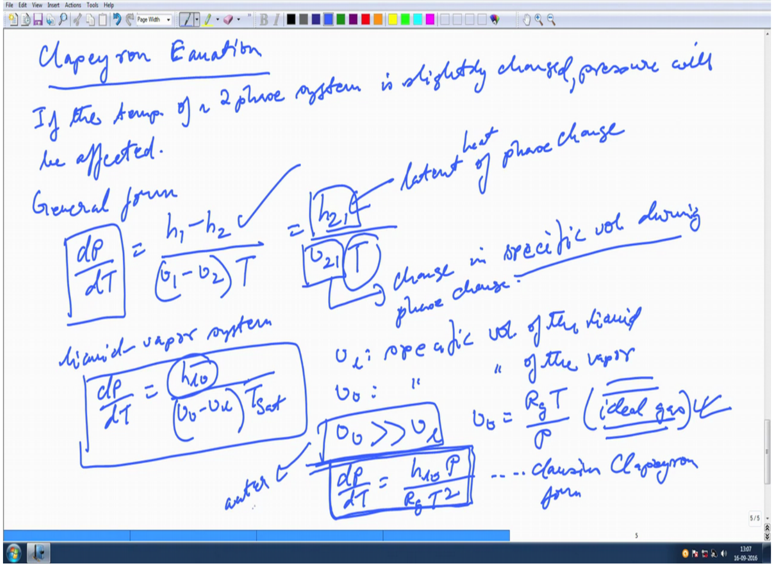
From the second one we get P1 = P2 right and from the third one we get Mu1 = Mu2 right. This is valid for any two phase system right. So, the important conclusion that we have drawn out of here is as follows. We have combined this and we have shown that for a closed system okay. You have the temperature between the two phases should be the same.

So, the two phases for the two phases to exist in equilibrium right this is for two phases in equilibrium okay. When the two phases are in equilibrium the temperature between the two phases should be equal, the pressure between the; pressure in the two phases should be equal and the chemical potential between the two phases should also be equal correct.

So, that gives us; so this is valid for any two phase systems okay which are in equilibrium with each other. That you can show through extrapolation and in control other methodologies as well that this entire thing that we have shown these are important parameters that we have shown that the chemical potential is equal across the two phases right okay. So, that is an important observation okay.

So, for a single component two phase systems we have seen what is the criteria for the two phases to exist in equilibrium.

(Refer Slide Time: 24:44)



Clapeyron Equation

If the temp. of a 2 phase system is slightly changed, pressure will be affected.

General form

$$\boxed{\frac{dP}{dT}} = \frac{h_1 - h_2}{(v_1 - v_2)T} = \frac{h_{21}}{v_{21}T}$$

latent heat of phase change

change in specific vol during phase change.

Liquid-vapor system

$$\boxed{\frac{dP}{dT} = \frac{h_{lv}}{(v_v - v_l)T_{sat}}}$$

v_l: specific vol of the liquid

v_v: " " of the vapor

$\boxed{v_v >> v_l}$

$v_v = \frac{R_g T}{P}$ (ideal gas)

water

$$\boxed{\frac{dP}{dT} = \frac{h_{lv} P}{R_g T^2}}$$

.... Clausius Clapeyron form

Now let us look at another important thing which also is you have encountered this is called the Clapeyron equation right. We will find the utility of these equations when you go to the droplet and other type of phenomenon right. Now in a Clapeyron equation what happens is that let us put the statement if the temperature of a two phase system is slightly changed right changed that means the system where in equilibrium.

The temperature is slightly changed the pressure will be obviously affected right the pressure will be affected right. So, if the pressure is affected okay then how what is the simple relationship between the temperature and pressure okay. If I have a change of temperature and a change of pressure how these two things are kind of related when the two phases are in equilibrium to each other right.

So, I would not do the derivation okay for the general form of the Clapeyron equation, the derivation you can look up your undergraduate books okay it should be there and I will explain what each and every term actually means so, but the change of the slope the change in pressure and the change in temperature okay.

So essentially it is a slope okay the slope is related to that means this is the relationship between pressure and temperature. This is related to the latent heat of the phase change that means the phase changes from 2 to 1 or 1 to 2 whatever that may be happening okay. So, it is the latent heat due to the phase change and this one is the change in specific volume during phase change okay.

So, this is a unique relationship that means that if you know the latent heat of phase separation and if you know the phase yet the specific volume change during the phase change. And if you know the temperature at which the phase change happens the change in pressure and the change in temperature can be related to each other right okay.

Now several relationships among temperature, pressure, volume and enthalpy change for a single component system exists. But the two phase system at equilibrium actually obeys a form like this right. Now for a liquid vapour system, now this is valid for any system right this for a liquid vapour system specifically dP by dT is given by hlv in that case 1 and 2 are the liquid and the vapour right.

That is given by Vb - Vl right and because this is given by the T saturation right. So, the T saturation is what it is so this particular relationship is the same but with a little bit of a change except that this is now the latent heat of vaporisation essential okay. Now here is the specific volume of the liquid right specific volume of the liquid.

And Vb is the specific volume of the vapour right now normally because of expansion okay the Vb is normally much, much greater than Vl right that is obvious because you take a small drop of water and if you expand if you just vaporise it okay because of the severe density change because this is nothing but the inverse of the density change the specific volume right. The vapour expands almost like thousand times right.

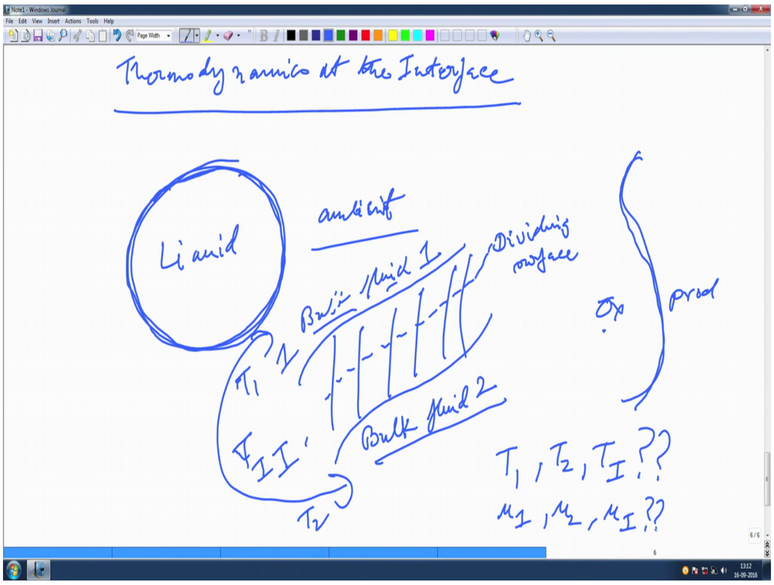
So, you have a thousand time change in volume just for say for example for water similar happens for other types of fluids as well right. So, and this Vb you can also write it you can consider this as an ideal gas and you can write it in this form as well right. So, considering that this is an ideal gas. Ideal gas is something which is basically you can disregard any compressibility effect okay in the ideal gas.

So, this dP by dT is given as hlv okay hlv into P divided Rg t square right. This particular form is called the Clausius Clapeyron form note it. So, this is the Clausius equation this particular slightly revised form is called the Clausius Clapeyron equation, clear on this particular part.

So, this is but perhaps so at this particular point what we have done is that we have just applied the ideal gas law as assumption and the fact that the density of the vapour is much, much less than the density of the liquid that means the specific volume of the vapour should be much, much higher than the specific volume of the liquid.

And I gave you the example of water and water vapour right where you do get a thousand times change in the volume okay. So, after this what we are going to do and we will just introduce the problem over here and if you continue in the next class. So, the first thing that we will do over here is that now that we know that what is the relationship between temperature and pressure when there is a phase change happening.

And when the phase actually is in equilibrium to each other what are the conditions that are needed. But one important thing that I told you in the first lecture was that what about the interfaces we have to know the thermodynamics of the interfaces.
(Refer Slide Time: 31:22)



So, I will just introduce the thing over here and go into the next lecture thermodynamics add the interfaces okay. So, what is thermodynamics of the interface let us look at the interface for example if this is a droplet of liquid, a raindrop say for example. This is ambient sorry ambient. So, what happens is that this liquid and the ambient is separated basically by this interface right.

Similarly you can have a bubble we all have seen if you blow a bubble okay. So, that is also you can blow a bubble inside a liquid also. So, you can see that there is an interface which is separating the two phase's right. And with the first class we said that this can be a nice geometric interface, it can be like a corrugated interface, it can be a lot of things okay.

Now this interface can be thin interface or it can be a thick interface also. So, there can be so if we zoom in into the interface perhaps you will see something like this. This is bulk fluid one this is phase bulk fluid 2 okay. And the interface is you know dividing surface okay. It is like a dividing surface an arbitrary function whatever you call it okay and that interface is mentioned that something like an I okay.

So, the two bulk fluids, so this can be liquid vapour, vapour liquid whatever solid vapour whatever you can think of okay. They are separated by any interfacial region basically it is like an interfacial region okay. So, this interfacial region can be very thin in most of the cases we consider it to be very thin. But we still need to know that what is the mechanism by which mass or heat transport occurs from this to this right, through the interface.

That is the most important thing that will affect all the calculations that you see over here okay. Here we of course the two phases are not mixed with each other okay. But it is basically also can be considered as a single substance which has two phases that in fluid one is the same is a different phase of the same substance like water and water vapour okay.

It can be it can be actually many thing it can be two in mixable liquids, it can be a single substance with two phases, it can be a mixture of gases in contact with a solid surface or it can be also be a chemically reacting interface like for example this can be a flame. If you look at a flame okay a candle flame for example or any other flame okay.

So, one side is oxidizer okay one side is a product right there is an interface which basically separates the two okay. Though these are of two different components there may be two different phases also that can be present okay. So, all these are interfacial phenomena which we need to know that how this interface actually behaves.

So, next class what we are going to try to establish is that what is the thermodynamics of this particular interface okay whether this interface is kind of a nice interface and what kind of a transport can happen okay. What is the, what are the equations that are valid across the interface for example if this temperature is T1, this temperature is T2 the interfacial temperature is TI.

What is the relationship between temperature T1, T2 and T I what is the relationship between them right. Also what about the chemical potential that means Mu1, Mu2, MI right. So, we need to know that how those chemical potentials actually ferry okay. So, this is the thing that we have.

So, these are the interfacial phenomena within the next class we are going to see that how this interface is actually vary okay how this interfaces can be described okay.