Course on Phase Equilibrium Thermodynamics
By Professor Gargi Das
Department of Chemical Engineering
Indian Institute of Technology Kharagpur
Lecture 22
Homogenous Open Systems

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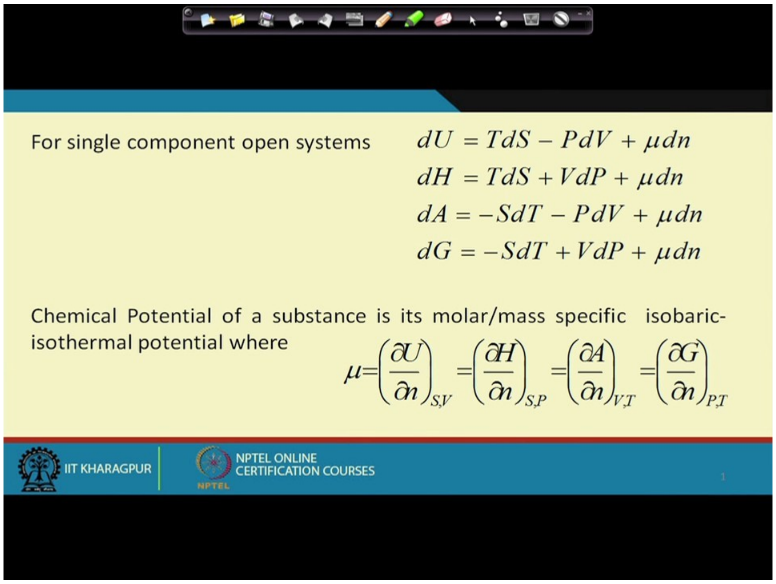

For single component open systems

$$dU = TdS - PdV + \mu dn$$
$$dH = TdS + VdP + \mu dn$$
$$dA = -SdT - PdV + \mu dn$$
$$dG = -SdT + VdP + \mu dn$$

Chemical Potential of a substance is its molar/mass specific isobaric-isothermal potential where

$$\mu = \left(\frac{\partial U}{\partial n}\right)_{S,V} = \left(\frac{\partial H}{\partial n}\right)_{S,P} = \left(\frac{\partial A}{\partial n}\right)_{V,T} = \left(\frac{\partial G}{\partial n}\right)_{P,T}$$

Well, hello everybody we continue our discussions on homogeneous open systems that we have started in the last class if you see in the last class we have derived these 4equations relating a thermodynamic potentials with the respective parameters for under different conditions of coupling between the system and the surroundings and we have defined a new term which we found for pure substances it is nothing but the molar Gibbs free energy and it was defined in this particular form.

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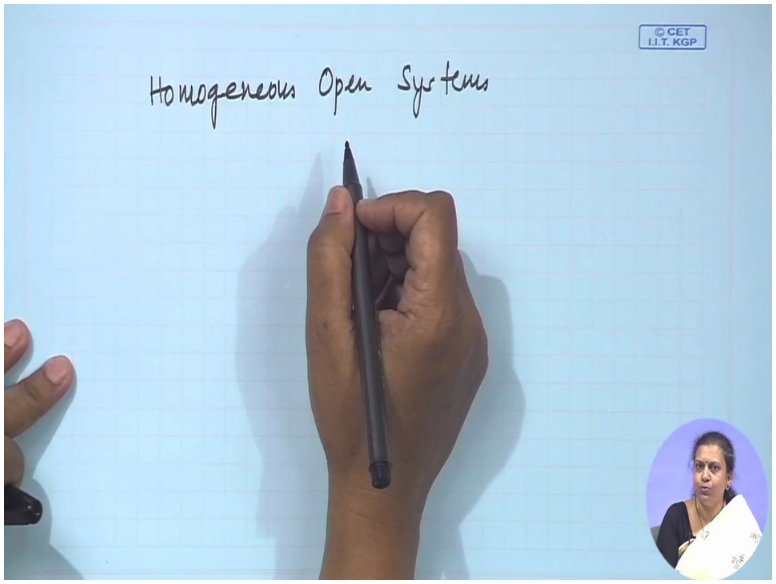

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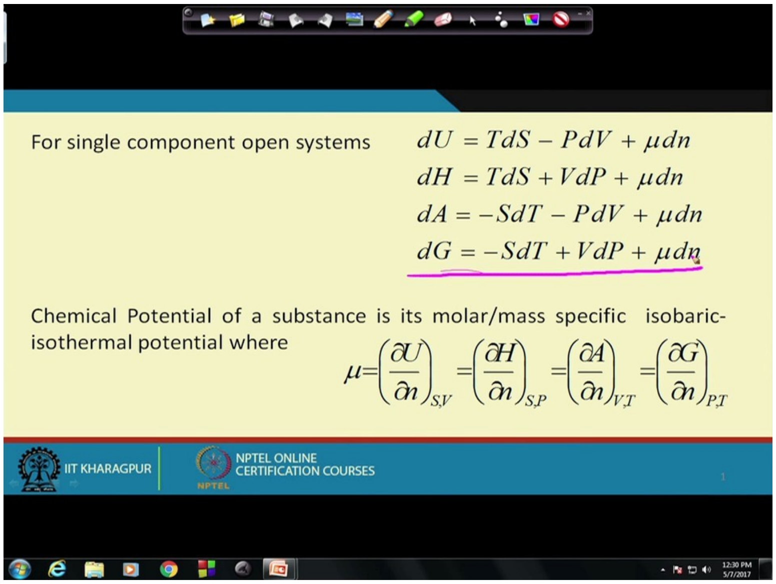

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Now we would like to extend the discussions that we had yesterday slightly further and we would like to discuss certain other aspects of homogenous open systems. Now since as I have already mentioned and you also know that the temperature pressure conditions or keeping constant temperature and pressure it's the most common thing that we encounter in practice. So therefore we are going to deal primarily with the equation which relates the Gibbs free energy with the other things.

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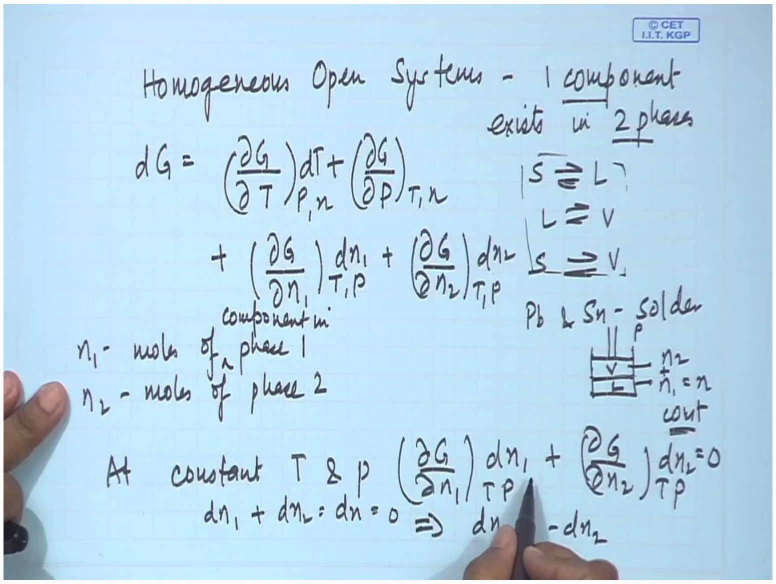

Homogeneous Open Systems - 1 component exists in 2 phases

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} + \left(\frac{\partial G}{\partial n_1}\right)_{T,P} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P} dn_2$$

$S \rightleftharpoons L$

$L \rightleftharpoons V$

$S \rightleftharpoons V$

Pb & Sn - solder

n_1 - moles of component in phase 1

n_2 - moles of phase 2

$n_2 + n_1 = n$

cont

At constant T & p $\left(\frac{\partial G}{\partial n_1}\right)_{TP} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{TP} dn_2 = 0$

$dn_1 + dn_2 = dn = 0 \Rightarrow dn_1 = -dn_2$

Now for the time being let me write it down for the time being I would like to deal with the simplest type of Homogenous open systems, what is it? It comprises of say one component it's a single component system which exists in 2 phases and let me tell you this is the most common type of phase transition that we encounter and the phase transitions are usually of the form solid to liquid or maybe liquid to vapor or maybe solid to vapor and so on, these are the most common transitions that we encounter that are also be some other type of transition for example an alloy of say a lead and tin which forms a solder that can also, here also we can have a similar type of phase transition.

So for the time being, what we do? We concentrate on one component 2 phase systems and we consider the simple or the simplest type of open systems that we can think of once we are conversant we are quite familiar with this then we go for heterogeneous closed systems or in other words we go for a system where a large of homogeneous open systems which constitutes a heterogeneous closed system.

Now let us see in this particular case we can write down dG as del G del T at constant P, n dT plus del G del P I have written it down several times in the last class plus del G del n 1 where I would like to remind you that n1 is the number of moles of phase1 say, n2 is moles of component it should be of component in phase 1 and this is moles of component in phase 2, so this is del G del n1 under constant T, P dn1 plus del G del n2 constant T,P dn2, right?

Now at constant pressure temperature conditions because usually we know that these types of phase transitions they occur under constant temperature pressure conditions. So under these conditions what do we get? We get del G del n1 T, P dn1 plus del G del n2 T, P dn2 this should be equal to 0. Now in the beginning I have told you that we are dealing with a single component in 2 phases and we assume that while, for example suppose say it is a liquid vapor mixture, right? Kept in a piston cylinder arrangement where the pressure is kept constant the temperature is kept constant we have got a liquid here we have got a vapor here.

Now if you consider the liquid only to be a system then it is an open system because there is mass and energy interaction between the liquid and vapor phase if we consider the vapor to be the system then again it is an open system but when we consider the liquid vapor combination to be a system then it is a closed system. Now what do we have here? We have say n1 moles here we have n2 moles here and we know that since the composite system is a close system.

So n1 plus n2 equals to n this should be something constant or in other words what I mean to say is dn1 plus dn2 equals to dn should be equal to 0 which automatically implies that dn1 should be equal to minus dn2. So therefore if you substitute in this particular equation then what do we get?

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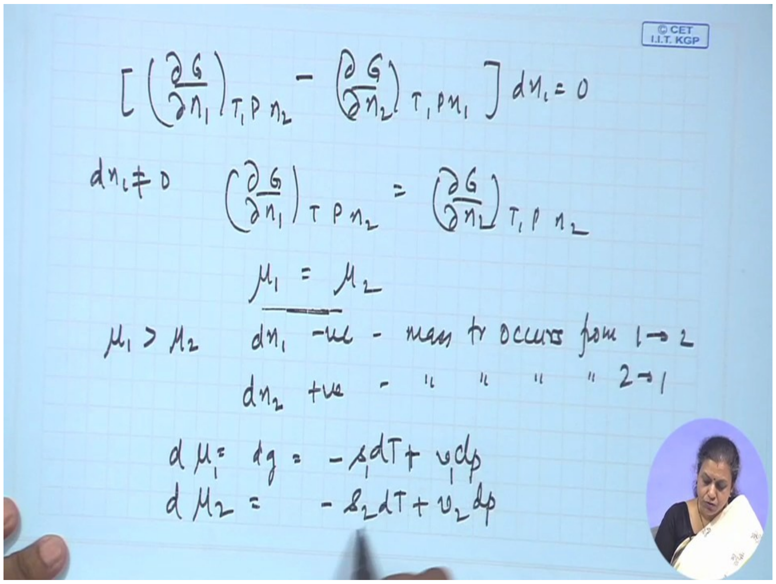

$$\left[\left(\frac{\partial G}{\partial n_1}\right)_{T,P\,n_2} - \left(\frac{\partial G}{\partial n_2}\right)_{T,P\,n_1}\right] dn_1 = 0$$

$$dn_1 \neq 0 \qquad \left(\frac{\partial G}{\partial n_1}\right)_{T\,P\,n_2} = \left(\frac{\partial G}{\partial n_2}\right)_{T,P\,n_2}$$

$$\underline{\mu_1 = \mu_2}$$

$\mu_1 > \mu_2$ $\quad dn_1$ -ve - mass tr occurs from $1 \to 2$

dn_2 +ve - " " " " $2 \to 1$

$$d\mu_1 = dg = -s_1 dT + v_1 dp$$
$$d\mu_2 = \quad -s_2 dT + v_2 dp$$

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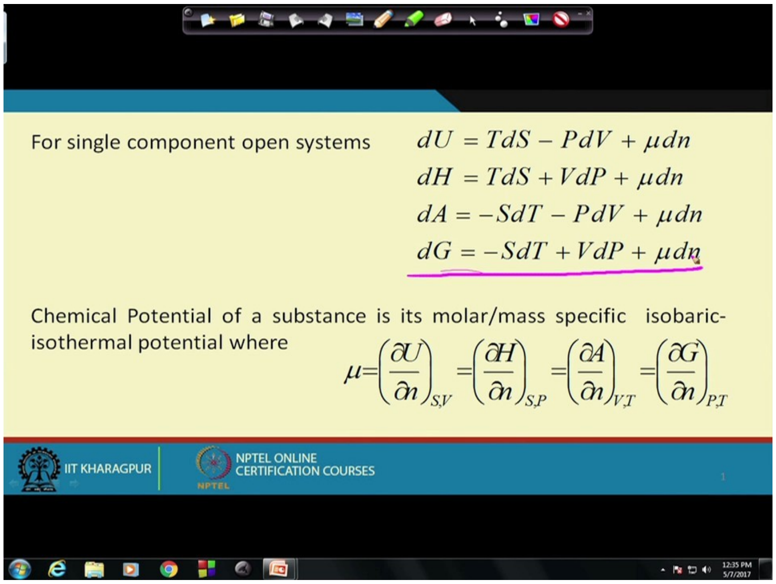

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We get in this particular equation then in that condition we get del G del n1 T, P n2 minus del G del n2 T,P n1 into dn1 is equal to 0. What does this imply? Since we know that dn1 is not equal to 0 so it automatically implies del G del n1 at T P n2 must be equal to del G del n2 at T, P n2. From yesterday we already know what is this? It is in fact it is already written here this is nothing but mu. So therefore from here we can write this down as dmu1 or rather mu1 is equal to mu2 under this condition.

So therefore if suppose transfer occurs under condition such that mui1 is not equal to mui2 then in that case there is going to be mass transfer till the time when mu1 becomes equal to mu2 and in the process of this mass transfer what do we find? We find that the system with the larger chemical potentials shrinks and the system with the smaller chemical potential it increases in size till the chemical potential of both the open systems

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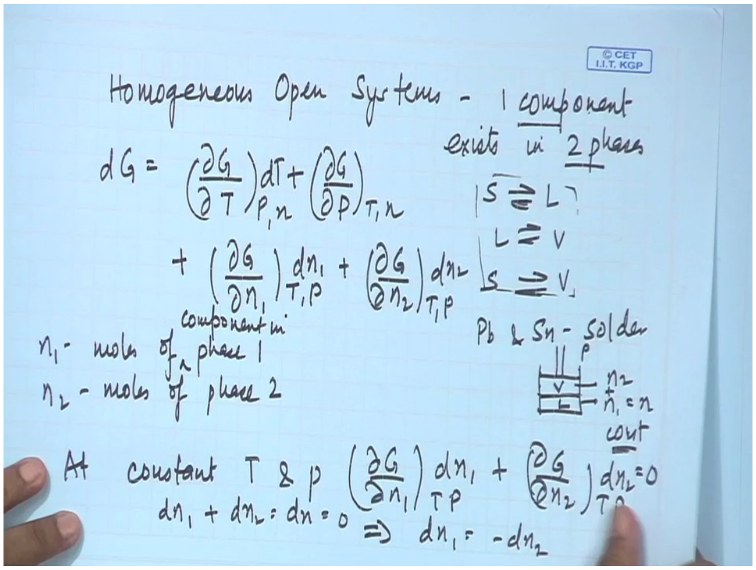

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$$+ \left(\frac{\partial G}{\partial n_1}\right)_{T,P} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P} dn_2$$

$S \rightleftharpoons L$

$L \rightleftharpoons V$

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Pb & Sn - solder

n_1 - moles of component in phase 1

n_2 - moles of phase 2

At constant T & p $\left(\frac{\partial G}{\partial n_1}\right)_{TP} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{TP} dn_2 = 0$

$dn_1 + dn_2 = dn = 0 \Rightarrow dn_1 = -dn_2$

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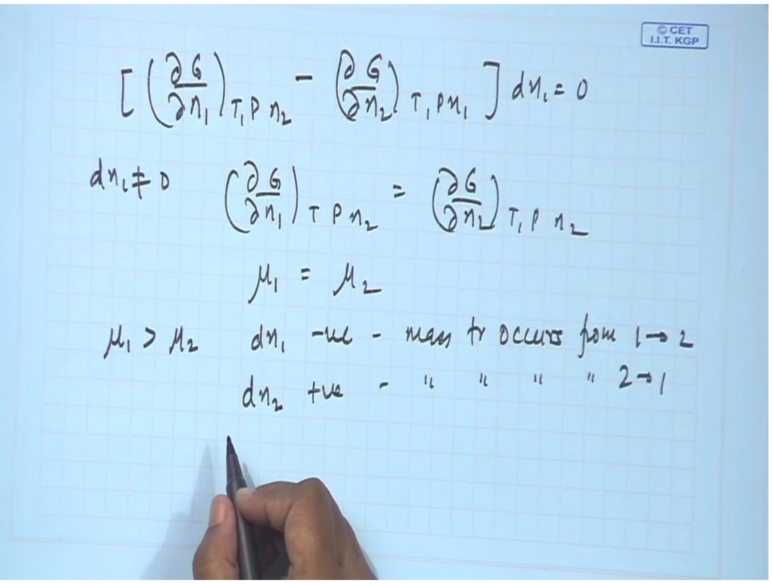

$$\left[\left(\frac{\partial G}{\partial n_1}\right)_{T,P\,n_2} - \left(\frac{\partial G}{\partial n_2}\right)_{T,P\,n_1}\right] dn_1 = 0$$

$dn_1 \neq 0$ $\quad \left(\frac{\partial G}{\partial n_1}\right)_{T\,P\,n_2} = \left(\frac{\partial G}{\partial n_2}\right)_{T,P\,n_2}$

$$\mu_1 = \mu_2$$

$\mu_1 > \mu_2$ $\quad dn_1$ -ve - mass tr occurs from 1 → 2

dn_2 +ve - " " " " 2 → 1

Say the liquid and the vapor under this condition they become equal moment they become equal we find that there is no other further interaction between the 2 systems they are under equilibrium condition. So to summarize if mu1 is greater than mu2 we know that the dn1 is negative and the mass transfer occurs from phase 1 to phase2 and vice versa if dn2 is positive then the mass transfer occurs from 2 to 1.

So just the way I have done I will repeat phase with the larger chemical potential shrinks and phase with the smaller chemical potential it goes till equilibrium is reached or in other words still mu1 becomes equal to mu2. Now this particular equation we can extend it further to find certain other characteristics of the transition boundaries, how?

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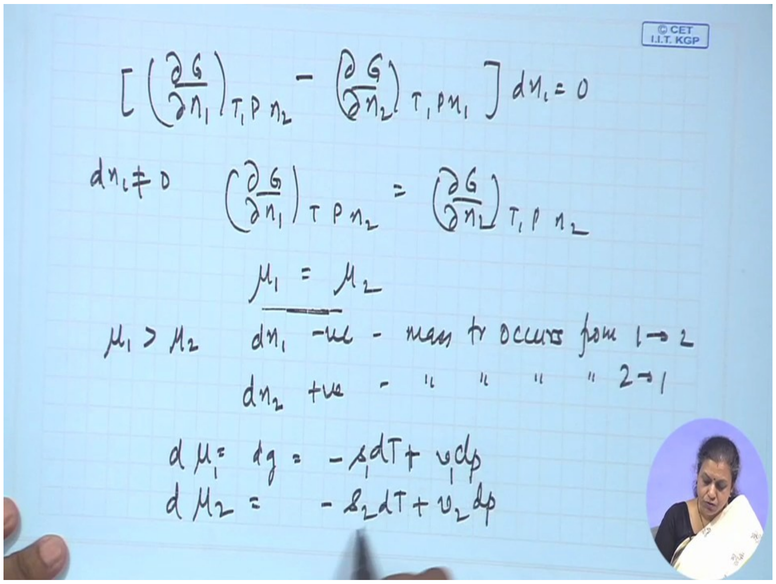

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dn_2 +ve - " " " " 2 → 1

$d\mu_1 = dg = -s_1 dT + v_1 dp$

$d\mu_2 = -s_2 dT + v_2 dp$

All of us know that what is d mu equals to? D mu it is nothing but equal to dG and we already know what is dg equals to again referring to this particular equation. Since dG has been written in terms of molar quantities, so therefore this equation with the number, with the different molar quantities. So therefore this becomes minus sdT plus vdp, right? So dmu1 it should be equal to minus s1dT plus v1dp, in the same way d mu2 this should be minus s2dT plus v2dp.

Now what do we know? We know that dmu1 should be equal to dmu2. So therefore for the 2 phases this should be equal to this and from there what do we get?

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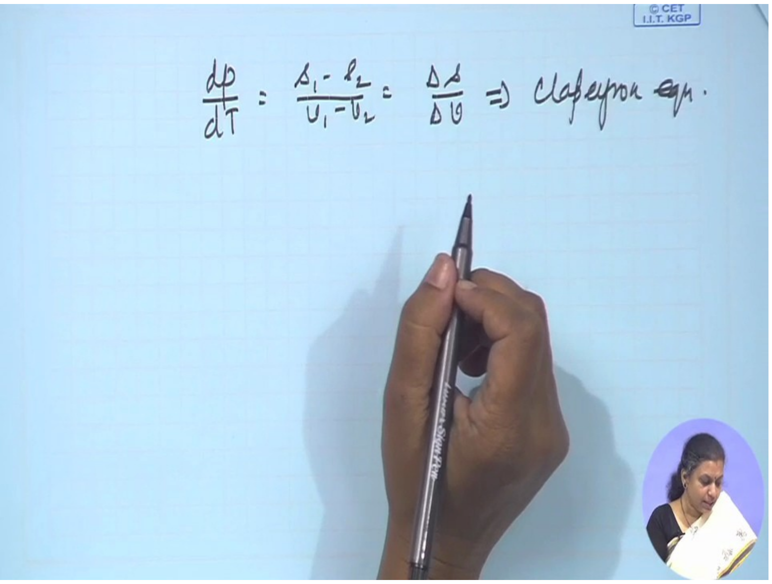

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$$\frac{dp}{dT} = \frac{s_1 - s_2}{v_1 - v_2} = \frac{\Delta s}{\Delta v} \Rightarrow \text{Clapeyron eqn.}$$

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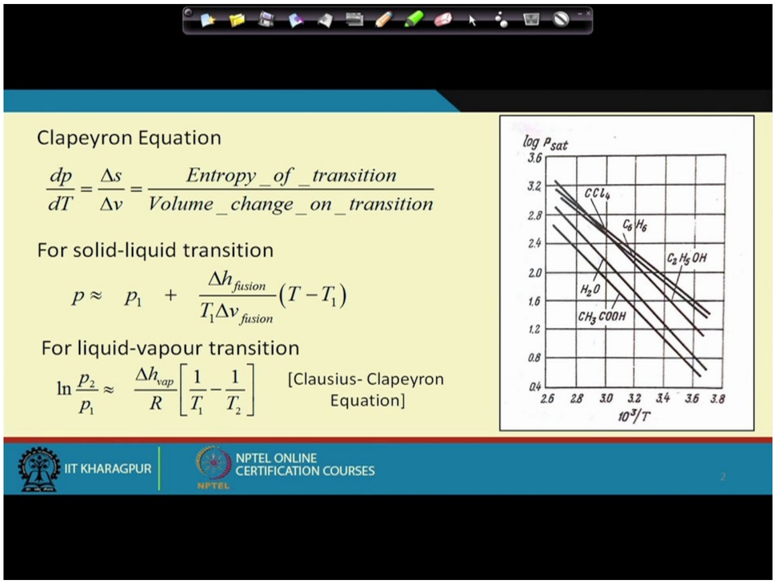

Clapeyron Equation

$$\frac{dp}{dT} = \frac{\Delta s}{\Delta v} = \frac{Entropy\_of\_transition}{Volume\_change\_on\_transition}$$

For solid-liquid transition

$$p \approx p_1 + \frac{\Delta h_{fusion}}{T_1 \Delta v_{fusion}}(T - T_1)$$

For liquid-vapour transition

$$\ln\frac{p_2}{p_1} \approx \frac{\Delta h_{vap}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$ [Clausius- Clapeyron Equation]

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From there we get the famous Clapeyron equation which can be derived as dp dT equals to s1 minus s2 by v1 minus v2 or in other words it is delta s by delta v which is nothing but the entropy of transition or the ratio of the entropy of transition with the volume change of this, so therefore this gives us the Clapeyron's equation you can see where we find that the slope of the pressure versus volume curve it is obtained from the slope of the pressure versus temperature curve it is obtained from the entropy of transition divided by the volume change on transition.

So therefore from this we find that the slope of the of the PT curve if we observe the slope of the PT curve which I have shown in the last class if you recollect the slope of the PT curves can be obtained from that particular equation, the equation which we say it is commonly known as the Clapeyron equation. So from this Clapeyron equation what are the things that we get? First thing is suppose we apply it there are number of things.

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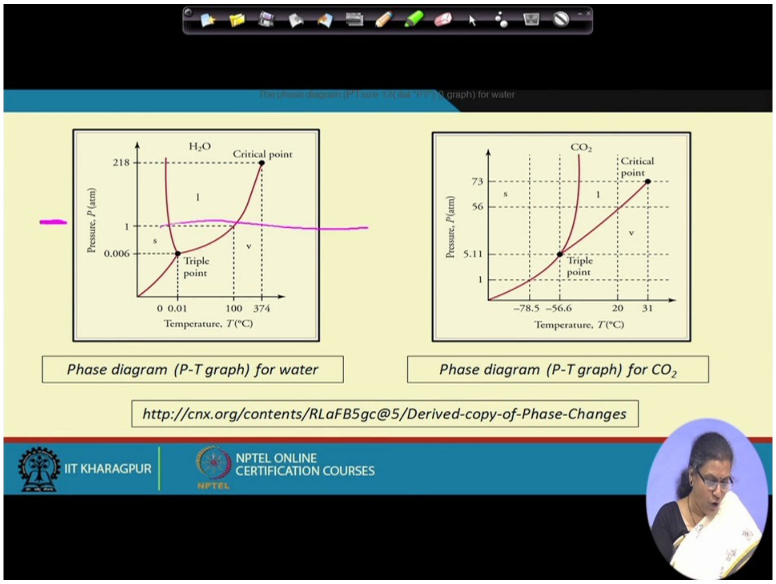

Phase diagram (P-T graph) for water

Phase diagram (P-T graph) for CO_2

http://cnx.org/contents/RLaFB5gc@5/Derived-copy-of-Phase-Changes

First thing is this can be applicable to any phase equilibrium problem say any phase equilibrium of any particular substance provided it is a pure substance we can apply it and if you observe the important part is we find that we can use the thermodynamic data, the data on delta s del delta v to predict the appearance of the phase diagrams and their forms, so therefore what I mean is we can predict the slopes of this PT curves for the different phases and we can also predict which graph is going to be steeper which is going to be less steep and we can do all these things using the thermodynamic data.

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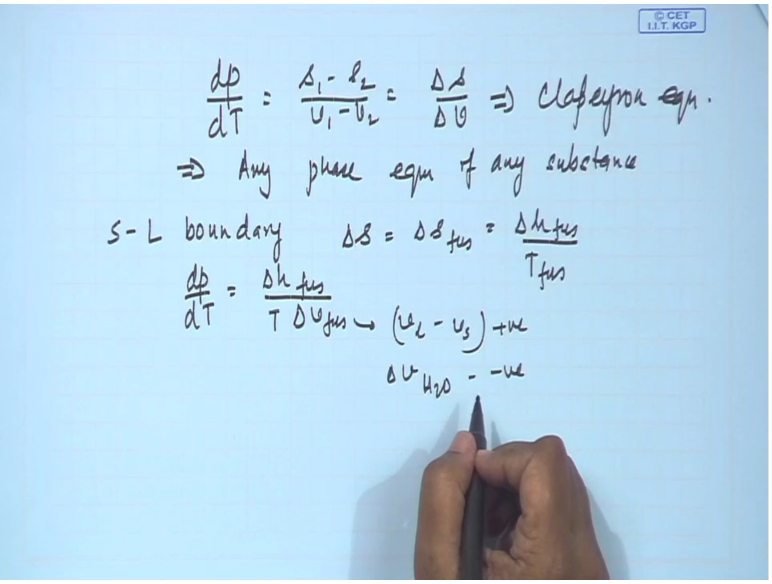
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$$\frac{dp}{dT} = \frac{s_1 - s_2}{v_1 - v_2} = \frac{\Delta s}{\Delta v} \Rightarrow \text{Clapeyron eqn.}$$

$\Rightarrow$ Any phase eqm of any substance

S - L boundary $\quad \Delta s = \Delta s_{fus} = \frac{\Delta h_{fus}}{T_{fus}}$

$$\frac{dp}{dT} = \frac{\Delta h_{fus}}{T \, \Delta v_{fus}} \rightarrow (v_l - v_s) \text{ +ve}$$

Δv_{H_2O} - -ve

Let us see what this particular equation reduces to? For example if we consider the solid liquid boundary when we consider the solid liquid boundary what is Delta s? Delta s is nothing but delta s fusion which is nothing but delta H fusion by the melting point of the solid so from there what do we get? We get dp dT is nothing but equal to Delta h fusion by T delta v fusion, right? Now usually what we find, usually this Delta v fusion is nothing but v liquid minus v solid.

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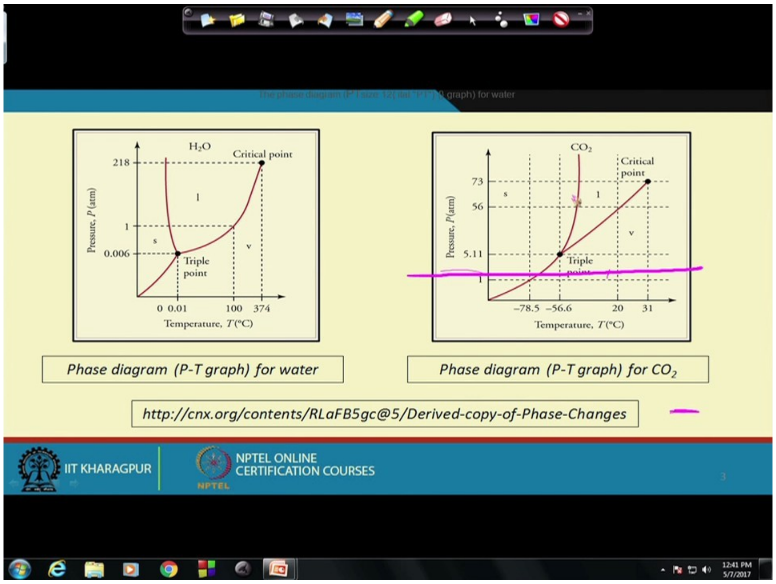

The phase diagram (P-T size 12{ital "P-T"} {} graph) for water

Phase diagram (P-T graph) for water

Phase diagram (P-T graph) for CO_2

http://cnx.org/contents/RLaFB5gc@5/Derived-copy-of-Phase-Changes

For most of the substances this is positive and therefore it is quite evident if you observe here the slope of this particular curve it is, we see that it that it is more or less positive. Now very interestingly if you find if you observe water then in that case we know that delta v for water that is going to be negative, why? Because yesterday also we discussed and you already know that the water it contracts on liquefaction.

So therefore if you observe the curve for water what you find? You find that there is a slight negative slope and that arises because of the negative value of Delta v fusion. We also see that in this particular case Delta v fusion is usually much smaller and that explains for the very steep curve the solid liquid transition curve for both the cases that I have depicted here and also for several other cases that you can you can see or you can take up in different textbooks.

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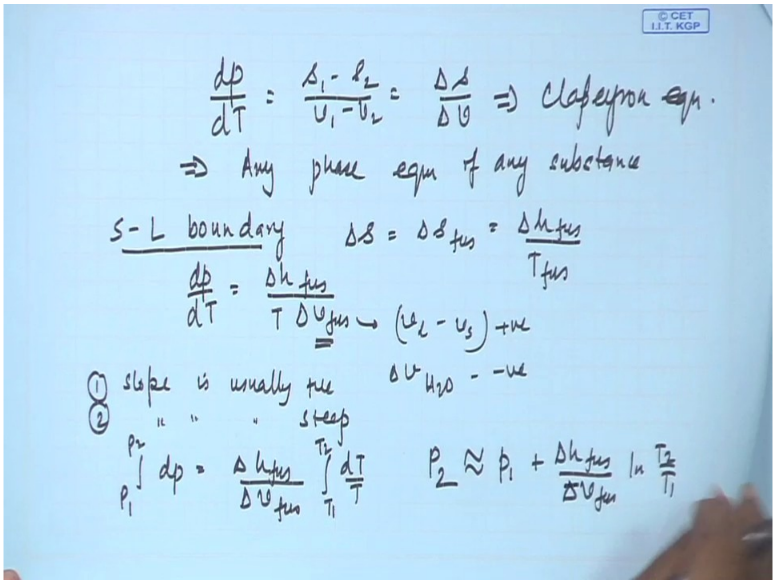

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$\Rightarrow$ Any phase eqm of any substance

<u>S-L boundary</u> $\Delta s = \Delta s_{fus} = \frac{\Delta h_{fus}}{T_{fus}}$

$$\frac{dp}{dT} = \frac{\Delta h_{fus}}{T \underline{\underline{\Delta v_{fus}}}} \rightarrow (v_l - v_s) + ve$$

① slope is usually +ve Δv_{H_2O} - -ve

② " " " steep

$$\int_{P_1}^{P_2} dp = \frac{\Delta h_{fus}}{\Delta v_{fus}} \int_{T_1}^{T_2} \frac{dT}{T} \qquad P_2 \approx P_1 + \frac{\Delta h_{fus}}{\Delta v_{fus}} \ln \frac{T_2}{T_1}$$

So therefore the conclusion is that for the solid liquid boundary we find that the slope is usually positive except some examples like water, antimony, bismuth and other thing is slope is usually very steep and so therefore from here we can we can easily integrate this equation as well and on integrating this equations say from a pressure P1 to P2 and assuming that Delta h fusion and Delta v fusion they are more or less constant with pressure.

We can get an expression like the final pressure can be obtained as the initial pressure plus Delta v fusion ln T2 by T1. So in this particular equation if we know the total number of parameters are 1, 2, 3, 4, 5, 6 out of these if we know 5 of the parameter we can find out the sixth one. Well, this was for the solid liquid boundary.

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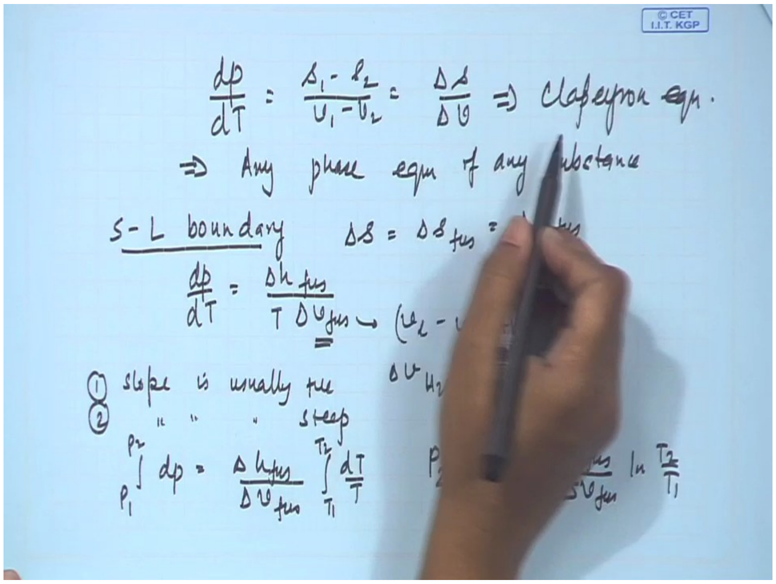

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$$\frac{dp}{dT} = \frac{\Delta h_{fus}}{T\, \underline{\underline{\Delta v_{fus}}}} \rightarrow (v_L - $$

Δv_{H_2}

① slope is usually +ve

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$$\int_{P_1}^{P_2} dp = \frac{\Delta h_{fus}}{\Delta v_{fus}} \int_{T_1}^{T_2} \frac{dT}{T}$$

P_2 ... $\frac{}{\Delta v_{fus}} \ln \frac{T_2}{T_1}$

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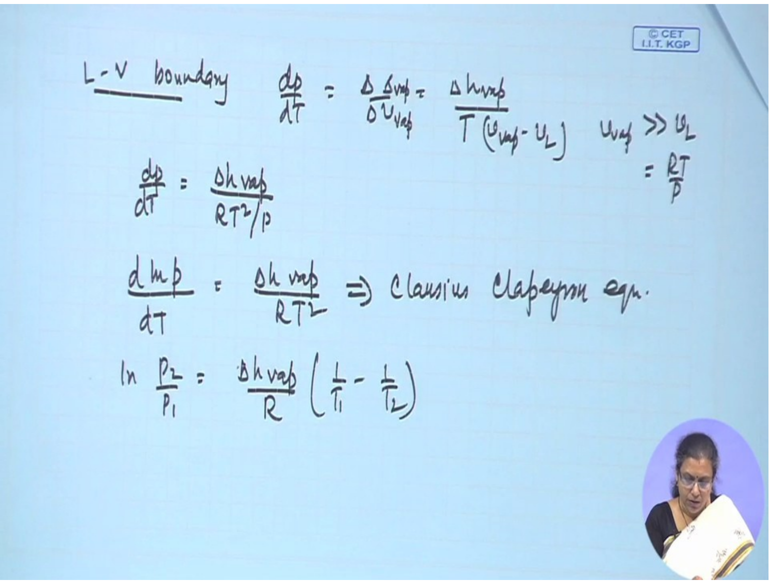

L-V boundary $\frac{dp}{dT} = \frac{\Delta s_{vap}}{\Delta v_{vap}} = \frac{\Delta h_{vap}}{T(v_{vap} - v_L)}$ $v_{vap} \gg v_L$ $= \frac{RT}{p}$

$$\frac{dp}{dT} = \frac{\Delta h_{vap}}{RT^2/p}$$

$$\frac{d \ln p}{dT} = \frac{\Delta h_{vap}}{RT^2} \Rightarrow \text{Clausius Clapeyron eqn.}$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta h_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Now let us apply the same equation to the liquid vapor boundary as well. So if we apply it to the liquid vapor boundary starting from the same Clausius Clapeyron equation we know dp dT this is equal to delta s by delta v. So therefore when it is liquid vapor then this is going to be delta s vaporization and the delta v vaporization.

So this is nothing but delta h vaporization by T the boiling point temperature into v vapor minus v liquid, now in this particular case usually unlike the solid liquid transition we know that usually the v vapor is much greater as compared to the v liquid and we also know that for low to moderate pressures this can be equal to, this obeys the ideal gas equation.

So from here we can write this down as dp dT is nothing but equal to delta h vaporization by RT square by P or we can also rearrange to write to denote dln P dT is nothing but equal to Delta h vaporization by RT square and this particular equation is known as it is a very famous equation it has got a lot of applicabilities and this equation is known as the Clausius Clapeyron equation, on integrating this equation what do we get?

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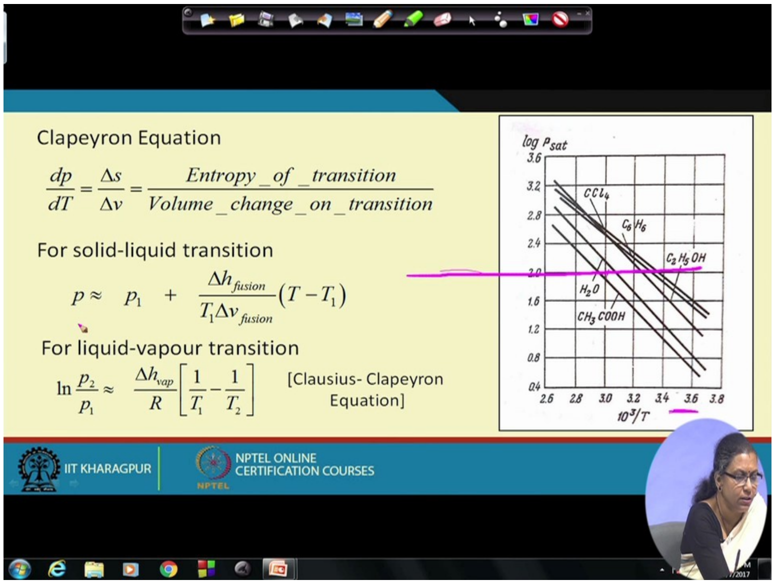

Clapeyron Equation

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For solid-liquid transition

$$p \approx p_1 + \frac{\Delta h_{fusion}}{T_1 \Delta v_{fusion}}(T - T_1)$$

For liquid-vapour transition

$$\ln\frac{p_2}{p_1} \approx \frac{\Delta h_{vap}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$ [Clausius- Clapeyron Equation]

On integrating this equation we get ln P2 by P1 this is equal to delta h vaporization by R into 1 by T1 minus 1 by T2. So therefore what does this imply? This implies, so therefore I have just written down the equations which we were discussing for solid liquid transition this is the equation for liquid vapor transition the Clausius Clapeyron equation has been derived and from this equation it is quite evident that ln P versus 1 by T should be a straight line.

And here I have depicted for a large number of liquids the log P saturated versus the 1 by T and we find the linear nature of the curve for all the substances despite the large number of assumptions which are inherent in this particular derivation. We will discuss the assumptions shortly after we deal with the solid vapor boundary.

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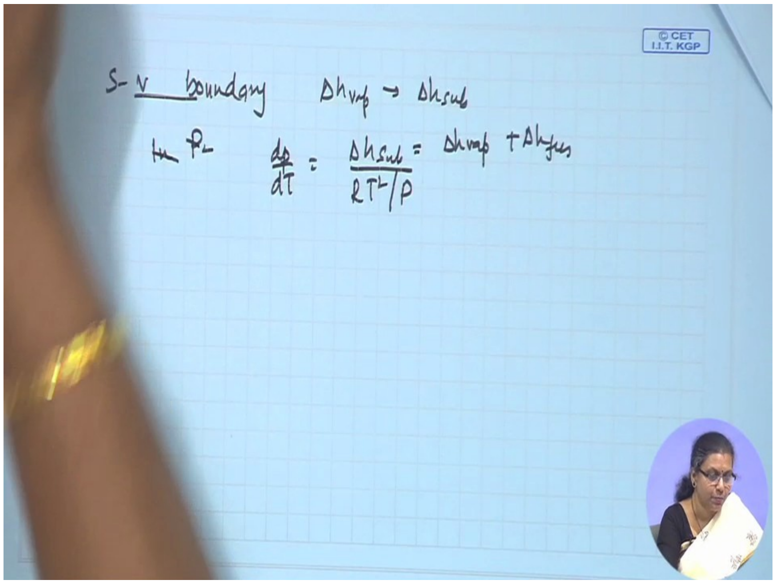

S-V boundary $\Delta h_{vap} \rightarrow \Delta h_{sub}$

ln P $\quad \frac{dp}{dT} = \frac{\Delta h_{sub}}{RT^2/P} = \Delta h_{vap} + \Delta h_{fus}$

Now in the solid vapor boundary also it is almost the same thing and the only thing that we do is we replace Delta h vaporization with Delta h sublimation.

As a result of which the equation which we obtained in these particular cases ln P or else I will write the better form dp dT is nothing but Delta h sublimation by RT square by P and keeping in mind that Delta h sublimation is nothing but delta h vaporization plus Delta h fusion this automatically explains that if you observe the PT the curve you will see that the solid vapor transition line it is much steeper as compared to the liquid vapor transition line and this can be explained from the fact that it arises since delta h sublimation is involved in the solid vapor the PT curve of the solid vapor transition curve and Delta h sublimation is much greater as compared to Delta h vaporization.

So therefore from here we find that generally for transition for the condensed phase to the vapor phase we find that the equation can more or less be written in the form as log P or log 10 P it is something of A minus B by T the equation is something of this form and from this log P or ln P in whatever way you wish you can write it down and you see the utility of this particular equation.

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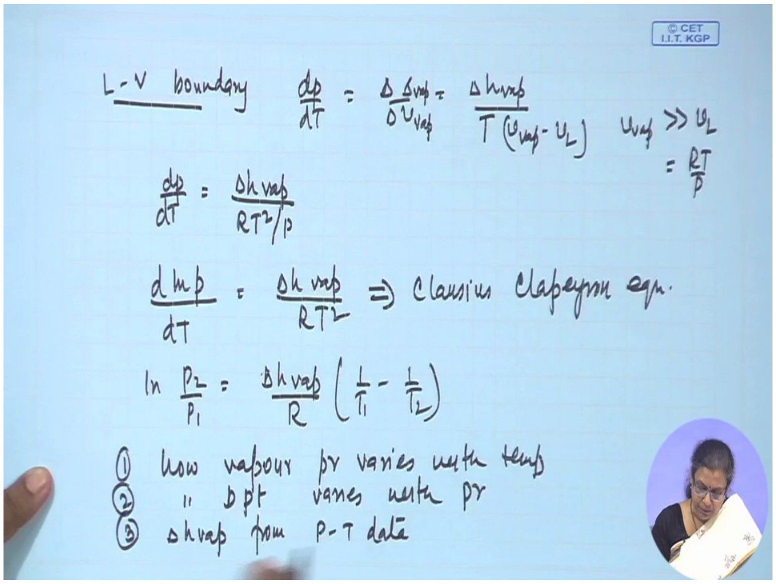

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L-V boundary $\frac{dp}{dT} = \frac{\Delta s_{vap}}{\Delta v_{vap}} = \frac{\Delta h_{vap}}{T(v_{vap} - v_L)}$ $v_{vap} >> v_L$ $= \frac{RT}{p}$

$$\frac{dp}{dT} = \frac{\Delta h_{vap}}{RT^2/p}$$

$$\frac{d \ln p}{dT} = \frac{\Delta h_{vap}}{RT^2} \Rightarrow \text{Clausius Clapeyron eqn.}$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta h_{vap}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

① how vapour pr varies with temp
② " b pt varies with pr
③ Δh_{vap} from P-T data

The utility of this particular equation or even the equation written in this form is first thing we can predict the P versus T curve from thermodynamic data on latent heat of vaporization. So therefore from here the first thing that we can find out is that how vapor pressure varies with temperature this is the first thing that we can find.

The other thing that we can find is how boiling temperature or boiling point varies with pressure. And the other interesting thing which we can find is we can find out Delta h vaporization from PT data this is the other important thing we can find data on Delta h vaporization as well as Delta h sublimation both of them and from the data.

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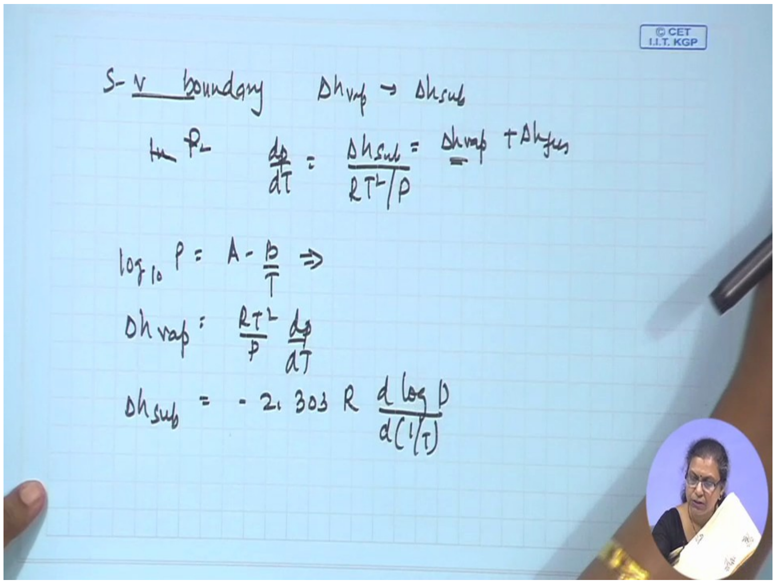

S-V boundary $\Delta h_{vap} \rightarrow \Delta h_{sub}$

$$\frac{dp}{dT} = \frac{\Delta h_{sub}}{RT^2/p} \qquad \Delta h_{sub} = \Delta h_{vap} + \Delta h_{fus}$$

$$\log_{10} P = A - \frac{B}{T} \Rightarrow$$

$$\Delta h_{vap} = \frac{RT^2}{P}\frac{dp}{dT}$$

$$\Delta h_{sub} = -2.303\, R \frac{d \log P}{d(1/T)}$$

From here if we try to find out Delta h vaporization it is nothing but equal to RT square by P dp dT. Similarly Delta h sublimation it is nothing but equals to we can write it down in this particular form. So therefore we find that from these equations which we have derived from the basic equation of homogeneous open systems the simplest type comprising of single component and 2 phases, what do we find?

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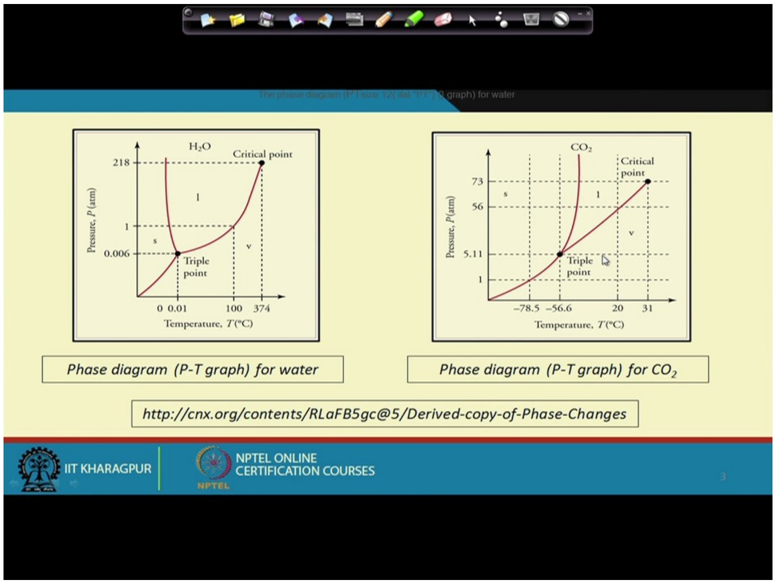

Phase diagram (P-T graph) for water

Phase diagram (P-T graph) for CO$_2$

http://cnx.org/contents/RLaFB5gc@5/Derived-copy-of-Phase-Changes

We find that we are in a position to predict the slopes of the PT curve here and also if we know the slope we can predict the heats or the enthalpies involved in the transition criteria. Now we need to remember despite the success of the Clausius Clapeyron equation it has got a large number of assumptions. Now what are the assumptions?

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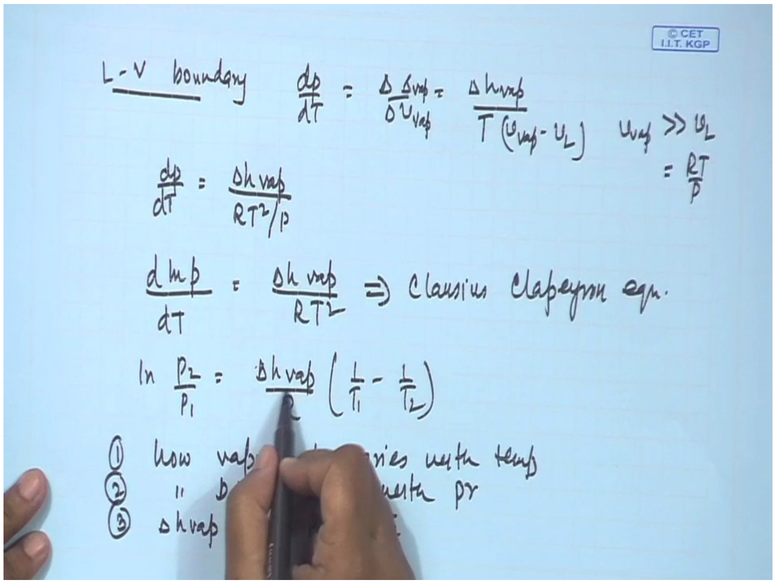

L - V boundary $\frac{dp}{dT} = \frac{\Delta s_{vap}}{\Delta v_{vap}} = \frac{\Delta h_{vap}}{T(v_{vap} - v_L)}$ $v_{vap} >> v_L$

$= \frac{RT}{p}$

$$\frac{dp}{dT} = \frac{\Delta h_{vap}}{RT^2/p}$$

$$\frac{d \ln p}{dT} = \frac{\Delta h_{vap}}{RT^2} \Rightarrow \text{Clausius Clapeyron eqn.}$$

$$\ln \frac{p_2}{p_1} = \frac{\Delta h_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

① how vap [illegible] ries with temp

② " [illegible] with pr

③ Δh_{vap} [illegible]

The first and the most serious assumption is for all these integrations that we have done here I have assumed the basic thing that delta h vaporization is constant only under that condition I have come from this step to this step and this is the most drastic assumption.

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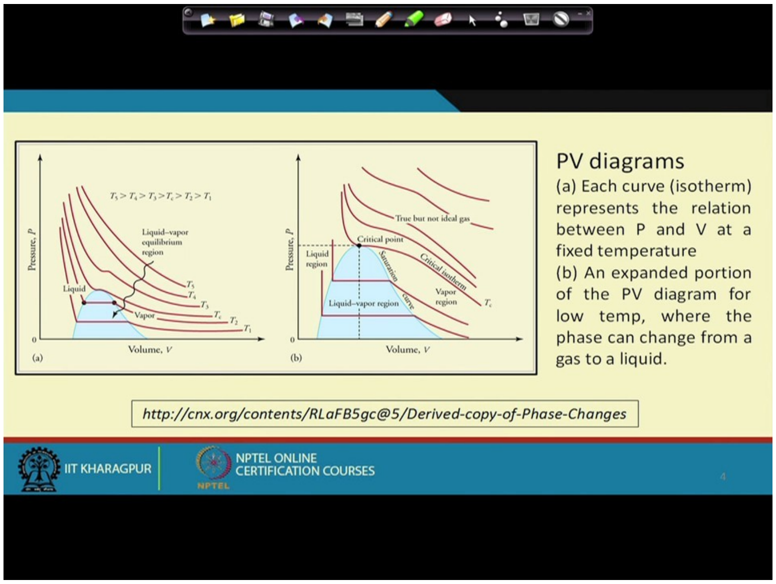

PV diagrams

(a) Each curve (isotherm) represents the relation between P and V at a fixed temperature

(b) An expanded portion of the PV diagram for low temp, where the phase can change from a gas to a liquid.

http://cnx.org/contents/RLaFB5gc@5/Derived-copy-of-Phase-Changes

Because if you observe the PV curves we can very well observe for the liquid vapor zone, we will be discussing this in the next class and then it will be clear to you how the most drastic assumption is regarding assuming the consistency of the of delta h vaporization the latent heat of vaporization. So we continue with this discussion in the next class.