Engineering Thermodynamics
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Module 8
Lecture No 53
Thermodynamic property relations: Clapeyron equation and Maxwell relation

Ok welcome back, in the last lecture we described the derivation Maxwell relation and as well as couple of other interesting aspect of the thermodynamic function to change the variables which are of interest to for us as a as a engineer ok in terms of controlling the variables which we can make use of in the experiments.

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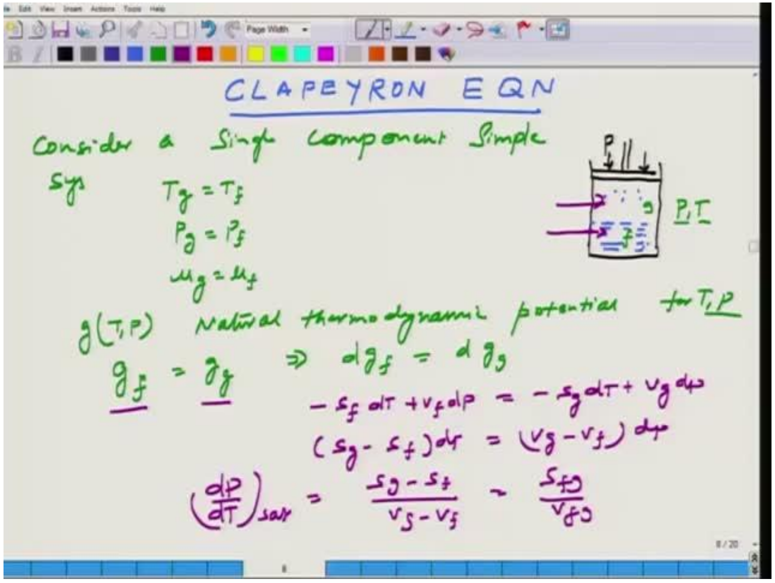

CLAPEYRON EQN

Consider a Single component Simple Sys

$T_g = T_f$

$P_g = P_f$

$\mu_g = \mu_f$

$g(T,P)$ Natural thermodynamic potential for T,P

$$\underline{g_f} = \underline{g_g} \Rightarrow dg_f = dg_g$$

$$-s_f\,dT + v_f\,dP = -s_g\,dT + v_g\,dP$$

$$(s_g - s_f)\,dT = (v_g - v_f)\,dP$$

$$\left(\frac{dP}{dT}\right)_{sat} = \frac{s_g - s_f}{v_g - v_f} \sim \frac{s_{fg}}{v_{fg}}$$

Ok so now I am going to make use of such expressions and we can start with something we call is clapeyron equation. So let us consider a single component, so let us consider a single component simple system ok, ok so and the situation is such that the pressure is applied, this is a massless let us say piston and here fluid and at this pressure and temperature this fluid undergoes phase separation leading to vapour phase which we say G and liquid phase which say F and we know at equilibrium your TG should be same as TF and pressure is F.

And as well as assuming that of course what we are assuming here the pressure is there is no change in the pressure in vertical direction you neglect that and as well as the chemical potential which we have not defined but we will make use of it here as something called Myu G and Myu F ok. Now the phase transition occurs at this P and T and we know that based on our last lecture that the variable which thermodynamic potential which has independent variables T and P is basically G ok. That is Gibbs free energy. So G becomes your natural thermodynamic potential ok for T and P ok.

Now given that this the fluid at equilibrium you have the same variables P and T at equilibrium your G of fluid is same as G of gas ok or in other word, DG of F is same as DG of G the vapour phase. Ok, so this is the condition for equilibrium, this has to be same at your PT for simple component system ok. And we can now make use of the the definition of DG which is SF DT plus VF DAP and this is same as minus SG DT plus VG DP or we can rewrite this as SG SFDT is VG.

So this is at the saturation condition because these two phases are at saturation condition and thus we can write this as DP by DT sat is SG minus SF VG minus VF or SFG VFG ok. So this is one expression which we came up. Now instead of making use of the equality of your Gibbs free energy for this two phase system at a given T and P which are at equilibrium we can also directly use Maxwells relation ok.

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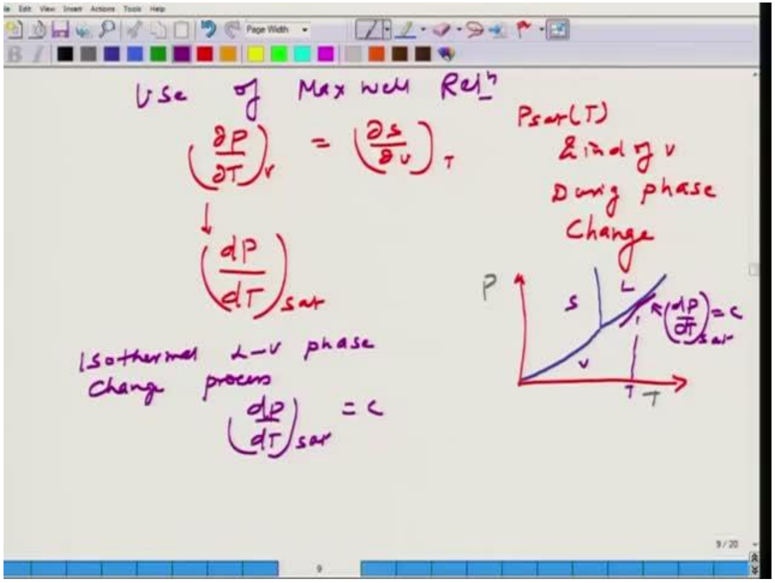

Use of Maxwell Rel^n

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

$$\downarrow$$

$$\left(\frac{dP}{dT}\right)_{sat}$$

Psat(T)
& ind of v
During phase
Change

Isothermal L–V phase
Change process

$$\left(\frac{dP}{dT}\right)_{sat} = c$$

So I will try to illustrate the use of Maxus relation. So of course we have four relations Maxwell relation so we can we will just use one of them which relates the derivatives of pressure with T ok because that is what we want. Now note that here for the case of your P, P sat is just a function of temperature right, ok it doesn't depend on the volume, so the Maxwells relation tells you that this derivative partial derivative is related to del S by del V at T ok. As I said P is just a function of temperature and independent variable at or during phase change ok, so what we can do is I can write this as simply DP instead of partial derivative.

Since it is independent of V I can write this as simple DP by DT ok and your sat as a as a instead of just V. Now let us look at ok your PT diagram here, ok so at a given some T, the slope here is going to be your DP by DT, so this is sat and this is going to be constant. For isothermal liquid vapour phase change process DP by DT sat is going to be constant ok, so this is the slope at this point, of course this is your liquid solid and vapour. So what we can do is, we know this slope now we can try to use this directly in the Maxwell relation and then we can try to integrate this in order to get the change in the entropy ok and with respect to the change in the volume.

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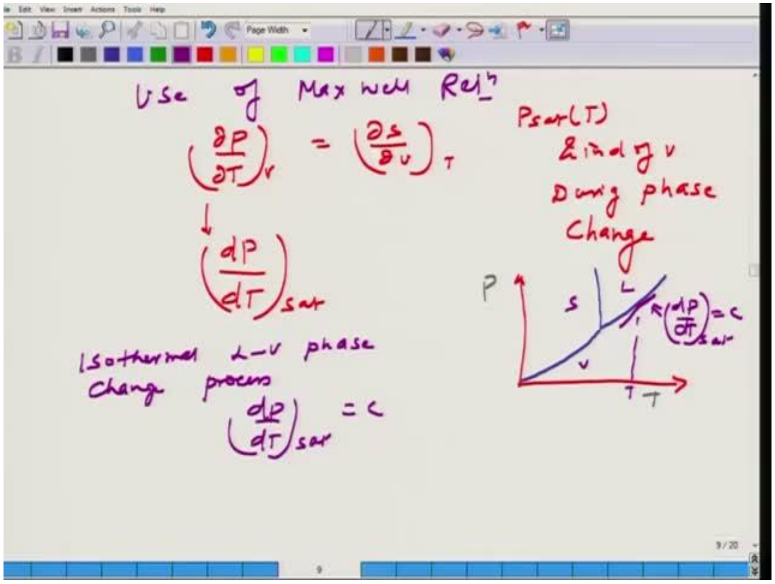
Use of Maxwell Relⁿ

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial s}{\partial v}\right)_T$$

$$\downarrow$$

$$\left(\frac{dP}{dT}\right)_{sat}$$

$P_{sat}(T)$

& ind of v

During phase Change

Isothermal L-V phase change process

$$\left(\frac{dP}{dT}\right)_{sat} = c$$

So let me just try to illustrate that, so if we integrate this Maxwell relation here, so what we can do is this left hand side is constant, so now we can integrate the right hand side and we can clearly get SG minus HF ok, this is integration, you had DS by DV is equal to DP at sat and then you have this VG minus VF, so this directly comes from your fact that DP by DT sat is DS by DV at constant temperature ok.

So this is for isothermal phase change, so I can write this as simply again SFG divided by VFG ok. Now it is clearly both this expression whether I made use of Maxwell relation or directly use of the Gibbs free energy equality you got the same expression ok. Now let me just work on this a bit, since P is constant ok during phase change I can use this DH as from the expression VDP is going to be simply DS because this is going to be zero ok.

Now I can integrate this DH TDS from fluid to let us say gas and this I can get because of the fact that the temperature is constant, this will be your SFG, so which essentially means HFG is TSFG ok. this aspect I can make use of it here and I can get this expression del P by del T sat as HFG something which I can calculate measure experimentally and of course this divided by TVFFG. Now this can also be generalised for any phase change, just not necessarily liquid vapour but any phase change from 1 to 2 ok, could be your vapour solid, could be any, any phase change.

So instead of using HFG I can write this as delta H for any phase change, this divided by T and this is delta V change in the volume of two phases. So this expression is called basically clapeyron equation is is in honour of the person who actually did this exercise. Now what we can do is we can make use of this clapeyron equation and try to simplify a bit for liquid vapour and solid vapour where we can consider that the volume of the vapour is substantially large compared to the liquid or for the solid ok.

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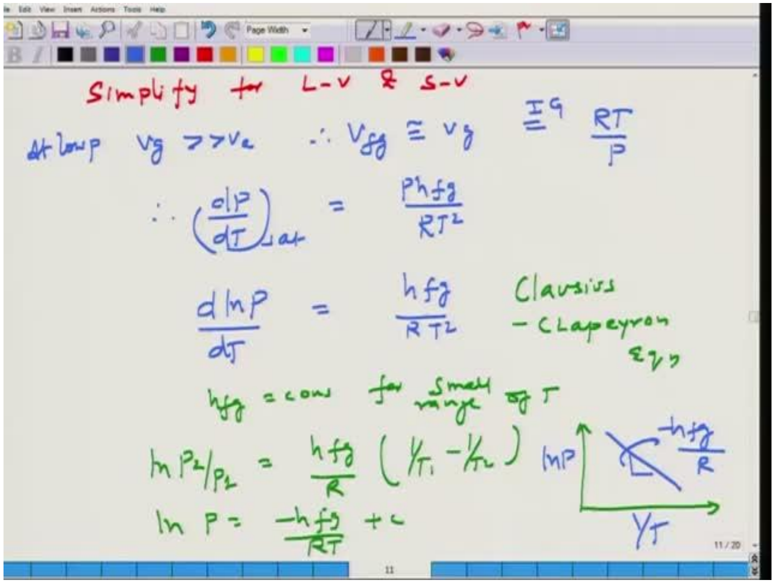

Simplify for L-v & S-v

At low P $v_g >> v_l$ $\therefore v_{fg} \cong v_g \overset{IG}{\equiv} \frac{RT}{P}$

$$\therefore \left(\frac{dP}{dT}\right)_{sat} = \frac{P h_{fg}}{RT^2}$$

$$\frac{d \ln P}{dT} = \frac{h_{fg}}{RT^2}$$ Clausius - Clapeyron Eqn

h_{fg} = const for small range of T

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

$$\ln P = \frac{-h_{fg}}{RT} + c$$

So let me just simplify this expression for liquid vapour and solid vapour, so let us consider VG VL for this would be let us say at low pressure, just consider the liquid vapour now, therefore VFG is going to be only VG and for ideal gas this is going to be simply RT by P ok. Thus I can write del P by del T sat as HFG and now if it is for the ideal gas will be your T and V is replaced by RT by P, so that becomes RT square and P comes in the numerator.

I can rewrite in this following form, I can bring P in here then it becomes DLNP DT and that is going to be HFGRT square ok, this is sometimes also called clausius clapeyron ok equation. So what we can do is we can further make use of this expression and integrate it considering HFG constant for small range of temperature and I can write in this as LNP2 by P1, is equal to HFG by R, followed by T1 minus T2 or in general I can write LNP is minus HFG by RT plus some constant ok.

So what does it mean that this expression can be used to obtain the heat of vaporization by just looking at the slope of any substance, mostly it is true for the gases if you take out the saturation vapour or vapour pressure the logopedic form as a function of 1 by T then you can get the slope and the slope would be HFG by R. Thus you can find out your heat of vaporization based on this particular slope ok.

So that will be the end of this lecture. What we are going to try is make use of this exercise particularly Maxwell relation and other expression which we have discussed earlier, that is your cyclic rule and and reciprocative relation eh to find out the changes in the internal energy and entropy and enthalpy ok. So I will see you in the next lecture.