Course on Phase Equilibrium Thermodynamics
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Lecture 23
Homogenous Open Systems(Contd.)

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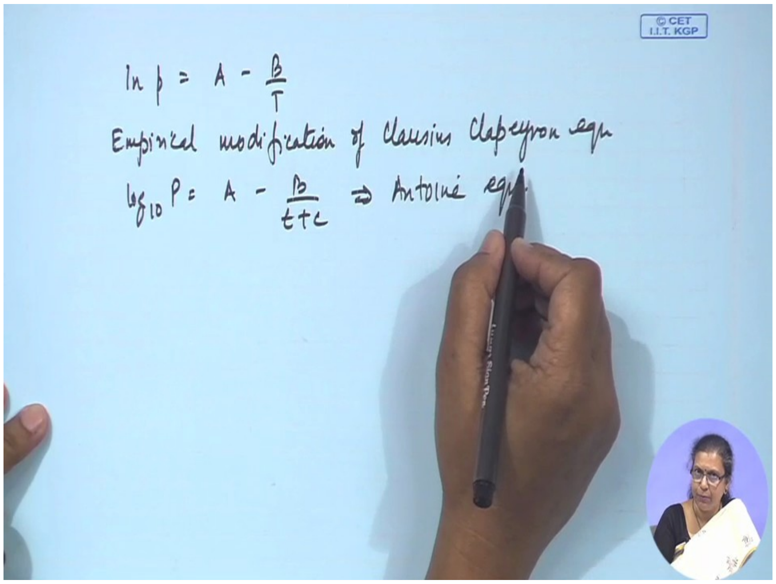

$\ln p = A - \frac{B}{T}$

Empirical modification of Clausius Clapeyron eqn

$\log_{10} P = A - \frac{B}{t+c} \Rightarrow$ Antoine eqn

Well to continue with our discussions where we have ended in the last class was I had derived the Clausius clapeyron equation, from the Clausius equation and the final derivation where I ended was the Clausius Clapeyron equation expressed in this particular form and we find that a more popular equation which relates vapor pressure with temperature is just a empirical modification of the Clausius Clapeyron equation, in fact that equation you must have heard and that equation is much more popular and that is used much more frequently, it is an empirical modification of the Clausius Clapeyron equation which is expressed as log 10 P equals to A minus B by t plus c.

In this equation if you, this equation is known as Antoine equation and for most of the purpose we will find that if you have to find out vapor pressure at some temperature or if you want to find out the boiling point at some particular pressure usually we use this particular equation if you compare there 2, we find that there are basically 2 differences one is, it is expressed in log10 whereas this is the 10 base and this is with the ln and the other thing we find that the parameter C is anything any value other than 273.15 Kelvin, so this equation is much more used.

Now coming back to the assumptions which were involved in Clausius Clapeyron equation despite the fact that it can be so successful and it is used so very frequently, possibly it’s thought that a fortune cancellation of the errors inherent due to the different assumptions gives or it's responsible for the success of the Clausius Clapeyron equation. Now what is the most drastic assumption? I have just mentioned it in the last class.

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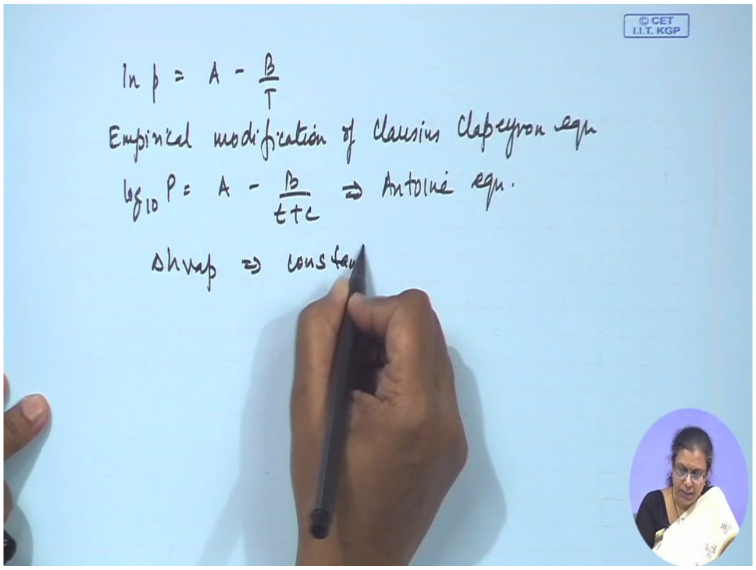

$\ln p = A - \frac{B}{T}$

Empirical modification of Clausius Clapeyron eqn

$\log_{10} P = A - \frac{B}{t+c} \Rightarrow$ Antoine eqn.

$\Delta h_{vap} \Rightarrow$ constan

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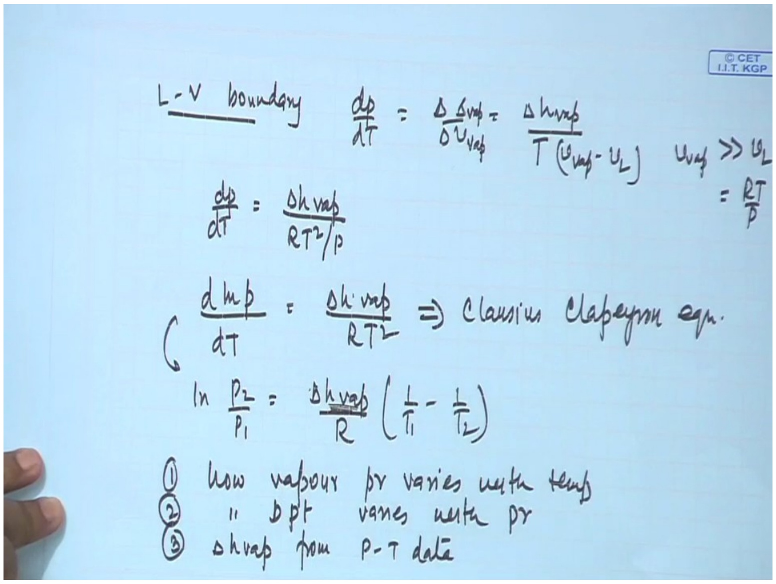

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L-V boundary $\frac{dp}{dT} = \frac{\Delta s_{vap}}{\Delta v_{vap}} = \frac{\Delta h_{vap}}{T(v_{vap} - v_L)}$ $v_{vap} >> v_L$ $= \frac{RT}{p}$

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

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

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

① how vapour pr varies with temp
② " bpt varies with pr
③ Δhvap from P-T data

The most drastic assumption is that I have assumed as I have assumed delta h vaporization to be constant based on which performs this particular integration in coming from this equation to this equation.

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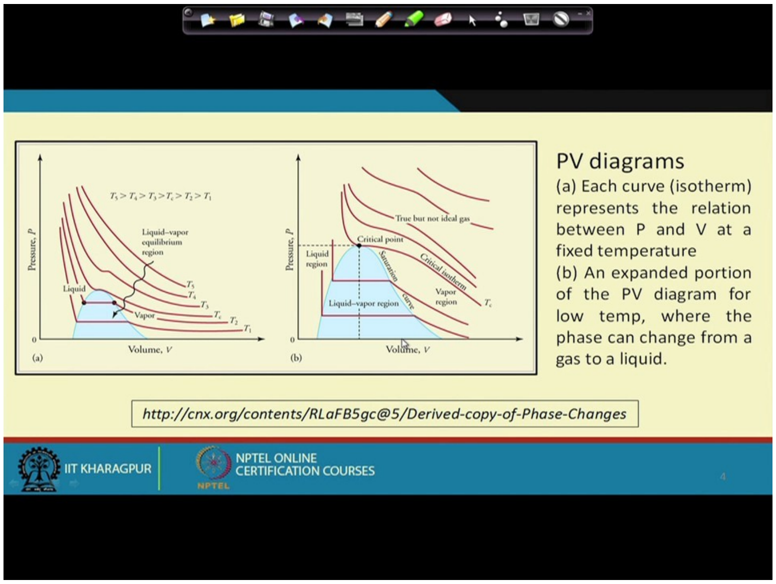

PV diagrams

(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

In reality we know that Delta h vaporization it is a significant function of temperature and this will be evident if you observe the Pv curves which I have shown in this particular diagram. We find that the liquid region exists at low in this particular region the vapor region exists under this particular region these are the isotherms which have been drawn the constant temperature isotherms and we will find that there is a dome where the liquid vapor both of them coexist when any particular system within this particular dome then it keeps on changing its composition, sorry.

It keeps on changing its phase from the pure liquid states to the pure vapor phase it keeps on changing its composition from the pure liquid state to the pure vapor phase and when it is inside the dome we find that depending upon its location it has different proportions of liquid and vapor. We find that as we go towards higher and higher pressures we find that this liquid vapor dome it keeps on becoming smaller and smaller.

And the horizontal portion which marks the phase change from the liquid to the vapor region that keeps on getting shorter and shorter till it reduces to a point at the critical point. So therefore at the critical point what we observe is the partial the molar volume of the liquid phase and the vapor phase they are the same and therefore none of the phases they can be distinguished from one another and under this particular condition we will find that the transition is not abrupt it is just continuous.

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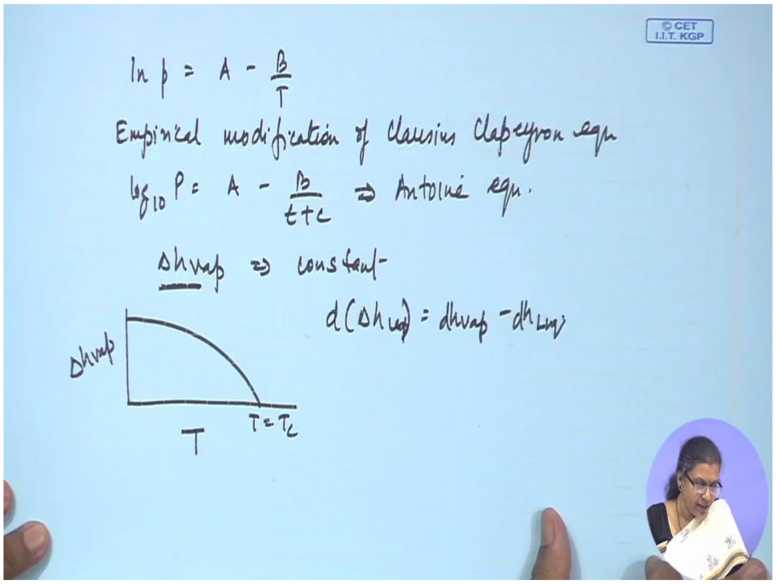

$$\ln p = A - \frac{B}{T}$$

Empirical modification of Clausius Clapeyron eqn

$$\log_{10} P = A - \frac{B}{t+c} \Rightarrow \text{Antoine eqn.}$$

$\underline{\Delta h}_{vap} \Rightarrow$ constant

$$d(\Delta h_{vap}) = dh_{vap} - dh_{Liq}$$

So therefore accordingly based on this if we plot delta h vaporization versus temperature we find that that the curve is something of this sort where delta h vaporization becomes 0 at T equals to Tc. So therefore from here it is quite evident that in no way delta h vaporization is constant unless we assume the 2 temperatures T1 and T2 over which the transition or over which the phase transition takes place are very close to one another.

So therefore my next attempt will be to find out the dependence of the latent heat of vaporization on temperature and this particular derivation this has been derived from the or rather this is known as Kirchhoff’s equation we know that the latent heat of vaporization this is nothing but equal to h vapor minus h liquid, so therefore d of this is going to give me this, right?

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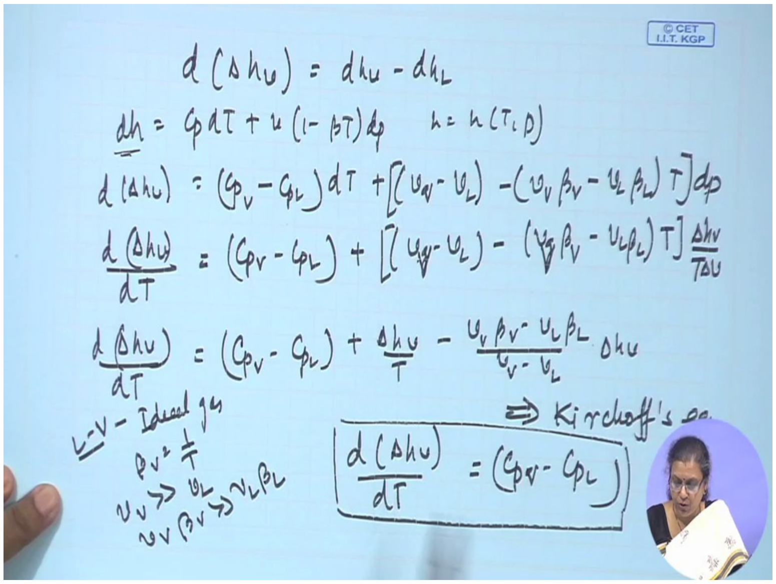

$$d(\Delta h_v) = dh_v - dh_L$$

$$\underline{dh} = C_p dT + v(1-\beta T)dp \qquad h = h(T, p)$$

$$d(\Delta h_v) = (C_{p_V} - C_{p_L})dT + [(v_V - v_L) - (v_V\beta_V - v_L\beta_L)T]dp$$

$$\frac{d(\Delta h_v)}{dT} = (C_{pV} - C_{pL}) + [(v_V - v_L) - (v_V\beta_V - v_L\beta_L)T]\frac{\Delta h_v}{T\Delta v}$$

$$\frac{d(\Delta h_v)}{dT} = (C_{pV} - C_{pL}) + \frac{\Delta h_v}{T} - \frac{v_V\beta_V - v_L\beta_L}{v_V - v_L}\Delta h_v$$

$\Rightarrow$ Kirchoff's eq.

$\underline{L-V}$ - Ideal gas

$\beta_V = \frac{1}{T}$

$v_V >> v_L$

$v_V\beta_V >> v_L\beta_L$

$$\boxed{\frac{d(\Delta h_v)}{dT} = (C_{pV} - C_{pL})}$$

Now this is the latent heat of vaporization it is dhv minus dhL. If you recall the property estimations for single phase substances that is in closed systems we had related h with measurable parameters T and P. If you recall those equations that we had derived dh was equal to CpdT plus v into 1 minus beta T dp, right when we were trying to express h as a function of T and P, fine. So therefore we can substitute this equation for the vapor phase and for the liquid phase in this particular equation once we substitute what do we get?

We get d delta hv this is nothing but equal to Cp vapor minus Cp liquid dT plus v vapor minus v liquid minus v vapor beta vapor minus v liquid beta liquid T into dp, right? We get this equation and from this equation suppose I would like to find out the variation of the molar latent heat of vaporization with temperature, what do we get? The equation is something of this sort vg minus vL minus vg sorry it's I missed it should be vv minus beta v minus vL beta L T, delta hv by T delta v, isn’t it?

What I have done? I have substituted dh from the basic equation that we have derived and then have substituted the Clausius clapeyron equation for dp dT in this particular case. So from there what do I get? I get d delta hv dT in this particular case it is nothing but equal to Cp vapor minus Cp liquid plus delta h v by T this and this cancels out minus Vv beta v minus vL beta L by Vv minus vL into delta hv and this particular equation this is known as the Kirchhoff's equation to predict the latent heat of vaporization in terms of temperature and pressure and this can find, so therefore this is the equation this is primarily for the liquid vapor transition.

Now what happens for the, and in this particular case it is important for us to remember that if we assume that the vapor phase is an ideal gas then for that case beta v is nothing but equals to 1 by T and again if we assume that beta v is much greater than vL as a result beta v beta v will also much greater than vL beta L and substituting all these things here we finally get d delta hv dT that is nothing but equal to Cp vapor minus Cp liquid.

The other terms we find they are going to cancel out, so therefore this particular equation gives us the variation of latent heat of vaporization with temperature.

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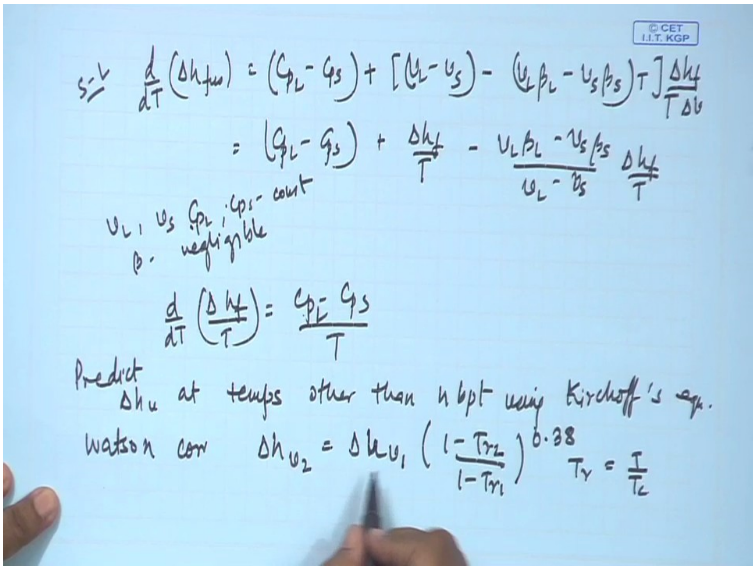

s-l $\frac{d}{dT}(\Delta h_{fus}) = (C_{pL} - C_{ps}) + [(v_L - v_s) - (v_L\beta_L - v_s\beta_s)T]\frac{\Delta h_f}{T\Delta v}$

$= (C_{pL} - C_{ps}) + \frac{\Delta h_f}{T} - \frac{v_L\beta_L - v_s\beta_s}{v_L - v_s}\frac{\Delta h_f}{T}$

v_L, v_s C_{pL}, C_{ps} - const

β. negligible

$$\frac{d}{dT}\left(\frac{\Delta h_f}{T}\right) = \frac{C_{pL} - C_{ps}}{T}$$

Predict Δh_v at temps other than n bpt using Kirchoff's eqn.

Watson corr $\Delta h_{v_2} = \Delta h_{v_1}\left(\frac{1 - T_{r2}}{1 - T_{r1}}\right)^{0.38}$ $T_r = \frac{T}{T_c}$

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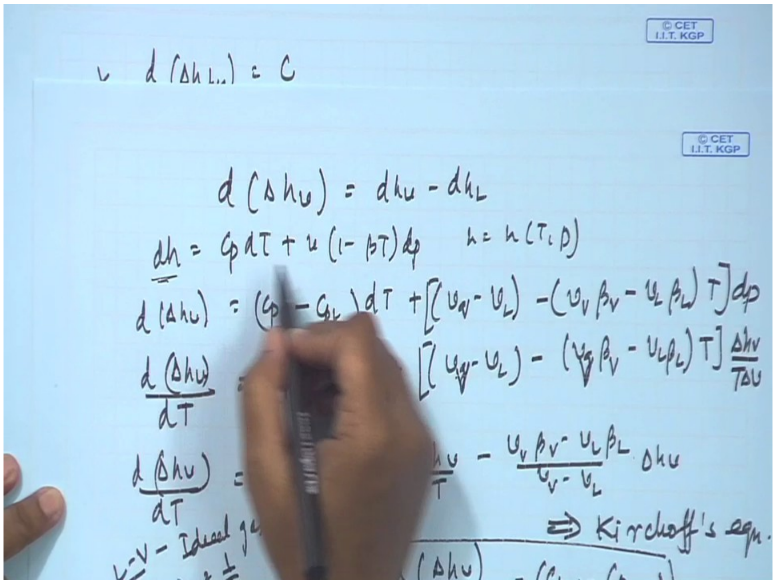

$d(\Delta h_{L..}) = C$

$d(\Delta h_v) = dh_v - dh_L$

$\underline{dh} = C_p\,dT + v(1-\beta T)\,dp \qquad h = h(T, p)$

$d(\Delta h_v) = (C_{p} - C_{L})\,dT + [(v_v - v_L) - (v_v\beta_v - v_L\beta_L)T]\,dp$

$\frac{d(\Delta h_v)}{dT} =$ [illegible] $[(v_v - v_L) - (v_v\beta_v - v_L\beta_L)T]\frac{\Delta h_v}{T\Delta v}$

$\frac{d(\Delta h_v)}{dT} =$ [illegible] $\frac{\Delta h_v}{T} - \frac{v_v\beta_v - v_L\beta_L}{v_v - v_L}\Delta h_v$

$\Rightarrow$ Kirchoff's eqn.

Now suppose I would like to find an identical thing for the solid liquid transition. In that particular case suppose I would like to find the delta h fusion then in that case here also I repeat the same thing I do the same thing I tried to substitute dhL minus dhs I write this in terms of Cps CpL etc and then the equation that I get is CpL minus Cps plus repeating VL minus Vs minus vL betaL minus vs beta s T into delta hf by T delta v, right?

From where again if I start substituting I get CpL minus Cps plus delta hf by T minus vL beta L minus Vs beta s by vL minus vs delta hf by T and if we assume that vL, vs your CpL, Cps all of these are constant and I also assume that quite naturally in both the solid and for the liquid they are incompressible liquids, so beta is negligible as a result of that in this particular case the equation reduces to delta hf by T which is nothing but CpL minus Cps divided by T.

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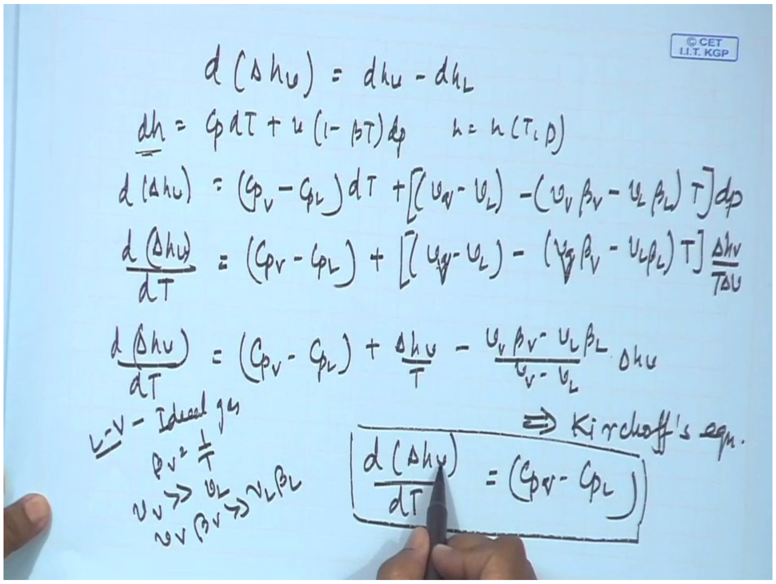

$$d(\Delta h_v) = dh_v - dh_L$$

$$\underline{dh} = c_p\,dT + v(1-\beta T)\,dp \qquad h = h(T, p)$$

$$d(\Delta h_v) = (c_{p_v} - c_{p_L})\,dT + \left[(v_v - v_L) - (v_v\beta_v - v_L\beta_L)T\right]dp$$

$$\frac{d(\Delta h_v)}{dT} = (c_{pv} - c_{pL}) + \left[(v_v - v_L) - (v_v\beta_v - v_L\beta_L)T\right]\frac{\Delta h_v}{T\Delta v}$$

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L-V - Ideal gas

$\beta_v = \frac{1}{T}$

$v_v >> v_L$

$v_v\beta_v >> v_L\beta_L$

⇒ Kirchoff's eqn.

$$\boxed{\frac{d(\Delta h_v)}{dT} = (c_{pv} - c_{pL})}$$

So therefore from here what did I get? If you observe that we could actually predict the variation of the latent heat of vaporization and the variation of the latent heat of fusion with temperature in terms of the specific heats of the 2 phases in fact it is important for you to remember that when I assumed that the latent heat is constant it means that I assume that this specific heats of both the phases in or in the respective phases remain constant with temperature.

And so therefore from these equations we can also find that we can predict delta hv at temperatures other than the normal the boiling point, we can predict delta hv at temperatures other than normal boiling point using the Kirchhoff's equation, okay and I would also at the end like to mention a few other equations which can be used for these purposes those equations are primarily empirical in nature.

One of the equations is due to Watson it is known as the Watson correlation which gives delta hv2 equals to delta hv1 1minus Tr2 by 1 minus Tr1 to the power 0.38 where 1 and 2 these two refer to the temperature of States one and two and Tr is nothing but the reduced temperature which is nothing but T by Tc.

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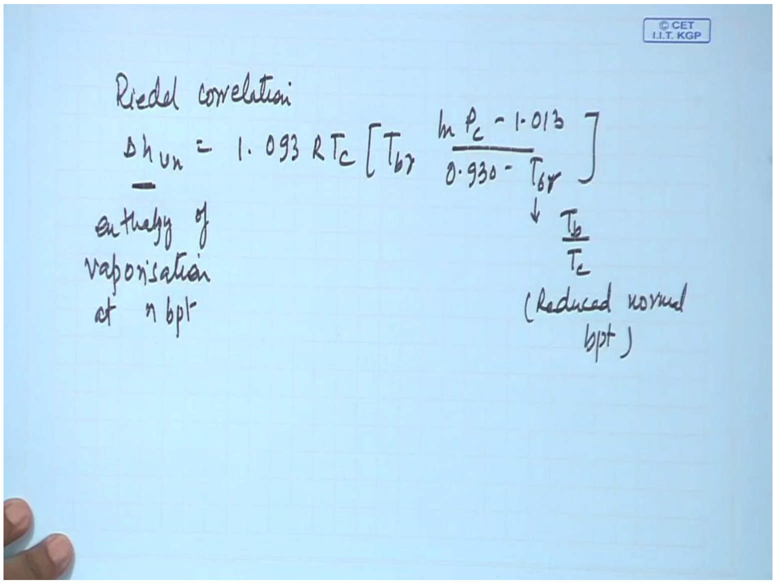

Riedel correlation:

$$\underline{\Delta h_{vn}} = 1.093\, RT_c \left[T_{br} \frac{\ln P_c - 1.013}{0.930 - T_{br}} \right]$$

enthalpy of vaporisation at n bpt

$T_{br} \downarrow \frac{T_b}{T_c}$ (Reduced normal bpt)

And for finding out the latent heat of vaporization at the normal boiling point this is easily estimated from another correlation which is known as the Riedel correlation. From here we can find out delta hvn it is nothing but 1.093 RTc Tbr ln Pc minus 1.013 by 0.930 minus Tbr. So therefore what I mean to say is and in this particular equation we will find delta hvn it is nothing but the enthalpy of vaporization at normal boiling point Tc is nothing but the critical temperature as we know Pc is nothing but the critical pressure and this equation Tbr is nothing but the reduced boiling point and reduced normal boiling point of the particular substance with which we are dealing with.

So therefore we can use the Riedel correlation to find out the molar latent heat of vaporization at normal boiling point.

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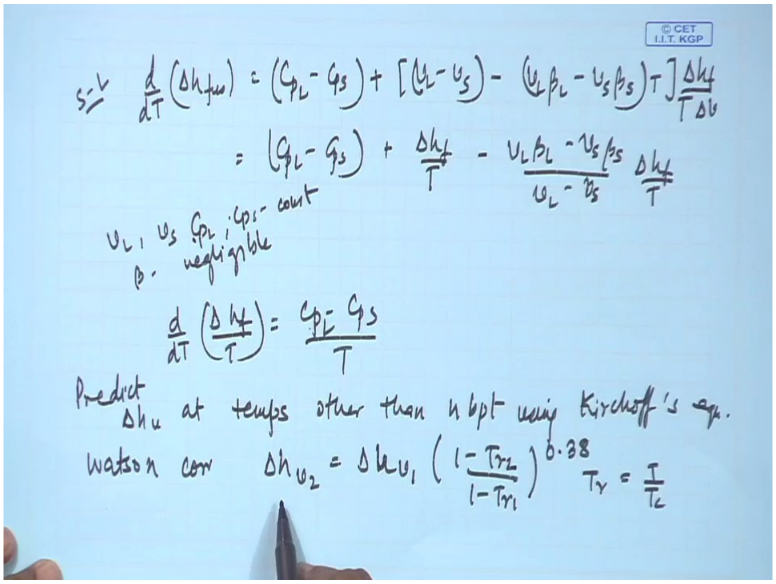

S-L $\frac{d}{dT}(\Delta h_{fus}) = (C_{pL} - C_{pS}) + \left[(v_L - v_S) - (v_L\beta_L - v_S\beta_S)T\right]\frac{\Delta h_f}{T\Delta v}$

$= (C_{pL} - C_{pS}) + \frac{\Delta h_f}{T} - \frac{v_L\beta_L - v_S\beta_S}{v_L - v_S}\frac{\Delta h_f}{T}$

v_L, v_S C_{pL}, C_{pS} - const

β - negligible

$\frac{d}{dT}\left(\frac{\Delta h_f}{T}\right) = \frac{C_{pL} - C_{pS}}{T}$

Predict Δh_v at temps other than n bpt using Kirchoff's eqn.

Watson corr $\Delta h_{v_2} = \Delta h_{v_1}\left(\frac{1 - T_{r2}}{1 - T_{r1}}\right)^{0.38}$ $T_r = \frac{T}{T_c}$

And then we can either use the Kirchhoff's equation or we can use the Watson correlation to find out the molar latent heat of vaporization at any temperature other than the normal boiling point.

So with this I would like to conclude this particular session on homogeneous on homogeneous open system, the simplest type of open system which comprises of just one component and it exists in 2 phases and we found that by using rather by using the basic equations of thermodynamics we could actually predict either the pressure temperature data from the thermodynamic data like molar enthalpy of vaporization or molar enthalpy of transition or the vice versa.

From here we could also find we could also deduce 2 equations namely the Clapeyron and the Clausius Clapeyron equation and I would like to remind you once more that the Clausius Clapeyron equation despite its large number of assumptions serves quite well for practical purposes but usually we use the Antione's equation to find out the vapor pressure, in the next class what we are going to do? We are going to deal with heterogeneous closed systems.

So initially what I did? We started our discussions with homogeneous closed system, in homogeneous closed systems we assume that it was made up of a single component or even if it is a mixture the composition of the mixture did not change and we tried to define a large number of properties for those particular systems and we tried to relate the measurable and non-measurable properties and the basis for that was Maxwell's equation.

After that we just relaxed the assumption further we went for homogeneous open systems and we deduced the Clausius Clapeyron equation, in the next class we are going to deal with the heterogeneous closed systems which comprises of a large number of homogeneous open systems which have been enclosed or rather which are enclosed by a boundary and the entire composite system does not interact with the surroundings with respect to mass transfer or with respect to volume transfer it can interact with respect to energy interaction. So we are going to deal with heterogeneous closed systems in the next class.