Course on Phase Equilibrium Thermodynamics
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Lecture 14
PvT Behaviour (Contd.)

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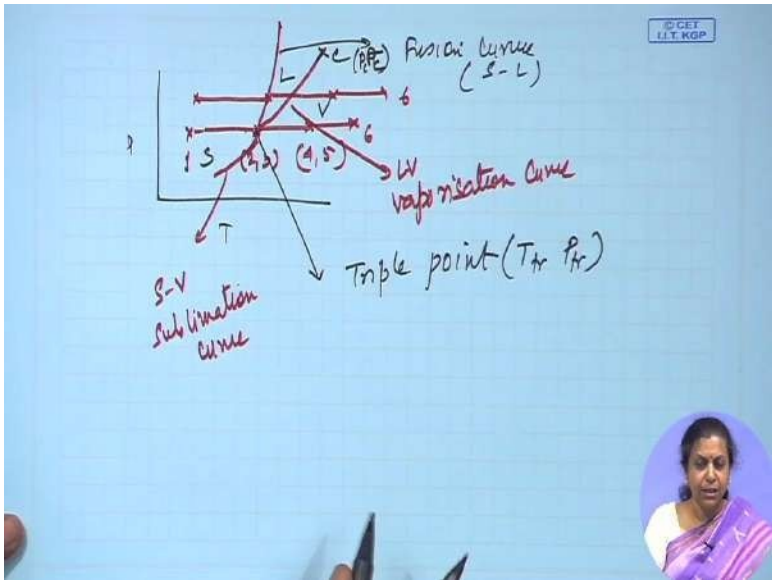

So therefore we had already discussed if you remember we had discussed the Pv and the Tv diagrams already the only thing which was left was the Pt diagram. Again we start with the same thing suppose we have pressure versus temperature, again we will we start with benzene at very low temperature it was one and then we keep on heating it at constant pressure it comes to some particular point and then there is change of phase since the change of phase occurs under isobaric, isothermal conditions, so therefore 2 and 3 they coincide here.

Then again it starts to heat, it heats till a quite till the liquid changes to a vapor phase again phases 4 and 5, if you recollect their transition from liquid to vapor that occurs at a particular point in this particular case and then the vapor continues to be heated. In this particular way we can keep on drawing these particular curves for different substance at for different specific volumes we can keep on drawing these particular curves.

And as we go on for higher and higher volumes we rather sorry higher and higher pressures, we find that these particular curves are there just the location of this saturation curves are different, again we again we join the different saturation point to give us saturation curves and under that case what do we get? We get something of this sort, this is going to be this, I could not throw them well, this and then this is going to be something of this sort, right?

So we find that we have a solid vapor transition curve which is nothing but the sublimation curve, okay. Now below this sublimation curve we have a solid here and then we have a liquid vapor this is known as the vaporization curve, it separates, this is the solid zone, this is the liquid zone and this is the vapor zone. So it separates the liquid and the vapor and we also have a fusion curve which marks the transition from the solid and liquid.

Again I would like to remind you that the fusion curve it can continue indefinitely as I have said but this particular curve it has to terminate at point C which is given by Pc, sorry yes Pc, Tc. So therefore this terminates here and this does not terminate and the sublimation curve also terminates all these 3 they terminate at the triple point which reduces to a point here, since this triple point is marked by a particular T triple point and P, right?

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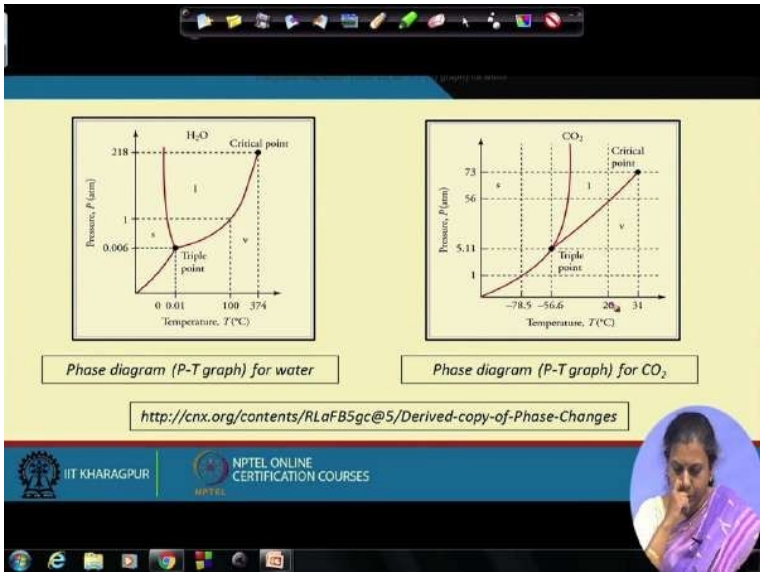

Phase diagram (P-T graph) for water

Phase diagram (P-T graph) for CO_2

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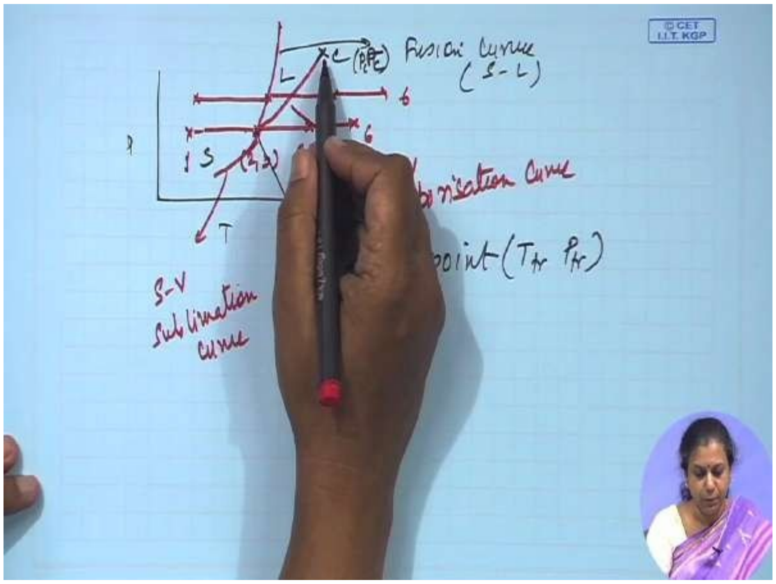

Where I would also like to mention one more thing which will be evident from this particular graph we find out that more or less the slopes of sublimation Curves and vaporization curves are always positive, the slope for sublimation curve is steeper as compared to the vaporization curve and usually the slope of the fusion curve is also positive, it is negative only for certain substances.

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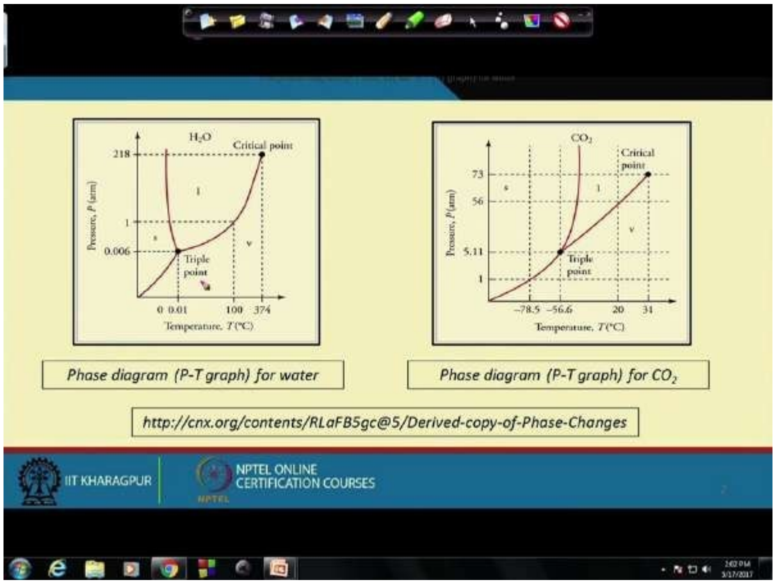

Phase diagram (P-T graph) for water

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

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

For example the most common substance that we come across which is water, now why all these things happen? You just you need to remember that water contracts on freezing but exactly why it happens and all the characteristics of the PT curves that we'll be dealing after a few more class where we will be dealing with equations like Clausius Clapeyron equation, Clapeyron equation all of these are going to tell you going to predict the slopes of this Pt curve and also the reasons for number of things that we observe in this particular case.

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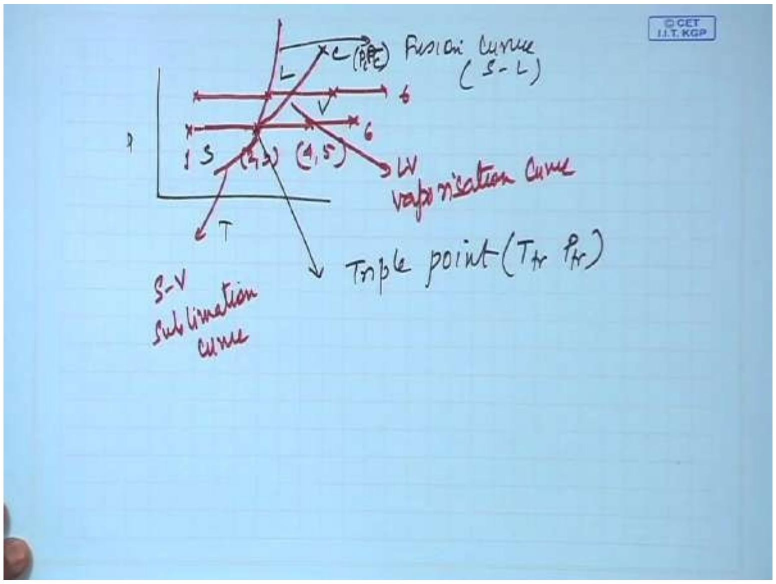

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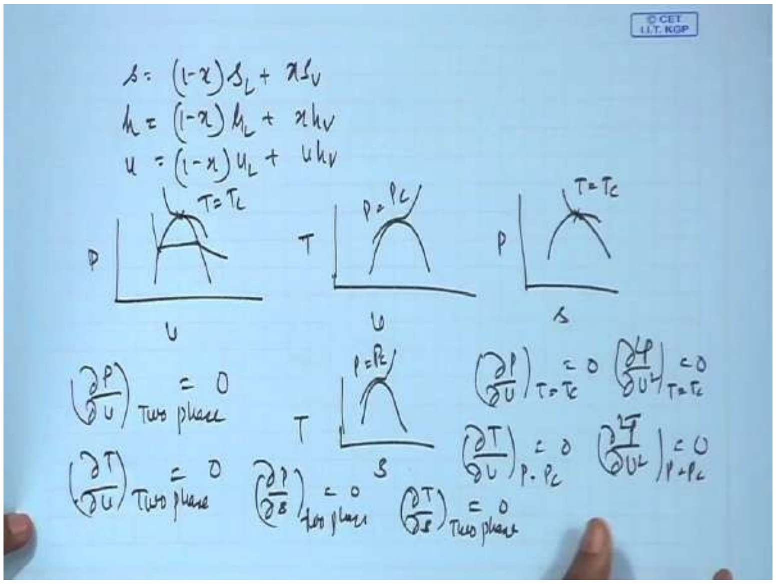

$s = (1-x)s_L + x s_V$

$h = (1-x)h_L + x h_V$

$u = (1-x)u_L + u h_V$

$\left(\frac{\partial P}{\partial v}\right)_{\text{Two phase}} = 0$

$\left(\frac{\partial T}{\partial v}\right)_{\text{Two phase}} = 0$

$\left(\frac{\partial P}{\partial s}\right)_{\text{Two phase}} = 0$

$\left(\frac{\partial T}{\partial s}\right)_{\text{Two phase}} = 0$

$\left(\frac{\partial P}{\partial v}\right)_{T=T_c} = 0$ $\left(\frac{\partial^2 P}{\partial v^2}\right)_{T=T_c} < 0$

$\left(\frac{\partial T}{\partial v}\right)_{P=P_c} = 0$ $\left(\frac{\partial^2 T}{\partial v^2}\right)_{P=P_c} < 0$

Now by this time you must have realized that this particular point the critical point here and the critical points which I have shown here these critical points they are constant characterizing the substance just like triple point's, right? So therefore for every substance if you want some very reliable property then definitely you would like to locate the triple point. Now as it is quite evident that it is easier to measure pressure temperature as compared to volume, so mostly what we do? We measure the critical pressure temperature and then try to predict the critical molar volume from these things, right?

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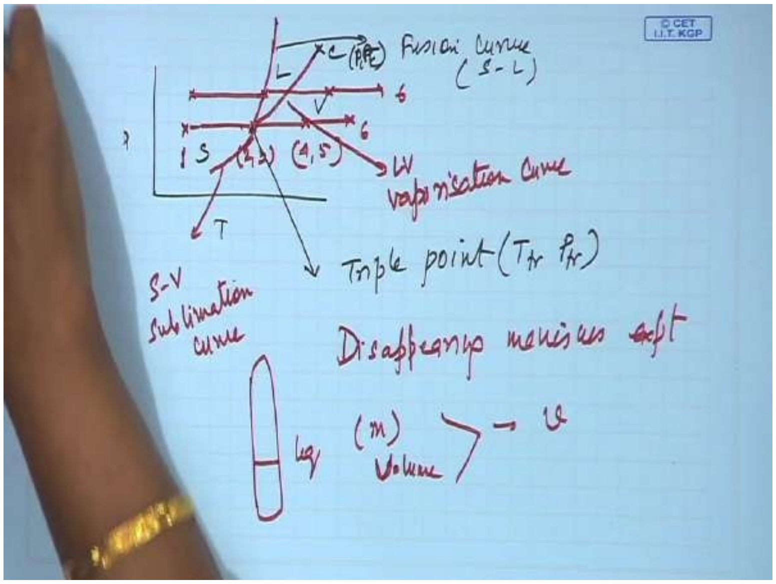

So therefore in order to determine this there is a very popular experiment which I will be mentioning in very brief which is known as the disappearing meniscus experiment, in this experiment it is a very common experiment which are performed in the chemistry laboratory. Usually this is performed with SF6 since its critical point is near about 45.5 degrees centigrade or something. So therefore it is easy to perform the experiment, what do you have? You have a closed sealed tube.

Now when you have a closed sealed tube what does it mean? And then here you introduce some portion of the liquid that you want whose critical point you want to measure. Usually the experiment as I have said their performed with SF6, right? Now what happens? In this particular system more or less you have introduced some amount of liquid, so therefore the mass remains constant and then since it is sealed from all ends so it's its total volume also remains constant, right?

So therefore what does it imply? It implies that the molar volume of the liquid that also remains constant, fine. Now under this condition if you start heating the tube, what you expect is going to happen? Quite naturally they are suddenly of which we would like to say that the moment you start heating the tube the liquid starts vaporizing and more and more vapor will be formed and then at one point the entire tube will be filled with the vapor.

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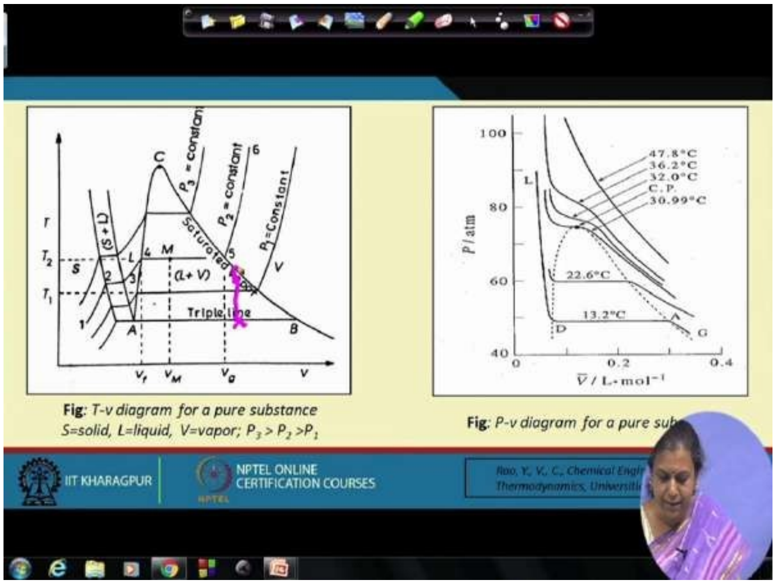

Fig: *T-v diagram for a pure substance*
S=solid, L=liquid, V=vapor; $P_3 > P_2 > P_1$

Fig: *P-v diagram for a pure sub*

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Now this will not always happen it will depend upon the molar volume with which we have started for example if I refer to the previous figure it is going to be evident to you. Suppose I refer to the previous figure when in this particular case it appears to you, yeah. If you just observe this figure it all depends from where you have started the experiments.

Suppose your molar volume was somewhere here. Suppose your molar volume was say somewhere here from here you start heating it, what do you what are you basically doing? You have kept the molar volume constant and you are increasing its temperature, fine. So therefore you keep on heating keep on heating what happens? You find that that you are shifting actually towards higher quality lines.

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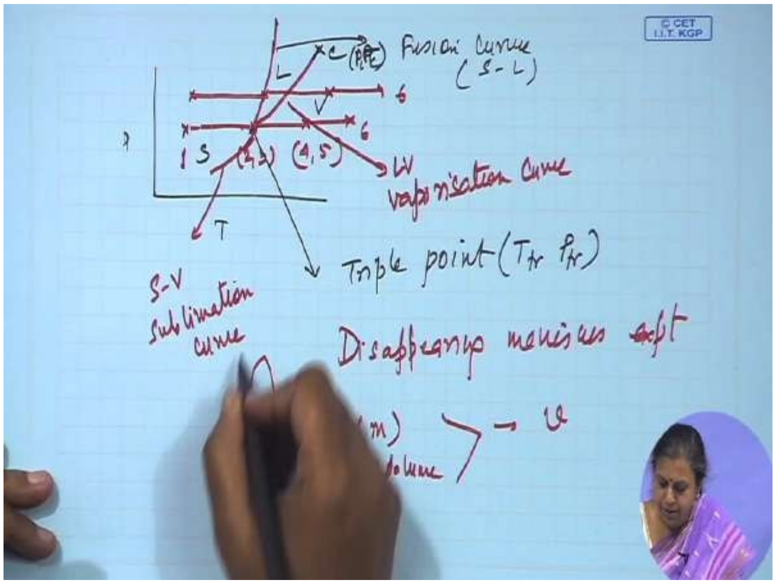

If you draw quality lines here, you are shifting towards higher quality lines till you reach the quality line x equals to one which is nothing but the saturated vapor curve and when you have reached this curve you find that your meniscus it keeps on decreasing till at one point it disappears and the whole thing is filled up with the vapor phase at you have entered your superheated vapor region, fine.

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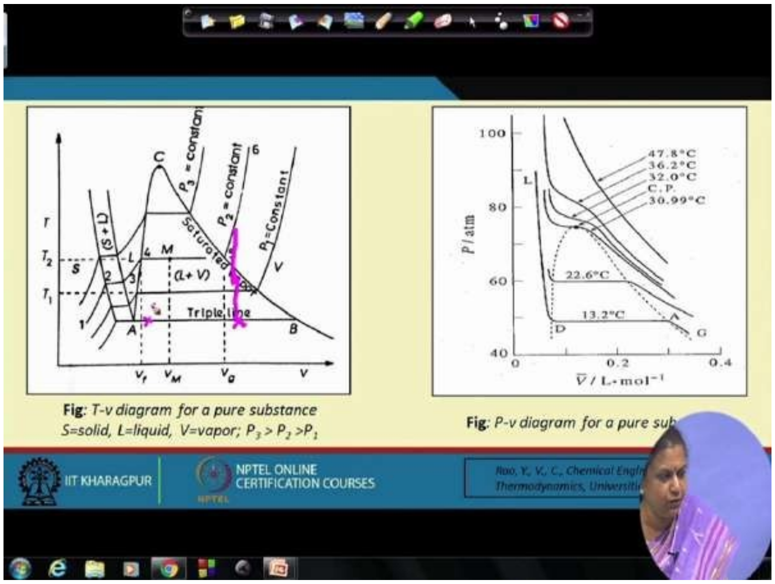

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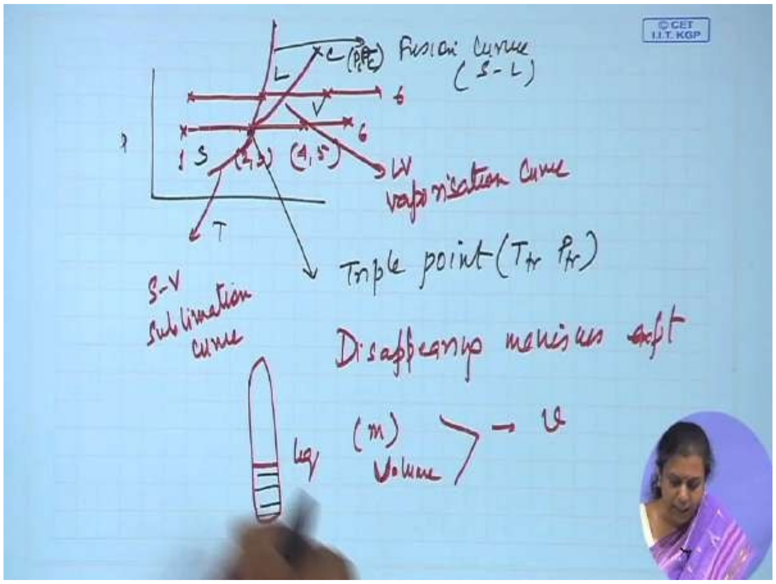

Suppose you are starting with a very low molar volume, yeah with a very low molar volume you have started. For example, say for instance you have started from somewhere here, right? Now you keep on heating it, what are you doing basically?

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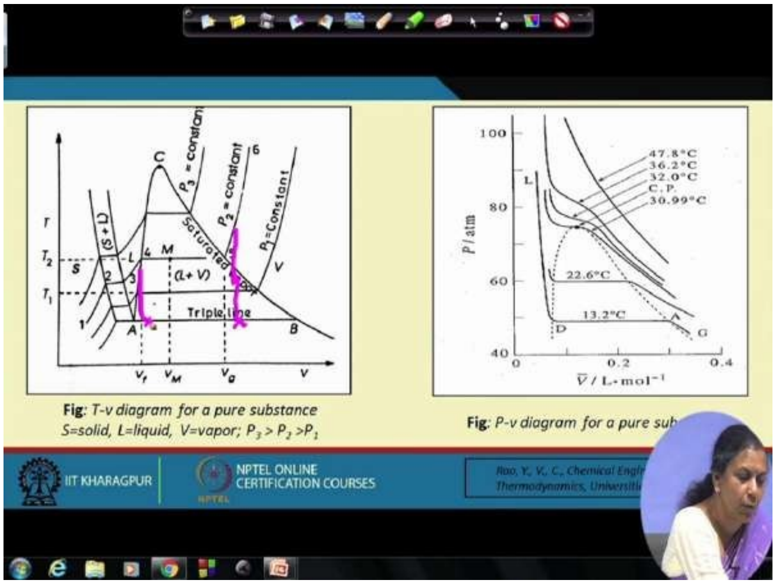

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Fig: P-v diagram for a pure sub

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Just notice you are following a vertical line, what are you doing here? You are going from a higher quality line to a lower quality line and then you keep on shifting quality lines till you reach x equals to 0 the saturated liquid curve and then if you continue the heating you have actually entered into the sub cool liquid region.

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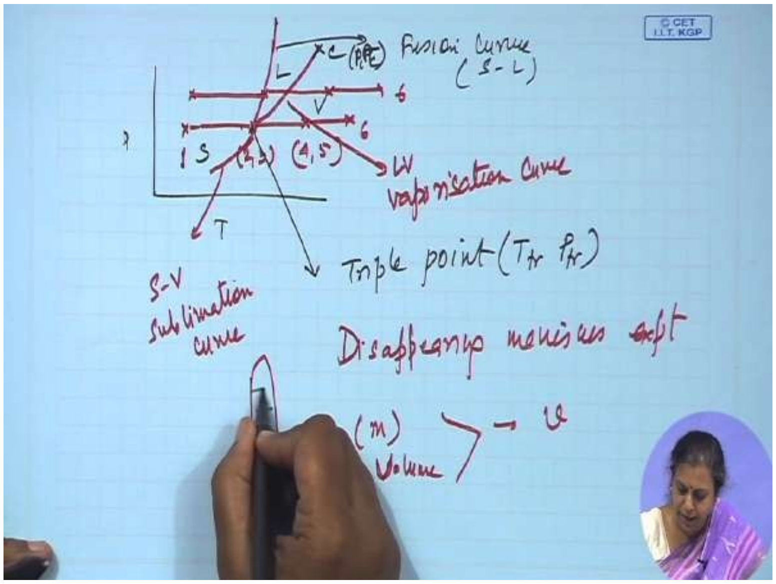

So in this particular case what happens? You find that your liquid meniscus it keeps on going up and the, this continues till finally the whole thing becomes filled up with the liquid. Now suppose you start the experiments with some particular volume of the molar volume of the mixture such that the molar volume it corresponds to the critical point.

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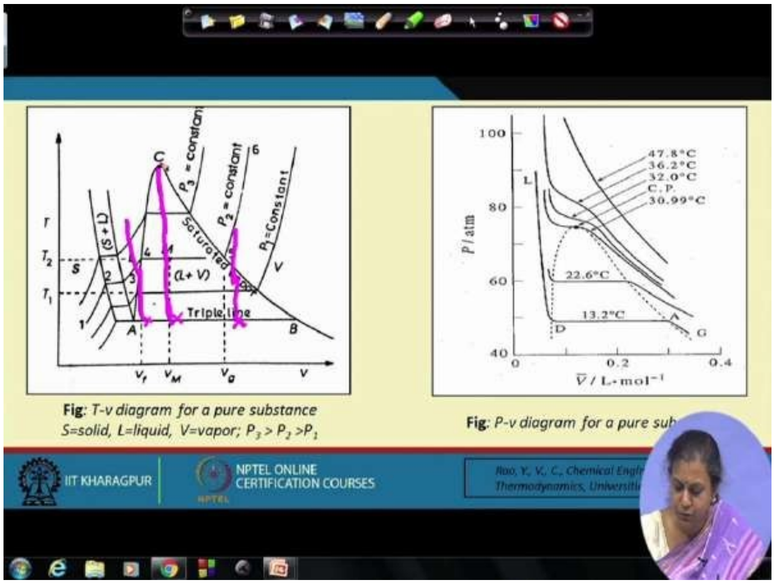

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S=solid, L=liquid, V=vapor; $P_3 > P_2 > P_1$

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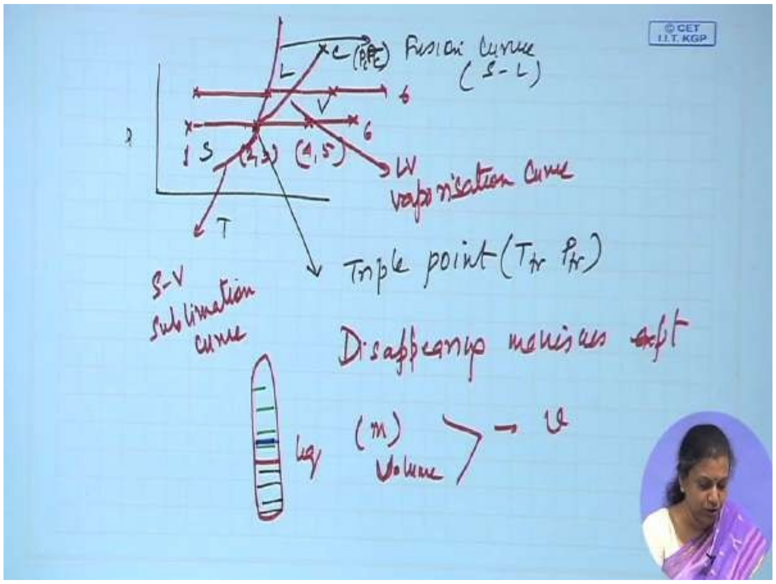

Now if you start heating it what will you expect? You are going vertical in the same way, please note that you are following a constant quality line in this particular case, you keep on following this constant quality line and continue the heating you will find that no matter how much you heat your line is going your meniscus will be remaining fixed at one your particular location it neither rises nor it falls, it simply remains constant at this particular portion and this thing it continues till you are reaching the critical point the moment you have reached the critical point the meniscus suddenly disappears.

And you know that this is the condition of, this is the critical condition at that particular condition if you measure the temperature and the pressure you are able to locate Tc and Pc, you can keep on performing the experiments you will find that the meniscus disappears comes back means you are just operating at this particular point, you just increase the heat again decrease the heat just decrease the heat again increase the heat. If you keep on continuing this you will find that the meniscus keeps on coming and going but it remains at one particular location and this corresponds to your Tc and Pc. So by this a very easy way of finding out the critical temperature and once you have found out the critical temperature then from the critical temperature it is much easier to find out the critical volume.

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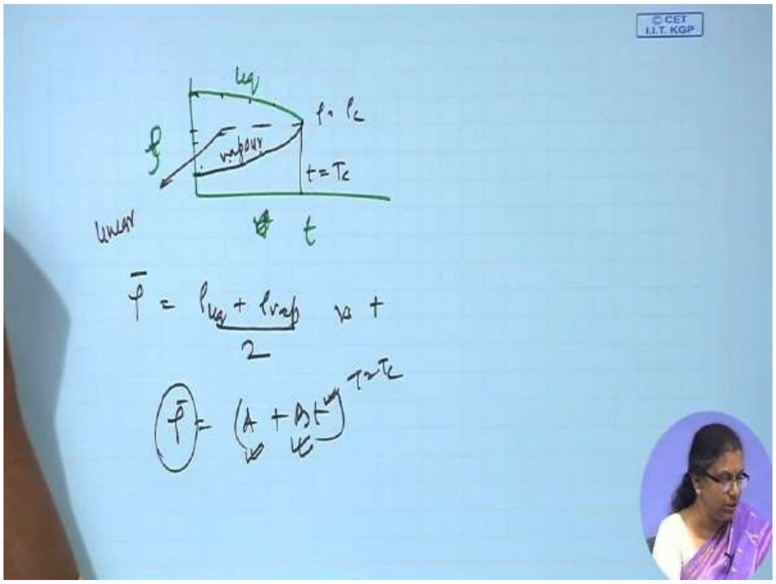

Just I will show you what exactly happens, suppose this is the critical temperature and suppose this is rho or in other words we can also plot the critical the volume also in this particular case. Exactly what are we, are we doing here? So therefore or in this plot rho versus T that is going to be easier. So what do we do? Suppose for the liquid we are plotting the orthobaric density which means the densities along the liquid vapor coexistence curve, what do we find? As we keep on heating the liquid density keeps on decreasing, right? The liquid density, this is rho liquid it keeps on decreasing because good the liquid expands and it also vaporizes at the same time.

What happens to the vapor? Much amount of vapor is being added and also we find that the vapor it expands, so we find that the liquid density keeps on decreasing the vapor density keeps on increasing till at T equals to Tc both the densities they become identical, right? So therefore here also we find that that if you would be plotting the rho bar which is nothing but rho liquid plus rho vapor by 2.

If you are plotting this versus temperature then we find usually this is the slope of this particular curve and this particular curve it is usually linear in nature and the slope it can be obtained as rho bar equals to A plus Bt, right? So from here you can find out A and you can find out B and then you can find out rho bar at T equals to Tc, so this is a standard way of finding out T equals to Tc or the critical conditions for pure component substances.

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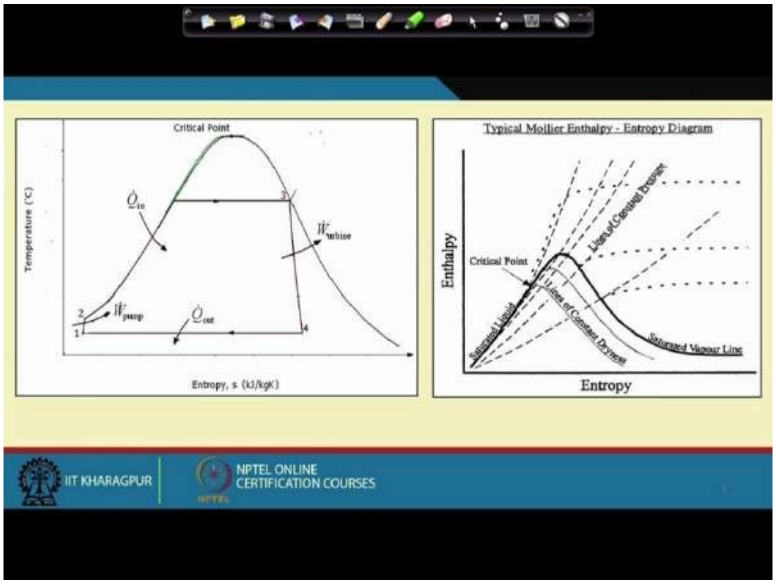

So apart from this I would like to say these are the basic phase diagrams but the phase diagrams which we use mostly for our purposes as you already know that those phase diagrams are primarily apart from these phase diagrams they are primarily the temperature entropy and more common is the enthalpy entropy diagram which is commonly known as the mollier chart.

The importance of mollier chart is the first thing is, it can be plotted on an elongated scale and here if you observe you find that we have the isobaric lines and we have the these are the isobaric lines we have the, these are the isothermal lines and we have lines of the constant quality lines.

So therefore this particular curve it is complete in all respects and if we know the pressure and temperature of the different points and then we are in a position to go to find out its enthalpy to find out its entropy and if suppose the conditions are such that it lies within this 2 phase dome then in that case we can also find out the dryness fraction or the quality of the mixture.

So therefore usually we find that the mollier diagrams are the diagrams which we use most frequently in order to find out the properties measurable as well as non-measurable of pure component substances in the liquid phase mostly in the liquid phase, vapor phase as well as in the liquid vapor region.

Now this was all about the graphical representations of PvT behaviors apart from this naturally as I have already mentioned we need to have some equations when I tell you about the equations the first equation which comes to your mind naturally for the gas phase is nothing but the ideal gas equation this is the first thing which comes to your mind, isn't it?

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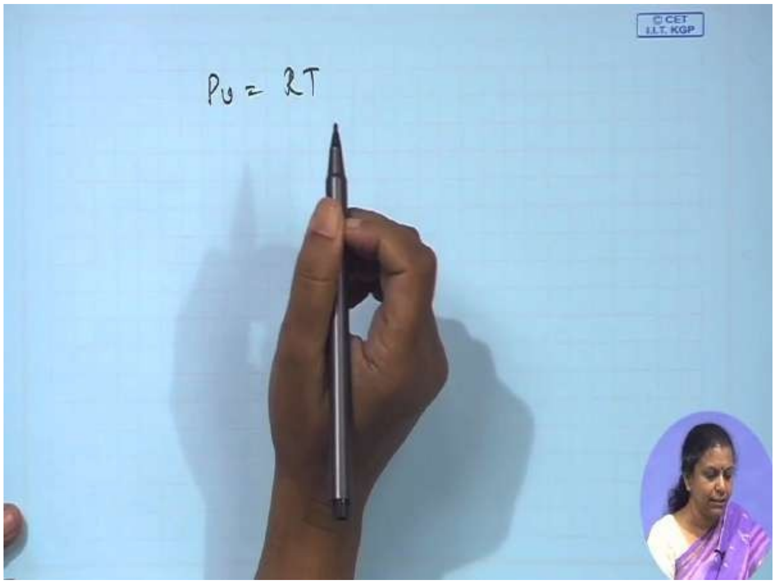

$Pv = RT$

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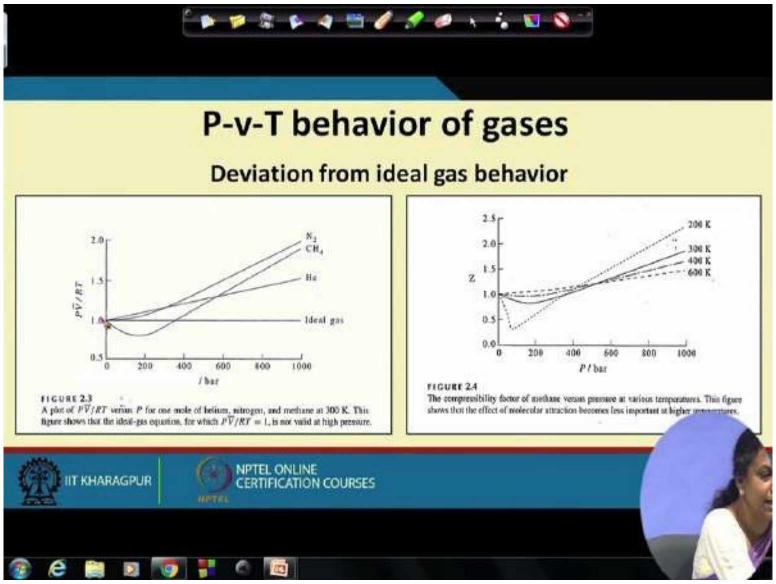

P-v-T behavior of gases

Deviation from ideal gas behavior

FIGURE 2.3
A plot of $P\overline{V}/RT$ versus P for one mole of helium, nitrogen, and methane at 300 K. This figure shows that the ideal-gas equation, for which $P\overline{V}/RT = 1$, is not valid at high pressure.

FIGURE 2.4
The compressibility factor of methane versus pressure at various temperatures. This figure shows that the effect of molecular attraction becomes less important at higher temperatures.

And we know as we all know that the ideal gas equation which is so very known to you for one mole it is Pv equals to RT we find that this is applicable only for this you all of you know this is applicable for very low not even low very low pressure and high-temperature and therefore this particular quantity z which is known as the compressibility factor which is nothing but Pv by RT this is equal to 1 for ideal gases and this is not equal to one for real gases, this you already know and I have just depicted this in the figures here where we show that that z is not equal to one for any particular real gas and as the temperature keeps on decreasing the deviation from ideality increases it is also a function of the measure of the gas.

So naturally since ideal gas equation does not suffice, what is the next thing? We would like to go for the different equations which would be predicting the PvT Behavior of the gases. Now what are the different equations that we have? The equations can broadly be classified in 2ways the first one is known as the PvT Behavior of the gases.

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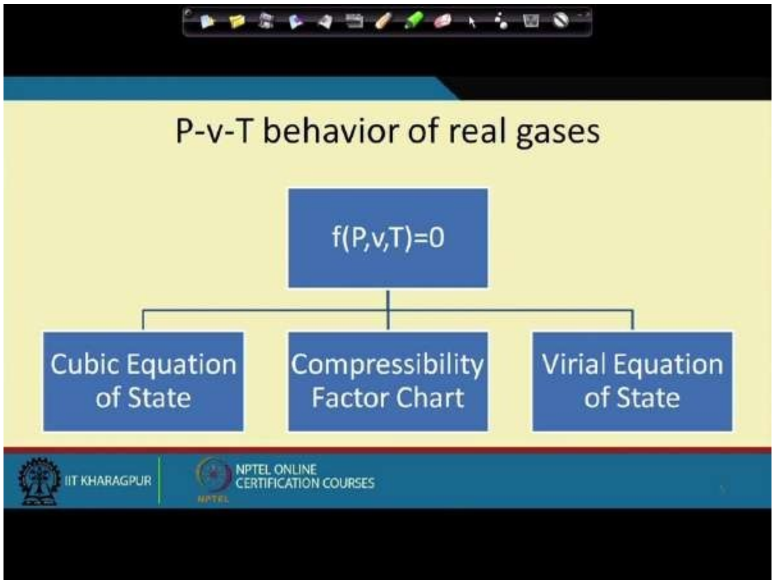

P-v-T behavior of real gases

f(P,v,T)=0

Cubic Equation of State

Compressibility Factor Chart

Virial Equation of State

So therefore they can be broadly classified in 2 ways, one is the cubic equation of state the immediate example of this, all of you are aware of is van der waals equation and the other one is the virial equation of state. When we are not sure whether the gas obeys any particular cubic equation or the virial equation we often refer to the compressibility factor chart which we will be discussing after we finish discussing these particular equations of states.

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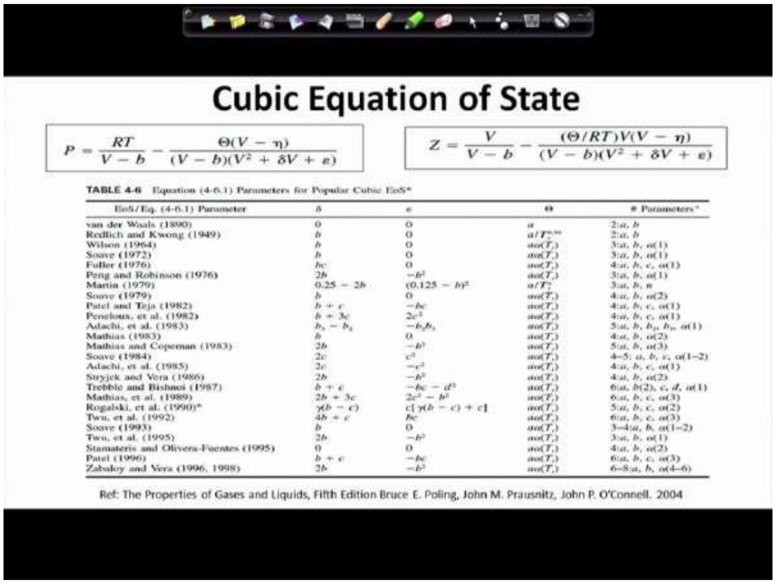

Cubic Equation of State

$$P = \frac{RT}{V-b} - \frac{\Theta(V-\eta)}{(V-b)(V^2+\delta V+\varepsilon)}$$

$$Z = \frac{V}{V-b} - \frac{(\Theta/RT)V(V-\eta)}{(V-b)(V^2+\delta V+\varepsilon)}$$

TABLE 4-6 Equation (4-6.1) Parameters for Popular Cubic EoS*

EoS/Eq. (4-6.1) Parameter	δ	ε	Θ	# Parameters*
van der Waals (1890)	0	0	a	2: a, b
Redlich and Kwong (1949)	b	0	$a/T_r^{1/2}$	2: a, b
Wilson (1964)	b	0	$a\alpha(T_r)$	3: a, b, $\alpha(1)$
Soave (1972)	b	0	$a\alpha(T_r)$	3: a, b, $\alpha(1)$
Fuller (1976)	bc	0	$a\alpha(T_r)$	4: a, b, c, $\alpha(1)$
Peng and Robinson (1976)	$2b$	$-b^2$	$a\alpha(T_r)$	3: a, b, $\alpha(1)$
Martin (1979)	$0.25-2b$	$(0.125-b)^2$	a/T_r^n	3: a, b, n
Soave (1979)	b	0	$a\alpha(T_r)$	4: a, b, $\alpha(2)$
Patel and Teja (1982)	$b+c$	$-bc$	$a\alpha(T_r)$	4: a, b, c, $\alpha(1)$
Peneloux, et al. (1982)	$b+3c$	$2c^2$	$a\alpha(T_r)$	4: a, b, c, $\alpha(1)$
Adachi, et al. (1983)	b_2-b_3	$-b_2b_3$	$a\alpha(T_r)$	5: a, b, b_2, b_3, $\alpha(1)$
Mathias (1983)	b	0	$a\alpha(T_r)$	4: a, b, $\alpha(2)$
Mathias and Copeman (1983)	$2b$	$-b^2$	$a\alpha(T_r)$	5: a, b, $\alpha(3)$
Soave (1984)	$2c$	c^2	$a\alpha(T_r)$	4–5: a, b, c, $\alpha(1-2)$
Adachi, et al. (1985)	$2c$	$-c^2$	$a\alpha(T_r)$	4: a, b, c, $\alpha(1)$
Stryjek and Vera (1986)	$2b$	$-b^2$	$a\alpha(T_r)$	4: a, b, $\alpha(2)$
Trebble and Bishnoi (1987)	$b+c$	$-bc-d^2$	$a\alpha(T_r)$	6: a, $b(2)$, c, d, $\alpha(1)$
Mathias, et al. (1989)	$2b+3c$	$2c^2-b^2$	$a\alpha(T_r)$	6: a, b, c, $\alpha(3)$
Rogalski, et al. (1990)*	$\gamma(b-c)$	$c[\gamma(b-c)+c]$	$a\alpha(T_r)$	5: a, b, c, $\alpha(2)$
Twu, et al. (1992)	$4b+c$	bc	$a\alpha(T_r)$	6: a, b, c, $\alpha(3)$
Soave (1993)	b	0	$a\alpha(T_r)$	3–4: a, b, $\alpha(1-2)$
Twu, et al. (1995)	$2b$	$-b^2$	$a\alpha(T_r)$	3: a, b, $\alpha(1)$
Stamateris and Olivera-Fuentes (1995)	0	0	$a\alpha(T_r)$	4: a, b, $\alpha(2)$
Patel (1996)	$b+c$	$-bc$	$a\alpha(T_r)$	6: a, b, c, $\alpha(3)$
Zabaloy and Vera (1996, 1998)	$2b$	$-b^2$	$a\alpha(T_r)$	6–8: a, b, $\alpha(4-6)$

Ref: The Properties of Gases and Liquids, Fifth Edition Bruce E. Poling, John M. Prausnitz, John P. O'Connell. 2004

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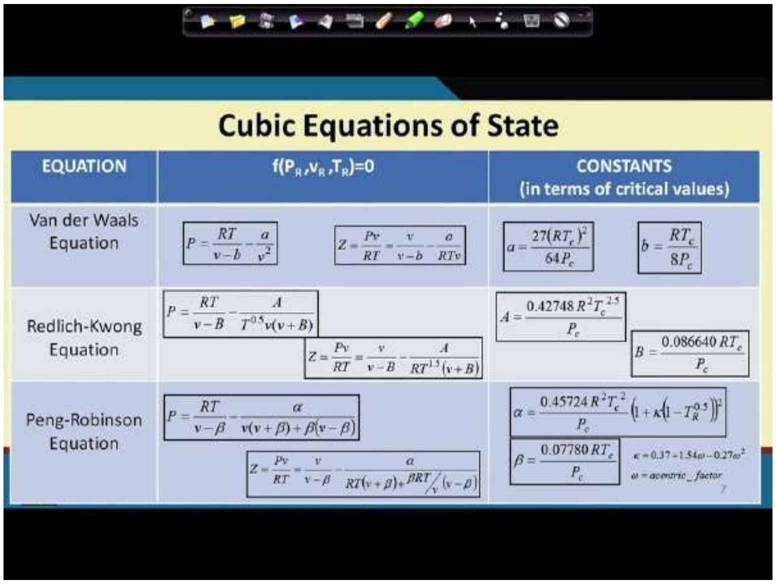

Cubic Equations of State

EQUATION	$f(P_R, v_R, T_R)=0$	CONSTANTS (in terms of critical values)
Van der Waals Equation	$P = \frac{RT}{v-b} - \frac{a}{v^2}$ $Z = \frac{Pv}{RT} = \frac{v}{v-b} - \frac{a}{RTv}$	$a = \frac{27(RT_c)^2}{64P_c}$ $b = \frac{RT_c}{8P_c}$
Redlich-Kwong Equation	$P = \frac{RT}{v-B} - \frac{A}{T^{0.5}v(v+B)}$ $Z = \frac{Pv}{RT} = \frac{v}{v-B} - \frac{A}{RT^{1.5}(v+B)}$	$A = \frac{0.42748\,R^2T_c^{2.5}}{P_c}$ $B = \frac{0.086640\,RT_c}{P_c}$
Peng-Robinson Equation	$P = \frac{RT}{v-\beta} - \frac{\alpha}{v(v+\beta)+\beta(v-\beta)}$ $Z = \frac{Pv}{RT} = \frac{v}{v-\beta} - \frac{\alpha}{RT(v+\beta)+\frac{\beta RT}{v}(v-\beta)}$	$\alpha = \frac{0.45724\,R^2T_c^{\ 2}}{P_c}\left(1+\kappa\left(1-T_R^{0.5}\right)\right)^2$ $\beta = \frac{0.07780\,RT_c}{P_c}$ $\kappa = 0.37 + 1.54\omega - 0.27\omega^2$ $\omega = acentric\_factor$

Now why is the cubic equations known as cubic equations or in other words to be more specific, what is the specialty of cubic equations? Now the general form of cubic equation don't get confused these are the whole lot of equations that have been proposed by different researchers the general forms being these but we are not going to deal with the host of these equations for your purpose be comfortable with primarily Van der waals equation which you already know and this equation is already known to you the functional form is already known to you and then there are 2 other equations which we will be using for conditions where the van der waals equations fails, right?

Now the functional form if you observe you will find for all of these what is the functional form? There are usually 2 constant equations where the constants are denoted by small a and small b for Van der waals, capital A capital B for Redlich Kwong and alpha and beta for Peng Robinson, we find that volume correction term is the same for all of them it's only with the intermolecular interaction which is represented by more and more complex equation in the different equation states.

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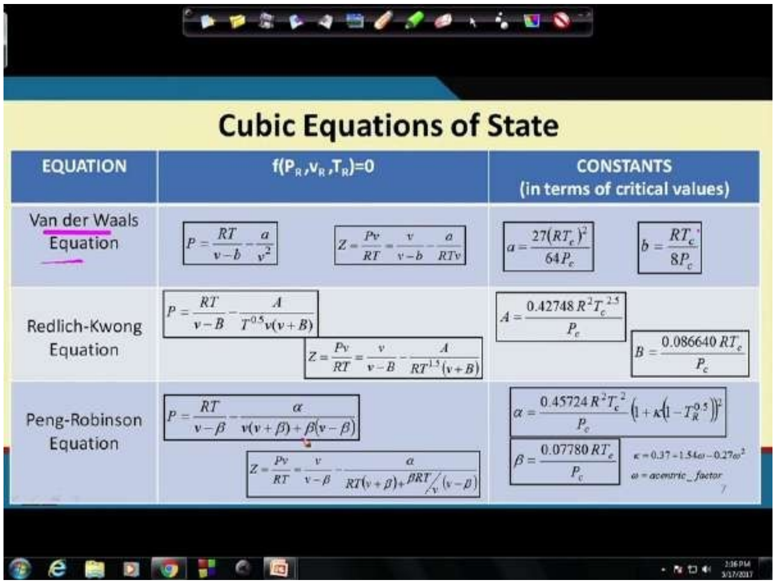

Cubic Equations of State

EQUATION	$f(P_R, v_R, T_R)=0$	CONSTANTS (in terms of critical values)
Van der Waals Equation	$P = \frac{RT}{v-b} - \frac{a}{v^2}$ $Z = \frac{Pv}{RT} = \frac{v}{v-b} - \frac{a}{RTv}$	$a = \frac{27(RT_c)^2}{64P_c}$ $b = \frac{RT_c}{8P_c}$
Redlich-Kwong Equation	$P = \frac{RT}{v-B} - \frac{A}{T^{0.5}v(v+B)}$ $Z = \frac{Pv}{RT} = \frac{v}{v-B} - \frac{A}{RT^{1.5}(v+B)}$	$A = \frac{0.42748\,R^2T_c^{2.5}}{P_c}$ $B = \frac{0.086640\,RT_c}{P_c}$
Peng-Robinson Equation	$P = \frac{RT}{v-\beta} - \frac{\alpha}{v(v+\beta)+\beta(v-\beta)}$ $Z = \frac{Pv}{RT} = \frac{v}{v-\beta} - \frac{\alpha}{RT(v+\beta)+\frac{\beta RT}{v}(v-\beta)}$	$\alpha = \frac{0.45724\,R^2T_c^2}{P_c}\left(1+\kappa\left(1-T_R^{0.5}\right)\right)^2$ $\beta = \frac{0.07780\,RT_c}{P_c}$ $\kappa = 0.37 + 1.54\omega - 0.27\omega^2$ $\omega = acentric\_factor$

Now let us see under what conditions each particular equation is applicable? This will be evident if we observe say the experimental pressure versus density data for ethane, okay. Here what do we observe? If we observe see this particular line it is the solid line it is the experimental curve which has been observed. Just note the Van der waals equation of state, we find that beyond 200 atmosphere it fails completely and under this particular circumstance we find more or less both the Redlick Kwong as well as the Peng Robinson equation of state both of them are applicable for this particular condition, okay.

And both of them are quantitative and if you observe closely you will find that the Redlich Kwong equation it appears to be slightly better as compared to the Peng Robison equation of state. Just to verify this I have given you one particular problem for calculating the molar volume of ethane this is also for ethane at 300 Kelvin 200atmoshperes, please do it with 3 particular equations of states and compare the answers that you get and compare the values with the experimental values from where you will be in a position to understand that Redlich Kwong equation is definitely better than Van der waals equation at higher pressures.

The other thing which I would want you to do is, there is also another thing let me explain before I go for this particular equation of state, now what is the specialty of cubic equations of state? The first specialty is, if you write it down in the form of the volume then what do you get? Then for all the equations you get a type where you find that it is cubic in volume. Now when this cubic in volume it should give you 3 roots?

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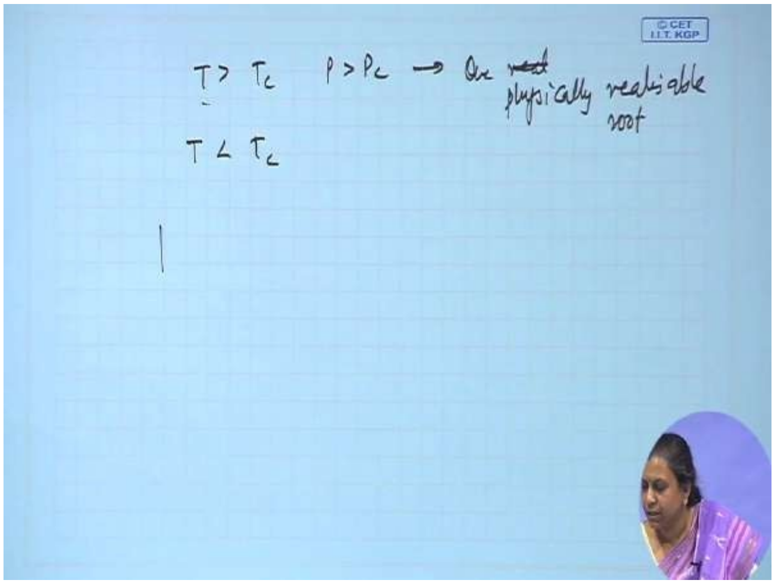

$T > T_c$ $P > P_c$ → One ~~root~~ physically realizable root

$T < T_c$

Now usually what do we find? We find that if you are working at conditions greater than T greater than Tc, P greater than Pc for this particular case you will find that there is just 1 physically realizable root I should write it down as 1 physically realizable root the other roots are complex just to give you a feel I have already given you 2 problems, do those 2 problems then you can take a few other problems you will find that when you are operating conditions much higher than the critical conditions than under those conditions you get one physically realizable root.

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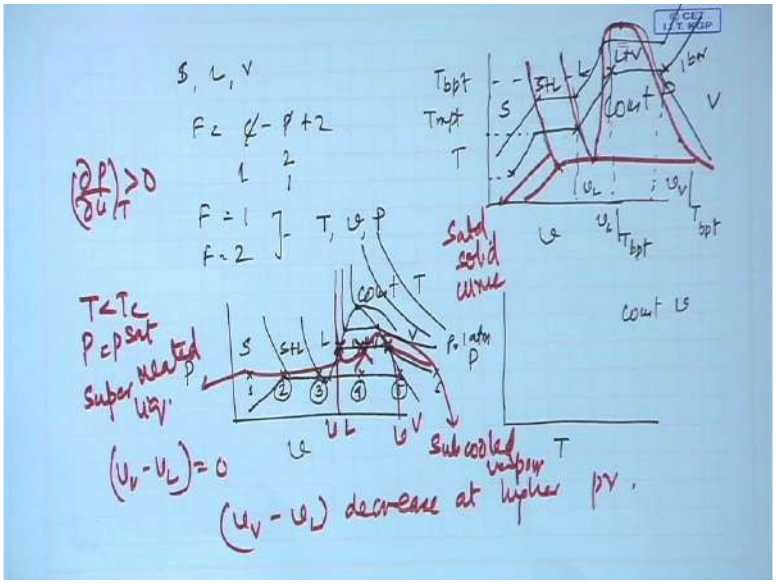

Now when you are working for conditions where T is less than Tc for that particular condition what do you get? That means what I mean to say you are working in this particular zone, in this particular zone here this particular zone here, you will find that under this condition you get 3 roots, right? One root the lower root it corresponds to the liquid volume the other root corresponds to the vapor volume and there will be an intermediate root which is the spurious root, why?

Because suppose you are trying to predict the behavior of the Pv behavior using any equation of state, it can be Van der waals, it can be Peng-Robinson it can be Redlich Kwong equation of state you will find none of the equation of states can predict this discontinuity in behavior, what they do? They predict a continuous curve, what is a continuous curve? Curve is something of this sort, this is what they predict, right?

Now we find that suppose for T less than Tc and P equals to the saturated pressure, which corresponds to this particular pressure under that condition if we work then we get one particular physically realizable root, what is a physically realizable root? It has to be positive, it has to be real and very important which it's not very evident it has to be greater than B, right?

The total volume of the gas has to be greater than the volume occupied than the molecules, fine. So therefore you will get 3 physically realizable roots if you are working within this liquid vapor dome, you will get one physically realizable root when you are working in this particular domain. So there and then we find that the isotherm or the isobar is predicted in this particular way where we find that the smaller volume it corresponds to the liquid volume this corresponds to vL, the large volume corresponds to Vv.

Now this particular region what does this correspond to? This particular region it correspond to sub cooled vapor which is a meta-stable state. What does this particular region correspond to? This corresponds to a super heated liquid which is again a meta-stable state, right? So therefore this region and if you find this region these 2 regions they are meta-stable states they can be obtained under very special conditions and if you observe this particular portion you find that for this particular portion del P del v at constant T is greater than 0 the slope is positive which cannot happen.

So naturally this particular region it is a spurious region, this region cannot exist as a result of which the intermediate root which you get has got no meaning. So therefore from here what do we conclude? We conclude 2 things the strength of cubic equations of state is that they can not only predict the volume or the behavior in the vapor phase they can also do so for the condensed phase and more importantly for the liquid vapor coexistence region.

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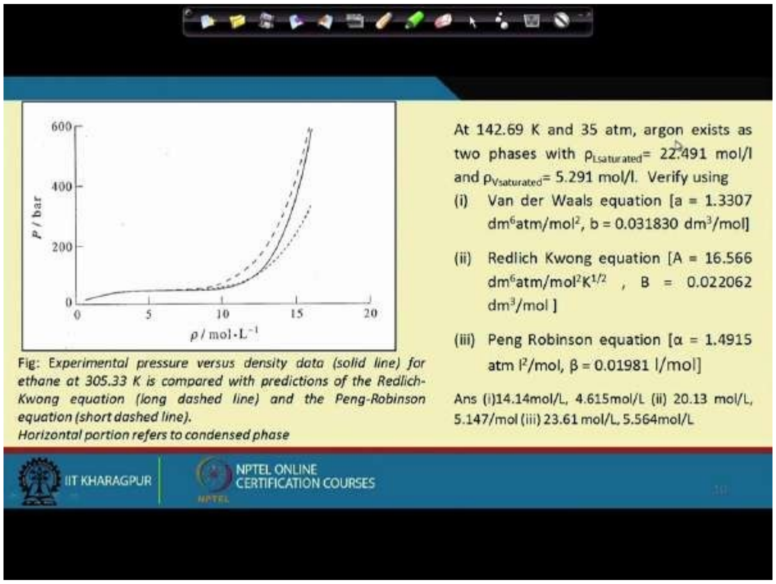

Fig: Experimental pressure versus density data (solid line) for ethane at 305.33 K is compared with predictions of the Redlich-Kwong equation (long dashed line) and the Peng-Robinson equation (short dashed line).
Horizontal portion refers to condensed phase

At 142.69 K and 35 atm, argon exists as two phases with $\rho_{Lsaturated}$= 22.491 mol/l and $\rho_{Vsaturated}$= 5.291 mol/l. Verify using

(i) Van der Waals equation [a = 1.3307 $dm^6 atm/mol^2$, b = 0.031830 dm^3/mol]

(ii) Redlich Kwong equation [A = 16.566 $dm^6 atm/mol^2 K^{1/2}$, B = 0.022062 dm^3/mol]

(iii) Peng Robinson equation [α = 1.4915 atm l^2/mol, β = 0.01981 l/mol]

Ans (i)14.14mol/L, 4.615mol/L (ii) 20.13 mol/L, 5.147/mol (iii) 23.61 mol/L, 5.564mol/L

So therefore we can predict the molar volumes for liquid state, vapor state and the liquid-vapor coexistence curve and just to show you 1 particular example I have given you one particular problem here, no not this problem sorry, this particular problem where I have the liquid argon and argon is exist in the 2 phases under this particular condition and the experimental density molar density of liquid argon and vapor argon are provided here. I would like you to verify this using the Van der waals, Redlich Kwong and the Peng-Robinson equation of state, remember for all of this you are going to get 3 roots for the volume.

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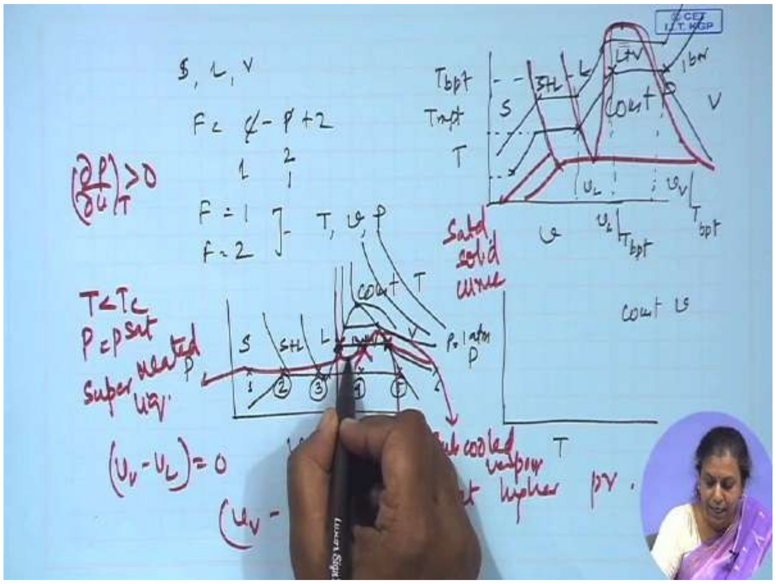

And the 3 roots as I have mentioned they correspond to 3 points joining the horizontal line such that the area under and the area above the horizontal line are equal. So from each of this you will get 3roots out of which the higher root will correspond to the vapor volume, the lower root will correspond to the liquid volume.

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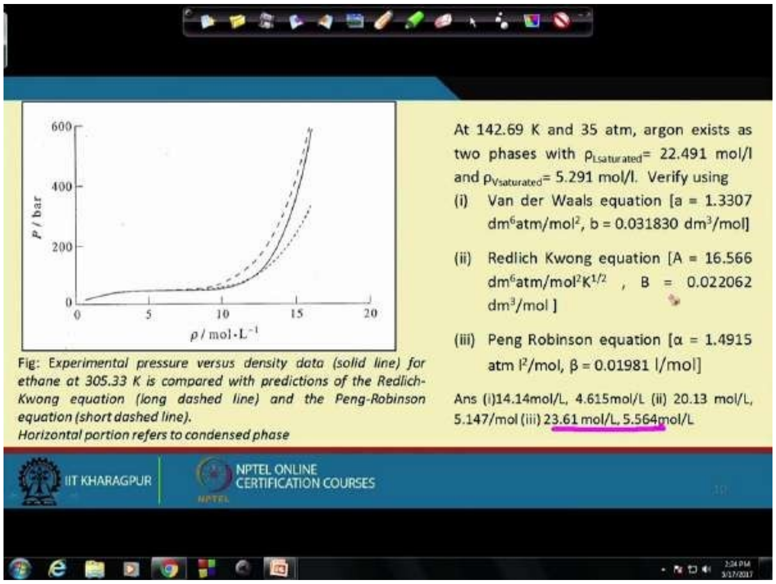

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Ans (i)14.14mol/L, 4.615mol/L (ii) 20.13 mol/L, 5.147/mol (iii) 23.61 mol/L, 5.564mol/L

And we find if you compare in this particular case is you are supposed to work out this problem, if you compare you find that the answer for the Peng-Robinson equation of state is this, sorry. The answer for the Peng-Robinson equation of state if you compare the different equation of states then what do you get? You get that the Peng-Robinson, yeah. You get that for the Peng-robinson equation of states whatever you have got these particular values they are closest to the experimental values.

Redlich Kwong equation of state they are slightly further off and Van der waals equation of state completely fails this is what I have tried to show in this particular curve. Van der waals equation could not be plotted because it was out of the range, if you observe here this is the Redlich Kwong curve, this is the vapor liquid coexistence portion the Redlich Kwong curve, this is the Peng-Robinson curve it shows that the Peng Robinson it's slightly better than the Redlich Kwong equation in the liquid vapor region.

So therefore among the different equations that I have suggested for the different equations what do we find? We find usually that the Peng-Robinson equation of state it is better for the liquid vapor coexistence curve, the Redlich Kwong equation of state is better for higher pressure conditions you are requested to workout examples and see it for yourselves.

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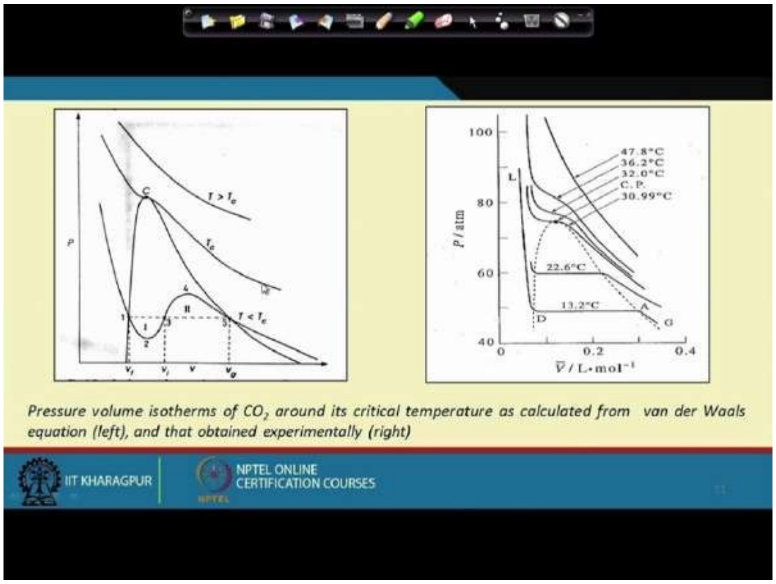

Pressure volume isotherms of CO_2 around its critical temperature as calculated from van der Waals equation (left), and that obtained experimentally (right)

And the strength of cubic equation of state is that it can predict the saturated volumes along with the vapor volumes. The weaknesses is that it fails to predict the condition in the liquid vapor dome the situation I have shown here and I have also compared it with the experimental situation, right? Here you get 3 physically realizable roots out of these 2 are meaningful and in this particular case you get just 1 physically realizable roots.

Now the other things which I would like to mention about the cubic equation of state is as you have already observed in the cubic equations of states what do we see? All of them comprise of some constants, right? Now these constants are completely empirical constants. Now each particular gas is going to have the different constants, it is very difficult to rather to find out or to or to accumulate or rather to collect the different constants for the different gases, fine.

So what people usually try to do is they try to express the constant of the cubic equations, say for instance for Van der waals it is a, b, for Redlich Kwong capital A capital B these things are their they people try to express them in terms of the critical constant, why?

Critical constant are much easily measurable as we have said they are much important much more constant as compared to other particular physical properties of pure substances, so in the next class or rather I will just be discussing very briefly this is left as an exercise for you in order to express the empirical constant in terms of the critical constants and then once we do it, we find that from the cubic equations of state we arrive to a very interesting equation of state which is known as a generalized equation which leads us to some more interesting results, thank you very much.