# **Thermodynamics of Fluid Phase Equilibria Dr. Jayant K. Singh Department of Chemical Engineering Indian Institute of Technology, Kanpur**

## **Lecture - 05 Review of the properties-part 2**

Welcome back, in this lecture we will continue the review of the properties continue from the previous lecture on the properties. So, we will start with the ideal gas equation of state, now the ideally from the perspective of thermodynamics we would prefer to have analytical equation of state, where it represent the state in terms of various different thermal properties such as PVT and one of the classical example is basically ideal gas equation of state.

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So, let me just first formally define what is any equation of state? An equation that relates the pressure temperature and specific volume, so this essentially will be your equation of state. So, equation of state is nothing, but some function which relates P V T and the simplest and the best known equation of state is ideal gas equation of state, in principle at low pressure and high temperature all gases approach ideal gas behavior.

So, typically a gas will behave like idle we call this conditions the gas it does not have any effective interaction between themselves and essentially there is no energy; that means, it can have a kinetic energy, but it cannot it does not have any potential energy ok.

So, such a of course, gross approximation for gases does wonderfully work in certain range selective regions and something which we will be talking about it. So, what is the equation of state for ideal gas is nothing, but PV is equal to NRT, where n is of code number of moles R is a gas constant and temperately is the temperature now of course, we cannot represent properties of many different.

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**OTHER EQUATIONS** van der Waals OF STATE Rerthelet Redlich-Kwang Beattie-Bridgeman Several equations have been proposed to Benedict-Webb-Rubin represent the P-v-Tbehavior of substances Strobridge accurately over a larger region with no Virial limitations **Van der Waals Equation of**  $\partial P$ **State**  $= 0$ ău Critical isotherm of a pure  $\partial^2 P$  $R<sub>1</sub>$ substance has an  $= 0$  $\partial v^2$ inflection point at  $RT_{\rm cr}$ the critical state  $a =$  $8P_c$  $64P$ This model includes two effects not considered in the ideal-gas model: the intermolecular attraction forces and the volume occupied by the molecules themselves. The accuracy of the van der Waals equation of state is often inadequate

Substances by simply ideal gas equation of state and thus for real fluids there are many equations states which has been developed one of the classical 1 due to wonder wall.

So, wonder Waal equation of state in early nineteen thirties the famed equation included the terms related to attractive forces between the molecules and effectively the volume of the molecules. So, this due to the attractions it was this volume and thus if you consider natural gas this is going to be 0 a is equal to 0 b is equal to 0 and you're going to get the same equation as an idle gas equation of state.

Now, in order to obtain the parameters a b for different fluids 1 can consider PV plot, and we know that at critical point there is inflection point or critical point is represented by the inflection point. Thus the criticality or the critical temperature and pressure can be used to evaluate the properties or valid this constant a and b.

So, using these 2 equation for the critical isotherms, we can obtain the values a and b and those you can use equation of state for many different substances, if you know the critical point of the substances you can directly get a l b for a specific fluid or gas, and this you can find out the equation of state control equation state for a specific gas.

Now, of course, including only this attractive force and this size is not good enough and that is the accuracy of the wonder Waal equation the state is often inadequate, and this is the reason that many different equations of state have been developed and this the listed are just like Burt Leigh, Rutledge Kwan and so forth.

Peng-robinson equation of state also and, so I will not describe in all our details something which we can use it and some aspect we will be using in the later part, but there are many different equations of stated some are popular and some are very specific (Refer Time: 04:22) is an equation of state is a motion one of the most popular equation of state for chemical systems.

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Example The gage pressure of an automobile tire is measured to be 210 kPa before a trip and 220 kPa after the trip at a location where the atmospheric pressure is 95 kPa. Assuming the volume of the tire remains constant and the air temperature before the trip is 25°C, determine air temperature in the tire after the trip. s an ideal gas<br>  $P_k = (210 + 95)PP^2$ <br>  $P_{k-1} = (225 + 15)P^2$ <br>  $T_{k-1} = (25 + 273)P^2$ <br> Consider air is an ideal gas

Particularly using idle gas, so this is an example where the gauge pressure of an automobile tire is measured to be 200 and 10 kilo Pascal before a trip, and 220 kilo Pascal after the trip at a location, where the atmosphere pressure is 95 kilo Pascal so; that means, the total pressure P 1 is equal to 210 plus 95 kilo Pascal, and P 2 is 220 plus 95 kilo Pascal and what is being said that assumed the volume of the tire remains constant and the air temperature before the trip is 25 ok.

So, it is a 25 plus 273.15 Kelvin, now what we need to find out is T 2, now this temperature 25 degree Celsius is way above the critical point, and it can be considered an ideal gas. So, considering a as an ideal gas we can simply use P 1 V 1 is equal to and T 1 P 2 V 2 is equal to N R T 2 and thus since the volume is constant P 1 by P 2 is equal to T 1 by T 2 and you can find T 2 from this simple relation.

You can plug these values in order to get the T 2. So, of course, ideal gas equation makes life easier in terms of its application, but it works out to be quite well even if you use equation of state very, very complex a to create constant equations 9, constraint equation 5, constant equations the value may not change for this particular example.

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Ok, but maybe it may change if the conditions are watch well below temperature settings, where it can be let us say saturated system and so forth. So, as I said our intention is to have some kind of equation of state, but many times we fail and for complex molecules is extremely difficult to have form a formulation with a function or the equation which relates  $P \vee T$  for all conditions, and thus property table is more popular for very commonly used fluid such as water refrigerant ok.

So, therefore, the properties are frequently presented in the form of tables now there are some properties which can be measured each easily, but others such as entropy and so forth. You need to use a some kind of relation from the measurable quantities in order to evaluate such a function. So, you know usually what we do is we measure and calculate all these properties, some are easily measurable, some are dependent on the measurable quantity and present in the table which in the convenient form, one of the properties enthalpy which is often encountered in control volume cases.



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So, typical table will look like this this is a ka table of saturated water, where we say is a pressure table the reason for that is that the first column is a pressure corresponding table is saturation temperature of this because the saturation water. So, saturation temperature and then you have saturated liquid vapour saturated liquid internal energy such a vapor into energy and the difference of that. So, U g minus U f is U f g and similarly that for enthalpy ok.

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So, to give you an example here, you have a case where the tank contains a saturated liquid at 90 degree Celsius. So, essentially on the T v diagram you since, T 90 degree Celsius is less than critical point and its saturated. So, it will be somewhere below here, but what would be the corresponding pressure for T 90.

So, we will look at specifically saturated water temperature table where the temperature is the first in the column. So, corresponding pressure will be your saturated pressure. So, here is a temperature and the corresponding pressure is 90 70.183 and this is where the system is because its saturated liquid it is not saturated vapor liquid otherwise it will have it would have been somewhere in between, and it is not certainly the saturated vapor otherwise it should have been here ok.

So, as I said for a given pressure and volume table or temperature column table these 2 points at the end one corresponds to saturated liquid, 1 correspond to saturated vapor for the case of or let us say 100 kilopascal, you have a saturated liquid here and saturated vapor of course, will have a different volume which will be substantially larger then the 1 contains by such was a liquid. So, for a case of 100 Pascal you are looking at a pressure table.

So, the 500 Pascal this will be your saturated Vf. So, V f is this and saturated Vg saturated vapor get a volume is going to be vg which will be 1.6941 meter cube per kg.

So, this is how we try to make use of the table in order to evaluate the volumes and other properties similarly, you can also find the corresponding Uf here, Ug here, Hf here, Hg here from the same table ok.



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So, what about when the system is at 2 phase mixture; that means, the vapor and liquid both so; that means, within the saturated regions. So, we in order to define such a case we need to find out the quality of it. So, quality is basically the relative amount of liquid and vapor and the way it is represented is the mass ratio of the mass of the vapor in the system; that means the ratio of the mass of the vapor and total mass ok. So, the total mass will be your m liquid plus vapor mf plus mg m x is equal to m vapor ok.

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So, you one can show clearly that having this definition, where m total is equal to m fluid plus m gas and x is m gas by m total, one can show that the average volume of the system is nothing, but Vf plus x multiplied by VG minus Vf, and similarly for internal energy similarly for enthalpy.

So, where s x in terms of the volume is going to be the Vg minus Vf divided by V fg. Now from the point of view of a plot if you look at P or T versus V you can use the diagram to find out x also for example, if b is at which our system is then we can use the length from a to b and a to see in order to get x here. So, this is directly from this expression ok.

Now, our in general you can write any property y average as Y f which means the property y of the fluid plus x multiplied by Y f g or the difference between the property Y in the gas phase a saturated gas phase and minus saturated liquid phase. So, in general Y average is going to be in between Y f and Yj and I could be Vu h. So, that is what we say here.

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So let me just make use of this understanding to do a simple example, widget tank contains 10 kg of water at 90 degree Celsius. If 8 kg of water is in the liquid form and the rest is in the vapor form, determine the pressure in the tank and the volume of the time. So, what we have is information is that it is at 90 degree Celsius and the total mass is given as 10 kg 8 kg is in the liquid form so; that means, the mass of the vapor is 2 kg. So, x is 2 kg by 10 kg this is going to be point 2 ok.

Now, we have been given ninety degree and certainly it is a saturated system. So, we are going to look at saturated water temperature table, which gives you the temperature and the corresponding pressure is this soapy set of the tank at 90 degrees Celsius is 70.183 kilo Pascal right. Now what is the volume of the tank, so volume of the tank we can simply use this information that the Vf and Vg is this. So, V is V f plus x V g minus V f that is of course, V f g. So, we can write down here the point  $0\ 0\ 1\ 0\ 3\ 6\ \text{plus}\ 0.2$ multiplied by 2.3593 ok.

So, that will get V here in terms of meter cube per kg, now in order to get the volume we need to multiply V by 10 kg. So, this is nothing, but V average right. So, V average by into 10 kg and that will give us the volume of the tank. So, tank volume, so a simple way of using the tables to get the information for this case ok.

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So, let us continue further with another example a mass of 100 gram of saturated liquid water is completely vaporized, at a constant pressure of 100 kilopascal and we have to determine the volume change and the amount of energy transferred to the water. So, what we have is a mass which is point 2 kg and the pressure is given here.

So, now essentially since if the pressure is here, we are going to make use of the saturated water constant pressure table and since it's already informed that there is a complete vaporization. So, it is going to be saturated system, so on a PV diagram it looks like this, so its 100 kilo Pascal and its being said that its completely vaporized from here to here, and we have been asked to find out the change in the volume from this to this and as well as the amount of energy transferred within this so; that means, what will be the difference here also.

So, we can directly take a look at the tables, the tables are given here 100 is given here pressure kilopascal corresponding Vfe is here. So, of course, a Vfg is 1.6941 minus this and the internal energy is given the difference between the gas and liquid is already given here, so we want to directly use this ok.

So, that means, the volume is point 2 multiplied by 1.6, let me say again 1.6941 minus point 0 0 1 0 4 3. So, that is going to be the volume of the system whereas, U is going to be 2408.2, which is nothing, but U fg multiplied by point 2, and that will be your

kilojoules. So, that is the delta U transferred in the system and this will be your delta V of the change in the volume.



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So, this is a example, of using the saturated water tables now of course, many times we obtain phases where the it is a superheated, which is basically this region now superheated region is in the right side of the saturated vapor line.

So, the way the way to represent or to find out this operated whether the system is at superheated let us say at a constant pressure is by looking at is property, they should be greater than the saturated property if this is the saturated vapor point, then the corresponding that is enthalpy is a g then if the system which is at superheated condition the enthalpy of that is room is going to be greater than sg. So, for this also we have tables are typically in terms of V U H and temperature for a given pressure. So, that is how we make use of such a superheated tables in order to solve problems related to superheated conditions.

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So, let us look at an example, so here we have a system which is at state where the pressure is defined and enthalpy is given, and we need to find out the temperature now since we don't know whether the system is at superheated or saturated or compress we need to first we find out what is the possible state of that.

So, the best way to do these to make use of first the condition of saturated water pressure table where we look at the condition here 0.5 mega Pascal, which is 500 kilo Pascal and look at the corresponding enthalpy of the vapor ok. Now, 2890 is certainly more than 2748.1 that is h is greater than sg and this it is in the super-heated vapour condition.

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So that is we should directly, take superheated water tables. So, there are many values we have to pick up a condition, where we should get P is equal to 0.5 mega Pascal. So, we take a values corresponding to P is equal to 0.5 mega Pascal and.

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Here you have v u h, so this is like v u h at the entropy. So, we will talk about that later, so within this we look at the value h is equal to 2890, and you can see that h is equal to 2890. So, this is our h here lies between temperature 200 and to 50, because 2890 is in between here so; that means, temperature is in between this now in this case in order to find precisely the temperature what we are going to do is we are going to do a linear interpolation.

So, very simple way to do that is we consider and the difference in the this 2 temperature 250 and 200, and the slope of the linear line from 250 to 200 will be the same as that in the temperature in between to 200, and that is what we are going to use that delta h divided by the temperature, and from here we rearrange this to get this temperature which comes out to be 216.3 degree Celsius ok.

So, what we are looking at is simply is the slope of the line from this 2 prime point. So, this is a common way of solving problems, where the data's are not given for each point and so we make use of linear interpolation.

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So in addition to the superheated vapor which is on the right side of this saturated vapor line you have a compressed liquid which is on the left side of a saturated liquid line on the P or T versus V plot. So, a compressed liquid line usually what we consider is for a given point, somewhere let us say here which is on a P is equal to 500 kilopascal at temperature 75 the property, we try we approximate to that of the liquid saturated liquid at the 75 degree Celsius. So, usually we approximate because the compressed liquid property depend on temperature more than on pressure.

So, in this case the pressure variations are usually neglected, but for enthalpy for example, the more accurate relation is even here. So, this is something which 1 can derive using thermodynamic relations and which we will be doing it in the later part of this course. So, what are the conditions for the compressed liquid? So, for corresponding to 75 degree Celsius the saturated point is here and at this point. So, this will be your P sat add that temperature of this system this is a P sat at the temperature of the system which is 75. So, basically the system is at 75 degree Celsius and 500 kilopascal ok.

So, if you look at it the pressure P here is greater than P sat at T. So, that is the condition which we have P should be greater than P set at a given temperature, in addition the temperature if you look at it for a given pressure that the T sat for this P is 151.83 and 75 is less than 151.83. So, the temperature is less than T sat at a given pressure. So, in general these 2 conditions will conclude that it is a compressed liquid, but in general all the properties such as your specific volume internal energy enthalpy will be less than the corresponding properties of the fluid at a given pressure or temperature so.

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That is how we define compressed liquid. So, let me now talk about the deviation of the properties from the ideal gas behavior, as we said that you know we are interested much to represent the properties or the state of the fluid in terms of some kind of equational state.

So, one way to look at is how much is a deviation from the ideal class is it possible to quantify the (Refer Time: 24:47), non-ideality in terms of very simple parameters and that is what the compressibility factor talks about it. So, now, the compressibility factor can be represented in terms of Pv is equal to ZRT well this is a molar volume. So, Z basically represent deviation from non-ideality for ideal gas that is equal to 1 for real guess it could be less than 1 or greater than 1, if you decrease the pressure such that it is 0, where the particles are far apart you to start behaving ideal gas.

So, what is the definition in general for low pressure it need not be like you know going to 0 or absolute 0, but in general Z is unity, when the gases are at low pressure or the high temperatures so, but what is the definition of low pressure at high temperature it is with respect to its critical point. So, the low pressure high pressure of a gas is high or low related to its critical temperature of pressure.

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So, in practicality or in general are you on a TV diagram this region would behave like idle gas behavior because the extremely low pressure, because yes it is extremely low pressure right. So, the pressure will decrease here all right and as well as this pressure because the temperature is quite high.

So, these 2 regions will start behaving more or less like ideal gas now the other important thing is right, now it was noted that if you reduce the properties such as your pressure temperature and volume by is critical point and many substances who are similar type sizes, they start behaving similarly in a reduced plot and this is the principle of corresponding state ok. So, if you reduce pressure by it is by the critical point of the fluid, and get a variable P R and similarly TR and VR.



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We can plot Z as a function of P are four different TR, and it appears that the many different substances which is here written here ethylene ethane and so forth. They all fall on almost similar on the same curve this is what is you know beautiful because essentially tells you that if you take out the characteristic property of the molecules in the form of the critical point then all behave similarly.

So, thus you can map this on a single curve which we call it compressibility chart, and which is nothing, but the Z here as a function of P R, now you can clearly see here that can be less than 1 as well as a certain condition it would be more than 1 ok.

So, if you want to find out Z just using the compressibility chart its quite easy for a given fluid for example, in this case any of this you need to find out for a given P, and let us say for given T you can get P R and T R using his critical point and then for given T R of y given P R and T R, you know exactly this line and then you can take Z and from there you can find out other properties, or for that matter if the Z is given and a specific an inner temperature is given that say you can use that in order to get the other unknowns. So, this is how the compressibility chart is used; now this is a simpler compressibility chart this there is more complete compressibility chart for.

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Many different systems this is something which we call in then cell about generalized compressibility charts. And it is designed such that it has a specific chart for low pressure and high pressures, and here you can find out that it can go the Z can also deviate from 1. Now in addition to PR and TR you have also VR.

In this case in order to simplify this exercise of course, this say something which is a commonly used in industry and 1 can also do an exercise on it or which I leave it to you. So, this was a very quick introduction to properties particularly the phase diagram utility of the tables and equation of state we will continue our discussion in the next lecture, see you in the next lecture.