Course on Phase Equilibrium Thermodynamics
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Lecture 16
PvT Behaviour (Contd.)

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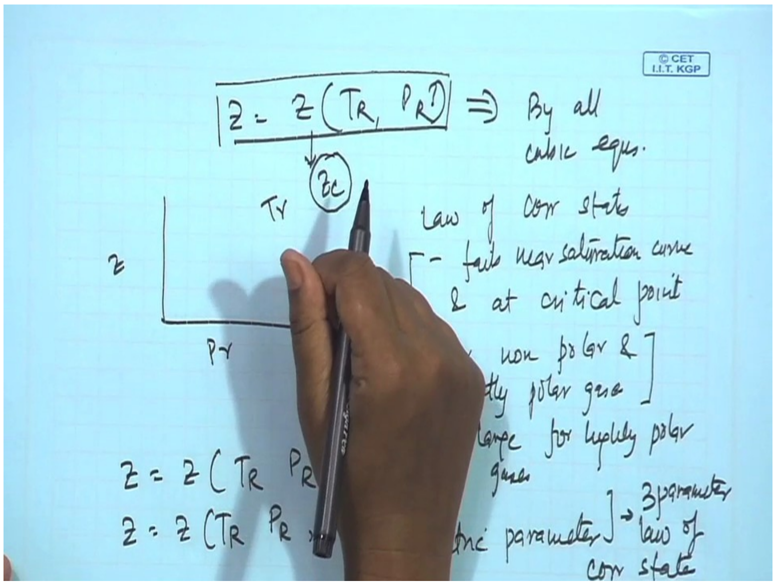

Well, to continue with our previous discussion where did we end? I had mentioned that normally this is very good but under certain circumstances we found that there is good amount of deviation therefore to improve predictions people started thinking about any particular third parameter which can be incorporated here which takes into account intermolecular interactions that is expected to improve the 2 parameter law of corresponding states.

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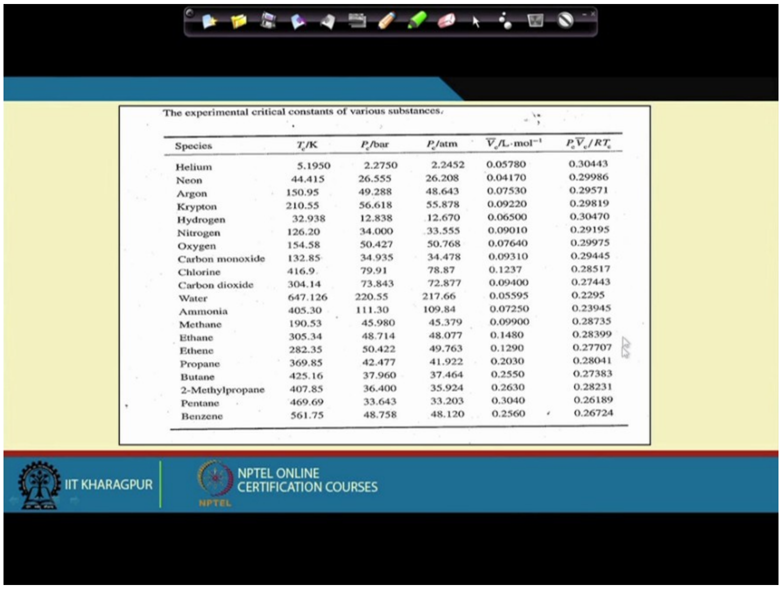

The experimental critical constants of various substances.

Species	T_c/K	P_c/bar	P_c/atm	$\overline{V}_c$/L·mol^{-1}	$P_c\overline{V}_c/RT_c$
Helium	5.1950	2.2750	2.2452	0.05780	0.30443
Neon	44.415	26.555	26.208	0.04170	0.29986
Argon	150.95	49.288	48.643	0.07530	0.29571
Krypton	210.55	56.618	55.878	0.09220	0.29819
Hydrogen	32.938	12.838	12.670	0.06500	0.30470
Nitrogen	126.20	34.000	33.555	0.09010	0.29195
Oxygen	154.58	50.427	50.768	0.07640	0.29975
Carbon monoxide	132.85	34.935	34.478	0.09310	0.29445
Chlorine	416.9	79.91	78.87	0.1237	0.28517
Carbon dioxide	304.14	73.843	72.877	0.09400	0.27443
Water	647.126	220.55	217.66	0.05595	0.2295
Ammonia	405.30	111.30	109.84	0.07250	0.23945
Methane	190.53	45.980	45.379	0.09900	0.28735
Ethane	305.34	48.714	48.077	0.1480	0.28399
Ethene	282.35	50.422	49.763	0.1290	0.27707
Propane	369.85	42.477	41.922	0.2030	0.28041
Butane	425.16	37.960	37.464	0.2550	0.27383
2-Methylpropane	407.85	36.400	35.924	0.2630	0.28231
Pentane	469.69	33.643	33.203	0.3040	0.26189
Benzene	561.75	48.758	48.120	0.2560	0.26724

So people started thinking about the third parameter, what did they observe? The first thing which people observed that if really all gases obey this 2 parameter law of corresponding states then from here all gases should have the same value of Zc, so what they did? They started finding out Zc for a large number of values which I have shown here.

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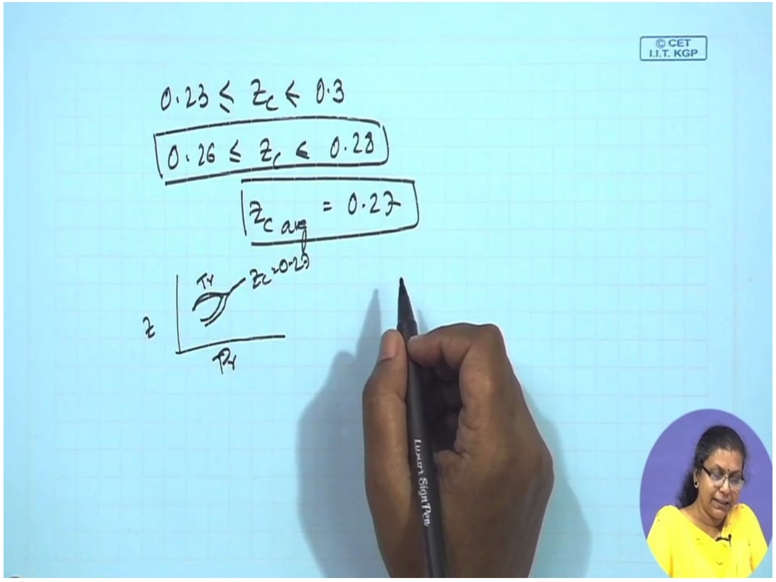

If you observe you find that the Zc values for the different gases they are definitely close to one another but there is a variation if you observe here that too these are mostly for non-polar molecules the variation is from 0.26 to 0.3 the variation occurs in this particular way. So therefore people thought that definitely the third parameter should be something or rather the third parameter should be the critical compressibility factor where in for 82 compounds when ZC was found out, it was found that ZC was varying from 0.23 to 0.30 with majority of T cases lying between this particular situation.

So therefore it was thought that when any gas obeys the 2 parameter law of corresponding states they should have a Zc average of 0.27 and whenever there is a deviation for this then Zc should be introduced as a third parameter and accordingly the third parameter law of corresponding states was introduced and lot of graphs of Zc were there and this was Zc equals to 0.27 any deviation was taken into account by separate graphs, right?

This was one class of thought this particular class of our or rather this particular definition it was given by the, it was given at the University of Wisconsin but the more popular approach is the thing which was suggested by the University of California, what they suggested? They thought that if the gases they correspond to the law of 2 parameter law of corresponding states then all the gases they should have the same saturated reduced pressure saturated vapor pressure at the same reduced temperature, right?

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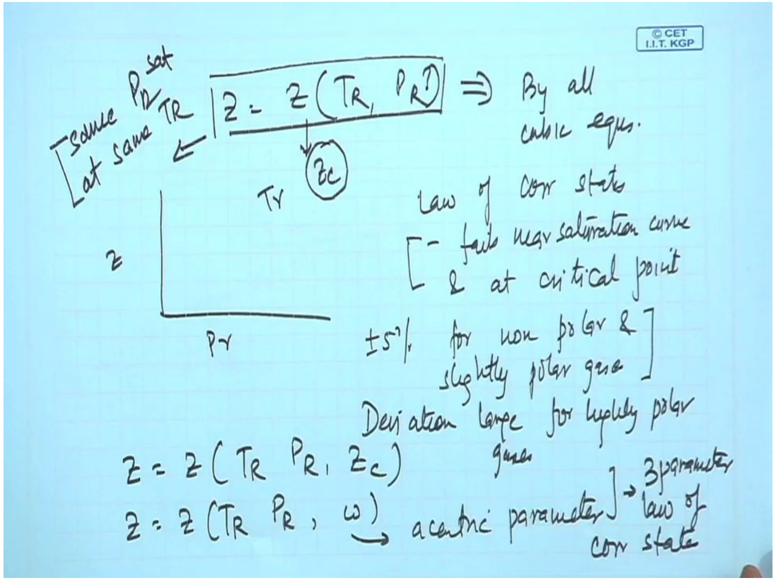

So therefore what this particular case again if I bring the 2, if this is applicable then all the gases they should have the same PR saturated at same TR this should happen but people found out that this is not the case, right? And this particular deviation was taken up as the third parameter in the 3 parameter law of corresponding states how was the deviation or how was this third parameter brought about?

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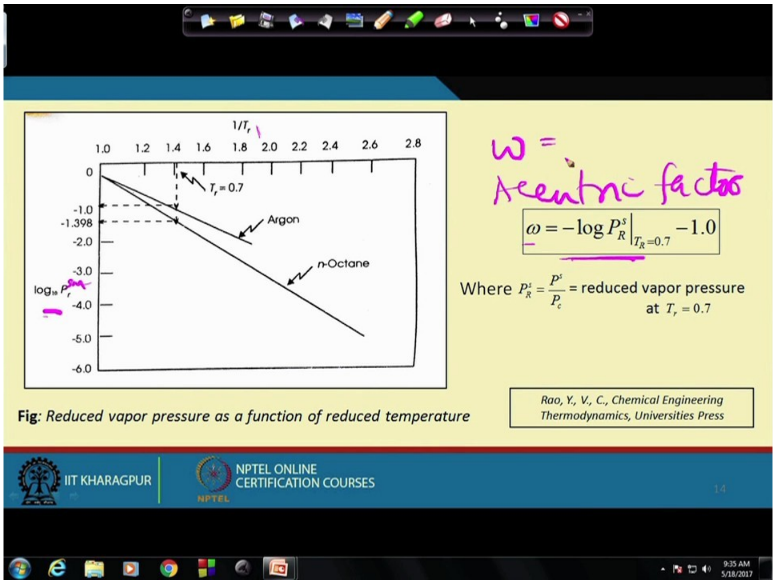

The third parameter was brought about by plotting if you find I have made it here by plotting log of PR saturated with 1 by TR, this is actually PR saturated, right? So therefore they plotted log 10 PR saturated as a function of TR and then they found that for different gases the slopes of these curves they were different and they assumed that definitely a perfect molecule should be one with completely spherical molecules that should be a perfect gas they are assumed Argon to be a perfect gas.

And then therefore they thought that the limiting value of omega should be such that omega equals to 0 for perfect gases with spherical molecules like Argon. Accordingly they defined omega in the way that I have mentioned here this was the definition of omega which gives minus log 10 PR saturated at TR equals to 0.7 minus 1.0, why? Because for argon we find this term becomes equal to one for argon and therefore omega becomes equal to 0 for argon. So they took up omega as this is known as an acentric factor and this gives you the deviation of the intermolecular potential of any molecule from that of a simple molecule or rather simple gas with spherical molecules, right?

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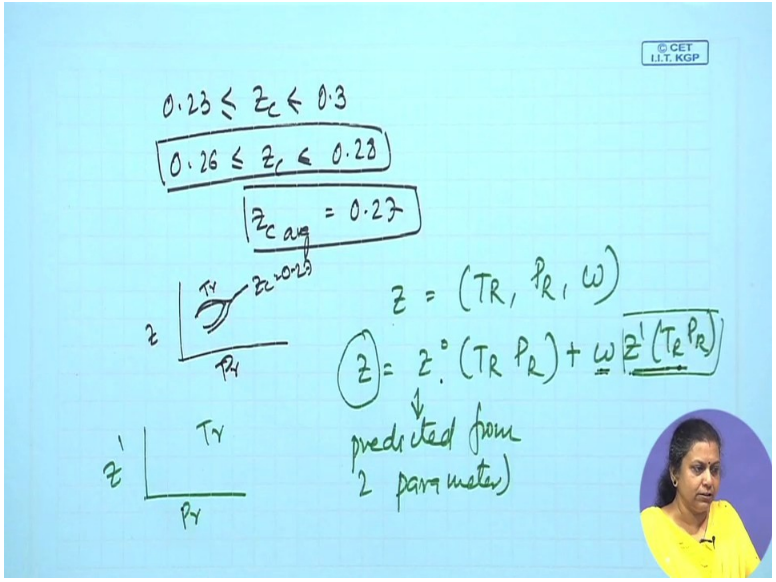
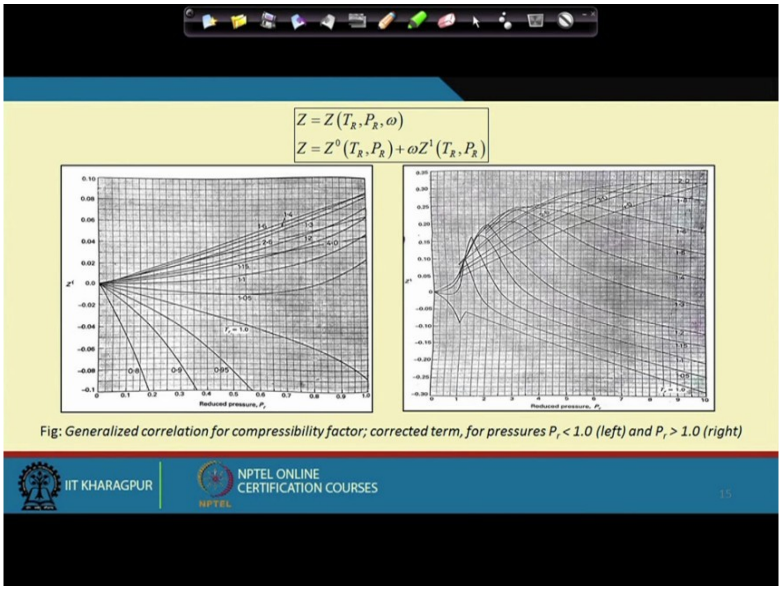


And this was taken up as the third parameter in the 2 parameter law of corresponding states which gave us z equals to TR, PR and omega and the functional form relating z with TR, PR, omega was something of this sort z where this is the z 0 predicted from 2 parameter model, right? And plus omega z1 TR PR this is the functional form relating Z with TR, PR, omega which gives you that for normal circumstances far removed from the critical conditions and the saturation curves for more or less not maybe polar molecules z can be obtained from the 2 parameter law of corresponding states, when there is some deviation then we need to find out omega.

Omega can be found out from the slope of PR, log PR saturated versus TR curve and then we need another set of equations to find out just like z versus TRPR we need another set of equations to find outside z1 as a function of PR with TR as parameter. So therefore along with z 0 additional similar curves were generated for z1 from which we could we can find out z0 and z1 for any particular gas evaluated its omega and accordingly calculate the compressibility factor for that particular gas.



Here I have just for your reference I have presented the z1 curves as well along with the z0 curves if you observe we have this z0 curves here and we have the z1 curves here and the omega curve here with all those things we should be in a position to predict the behavior of any particular gas even if you do not know which equation it corresponds to simply by assuming the 3 parameter law of corresponding states for greater accuracy and 2 parameter law of corresponding states for most practical applications.

Now this was all about the law of corresponding states and the use of compressibility factor charts and the cubic equations of state we need to remember that the cubic equations of state after all they are approximate in nature, right? Despite all the great advantages they are approximate in nature number 1 and they have certain empirical constants. Now a better theoretical basis or based on a better theoretical basis the real equation of state has been proposed.

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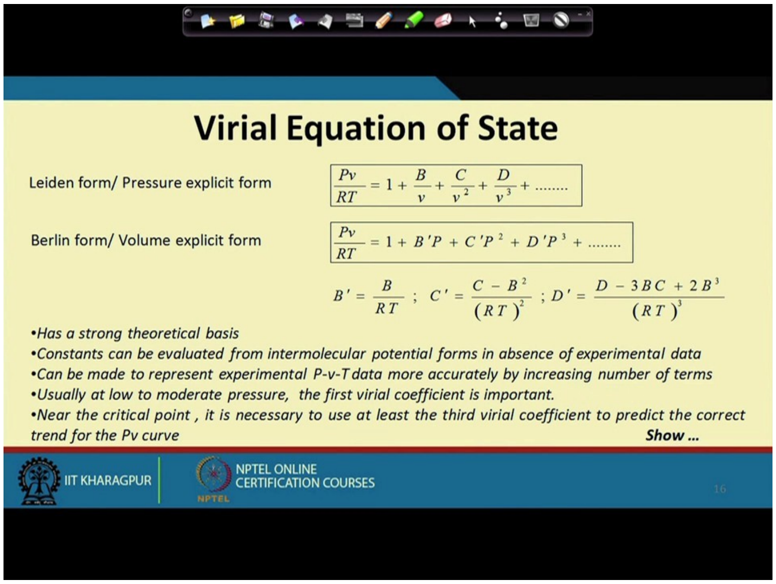

What is the virial equation of state? Let us see possibly all of you are aware of this particular equation of state it can be written in a pressure explicit form as well as in a volume explicit form as we have noted here and we find that these particular constants this BC etc this particular constants they give us the interaction between 2 molecules 3 molecules etc. Now if you observe this equation what do you find?

The first thing is, this equation has got some theoretical basis it is not entirely empirical, the next thing is you find that more or less for very low pressures high-temperatures you can neglect all the terms Pv by RT becomes equal to one, so it reduces to the ideal gas behavior. When it starts deviating from ideality the deviation is not very high we can just include the first parameter here, when the deviations are still higher we can include the higher-order terms.

So therefore depending upon the situation we can include more number of terms and thus incorporate the extent of deviation from non-ideality just by using one particular equation. Now the first thing is and the other important thing I also mentioned that the constants can be evaluated from intermolecular potential even when we do not have any particular experimental data. Now usually for the conditions which we come across we find that usually the first constant the B and the B primes they're mostly important.

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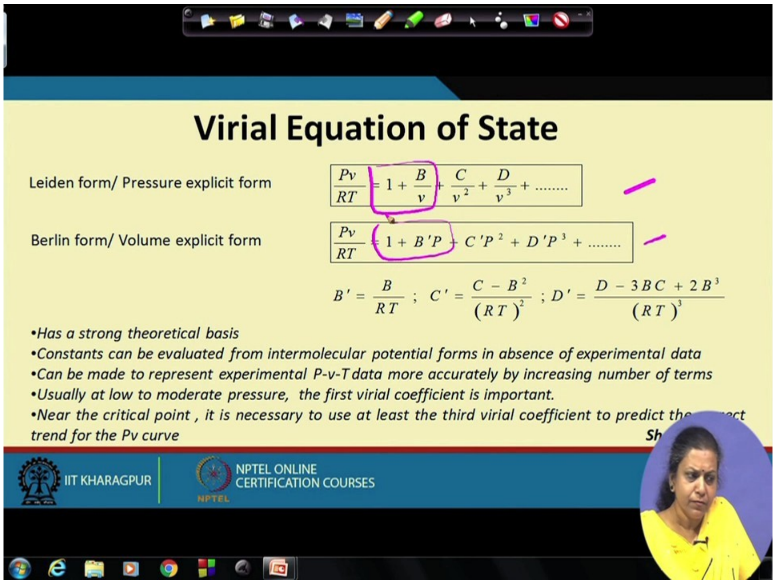

We usually for most practical purposes we can use that virial equation by truncating after the second term. So therefore this particular portion or this particular portion usually is sufficient for us and the relationships between the different constants have also been mentioned in this particular equation, right? So therefore there is not much that I have to say about the virial equations of state there is just certain thing which I would like to mention regarding the first constant which is usually much more important and which is of much greater concern for us.

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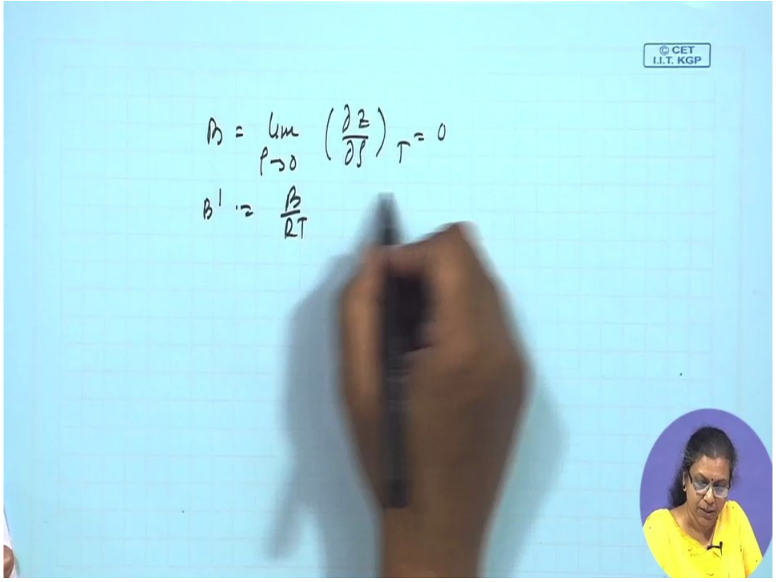

Now if you observe this particular constant, what do we find? There are certain important things that I would like to mention, first thing is if you take up this particular equation, what do you find? You find that your B, this is simply nothing but limit rho tends to 0 del z del rho at constant T equals to 0, right? So therefore what does it imply? And we know this B prime this is the relationship between B and B prime is that B prime this is equal to B by RT, fine.

So therefore if suppose we are plotting from this particular equation if you are plotting z versus P, what do you get? You get a linear equation you should be getting a linear equation at low to moderate pressures where we can just consider this part at low to moderate pressure we find that if we plot z versus P we should be getting a linear plot whose slope should be given by B prime or whose slope should be given by B by RT.

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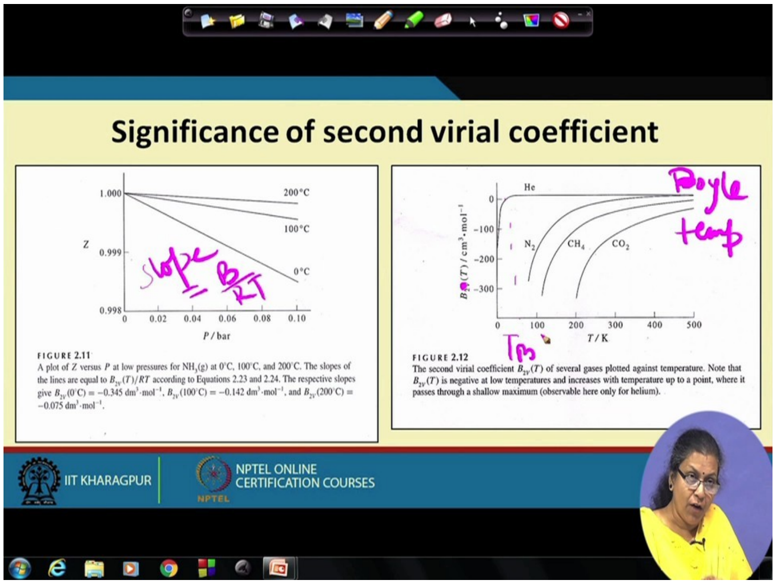

So therefore if we are plotting in this particular case then we find that the slope in this particular for each of the equation, what is the slope equals to? Slope is nothing but equal to B by RT remember one thing all these Bs and the Cs etc, all of them are functions of temperature and they are independent of the pressure or the density of the particular gas.

Again we find that if we plot this particular B, this is B basically if we plot this particular B with temperature we find that for very low temperatures the B is negative for all the gases and then under one particular temperature we find that the B becomes equal to 0, what does it imply? For low to moderate pressure it implies that definitely the B 0 means the gas is behaving ideally, so therefore it appears that at the condition where the temperature where V equals to 0 the gas behaves ideally it’s actually not so.

At the condition of the temperature where B equals to 0 the attractive and repulsive forces are equal to one another and this happens at a specific temperature which is again a property of the gas and this particular temperature is known as the Boyle temperature often denoted as, this temperature for each particular gas this temperature is denoted by TB.

For this particular case we find that the attractive and the repulsive parts of intermolecular attraction cancelled and the gas appears to behave ideally, provided we have neglected the effect of virial coefficient beyond the second. So therefore all these things are applicable for low to moderate pressure. So naturally finding out the first virial constant it’s quite important and there is a very easy way by which we can find it out again for understanding the very easy way we refer to the basic equation, what is this?

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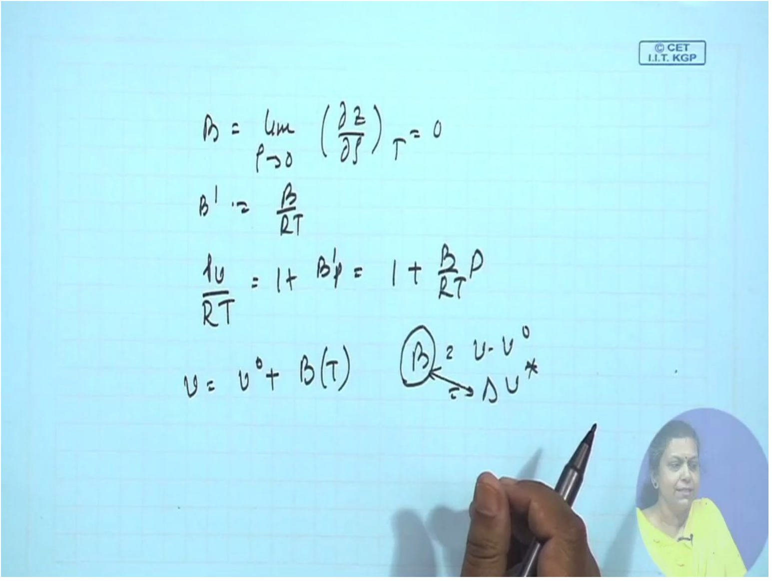

This is equal to B prime this is equal to 1 plus B by RT into P, agreed? Now if you multiply both sides where RT by P, what do we get? We get V equals to V0 plus B as a function of, it's a function of T, what is B equals to can you tell me? It's nothing but equal to V minus V0 which is nothing but equal to the residual volume for that particular gas at the pressure at any particular desired pressure.

So therefore we can find out data on the second virial coefficient from the data of residual volume if it's available at any particular pressure conditions provided we can neglect the contribution of third virial coefficient at higher terms. So therefore these are some of the few things that I wanted to tell you but before I end there is something interesting that I would like to mention.

I have already told you that when we are using the virial equations of state, when we are using the virial equations of state I have already told you that usually we are dealing with the first 2 terms or we come across the first virial coefficient which is important and I have also highlighted just because the first virial coefficient and one more thing for most of the cases this particular form is much more convenient. So we are mostly dealing with the coefficient B and I have also shown you the physical significance of B.

Now there is something interesting which I would like to tell you, while for normal circumstances the virial equation with 2 terms is sufficient at the critical condition we need at least 3 terms for a proper representation of the PvT Behavior, let us see how and why? I would like to show you that how near the critical condition we use at least the third virial coefficient for a correct prediction of the Pv behavior near the critical point.

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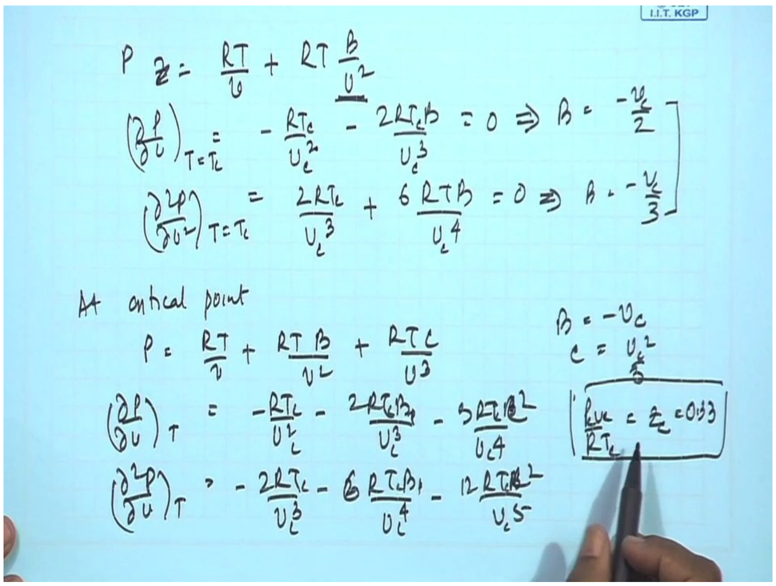

Let us see what happens if we start with just the 2 equations of state we truncate it after the 2 equations, what is it? This is RT by v plus RT B by V square, right? What is del p del? Sorry this is P equals to, what is del P del V at constant T? It is minus RT buy V square minus 2 RTB by V cube. What is del 2 P del v2 at constant T? This is nothing but equal to simply I am doing I am performing differentiations and nothing else I get the equation as this.

What happens at the critical point? At the critical point my T equals to Tc, this T equals to Tc, so accordingly here I should be getting I would be putting Tc Vc I will be substituting all the constants with the critical values, right? So once I do this and we know that at T equals to Tc both of them are 0. Now just observe the equations closely from this equation, what do you get? You get B equals to minus Vc by 2.

From this equation what do you get? Simply solve it and you find B equals to minus Vc by 3, so therefore you are getting inconsistent results if you are just considering 1 particular coefficient at the critical point. So therefore you get inconsistent results and you need to consider more number of terms for a correct prediction of the PvT Behavior near the critical point, what do we need to do then? For this particular case we if we consider more than one particular critical constants then we are dealing with this particular equation, right?

So in this case if we are performing del v del T, we get minus RT by V square minus 2 RT B1 by v cube minus 3RT B square by V to the power 4, again if we differentiate it once more we find out this equation becomes 6 RTB1 by v to the power 4 minus 12 RTB square by v to the power of 5, right? At the critical point again I would like to substitute everything with the critical constants, okay.

And then what do I have? I have got 2 particular equations B1 and B2 in this particular case sorry B and C I had written them in the form of B and C, this is B and this is C, I am sorry. This is B and this is C. So therefore from these 2 equations now we will find that we have from these 2 equations we will find that we have come to the state where B is equals to minus Vc and C is equals to Vc square by 3. So therefore we find that what the critical isotherm if you substitute these 2 values we find that Pv by RT which is nothing but Zc this reduces to 0.33 PcVc by R this reduces 0.33 at the critical point.

So from here what do we deduce? I deduce that it is fine to use the virial equation of state with just 2 terms for conditions far removed from the saturation curve and at the critical point but for conditions near the critical point in order to obtain consistent PvT behavior we at least need to consider 3 terms in the virial equation of state, right? So with this more or less I have completed the some of the discussions on the PvT.

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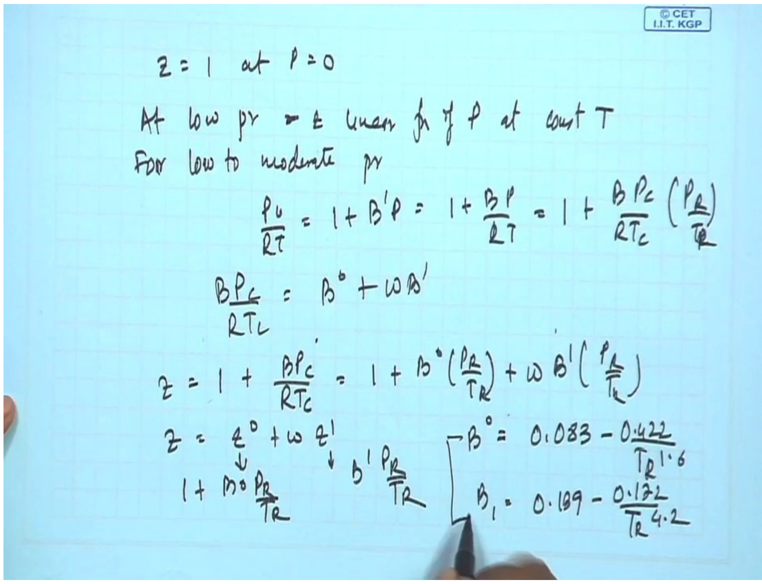

One more thing suppose I would like to mention is the generalized equations in terms of the PvT behavior or rather in terms of the virial coefficients. Now here we find that from generalized compressibility factor chart just the way I have deduced the compressibility factor chart from the cubic equations of state we should be able to predict the virial coefficients also from the generalized charts. So we know that z equals to one at P equals to 0.

So therefore we also know that at low pressure z it is a linear function of P at constant T, right? So for low to moderate pressures, what do we have? We have Pv by RT this is equals to 1 plus B prime P this is equals to 1 plus BP by RT which can be written as one plus B Pc by RTc PR by TR. For non-polar molecules we can write it down as BPc by RTc equals to B0 plus omega B1 and when you substitute this particular equation in the equation for z, we get z equals to 1plus BPc by RTc which is equal to one plus B0 PR by TR plus omega B1 PR by TR, right?

So from Pitzer correlation we know z is nothing but equal to z0 plus omega z1 from where we can say that z0 is nothing but 1plus B0 PR by TR and z1is nothing but B prime PR by TR and from here we can also deduce that B0 can be obtained as 0.083 minus 0.422 by TR to the power 1.6 and B1 can be obtained as 0.139 minus 0.172 by TR to the power 4.2, now these are the generalized virial coefficients called coefficients correlations which are applicable at low to moderate pressures for non-polar gases only. So therefore this reduces us to the rather so that we can also deduce the law of corresponding states using the virial equation just the way that we have done from the cubic equations of state.

So with this we would like to do a few problems so that you get much more conversant with PvT behavior of gases and then we proceed to find out how the PvT behavior of gases can be used in the equations to predict the enthalpy, entropy, internal energy, Gibbs free energy, Helmholtz energy and host of other new parameters that we will be introducing from the PvT behavior of gases? So this is all for the day and we proceed and we do a few problems in the next class.