

**Concepts of Chemistry for Engineering**  
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**Lecture 63**  
**Real gases- part 1**

Hello everyone, welcome to the module on intermolecular forces, and potential energy surfaces. We are still discussing on intermolecular forces, which exist between molecules and what is the role of those intermolecular forces on the properties of systems. So, in this particular lecture, we shall go ahead and look at how do intermolecular forces affect the properties of gases. And before we get there, let us just quickly recap on what we learned about intermolecular forces.

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**Brief recap**

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1. Dipole – dipole interaction
2. Hydrogen bonding
3. London dispersion or van der Waals interaction



In the previous lecture, we had seen about a water called as dipole-dipole interactions or to be more precise permanent dipole - permanent dipole interactions. And here, we had said that these interactions the interaction potential depends as  $1/r^3$ . And for this we are taking various examples like either two water molecules interacting or two molecules of acetone or any two molecules which are uncharged, but yet have a permanent dipole in their ground state can be described by this potential, which goes as  $1/r^3$  along with some factors, which also take into account the orientation of the two dipoles.

Going further, we had looked at another important interaction which is called as the hydrogen bonding, which we said it as a special case of a dipole-dipole interaction, because it has both components of a permanent dipole permanent dipole interaction and sometimes one can also

invoke electrostatic interactions to explain hydrogen bonding. And so, the exact decomposition is not very, very clear.

However, what is known is that both the factors that is electrostatic as well as the dipole-dipole do contribute towards hydrogen bonding, and this intermolecular interaction is ubiquitously found around us starting from biomolecules to water and whatnot. So, it is very important to at least understand and appreciate this.

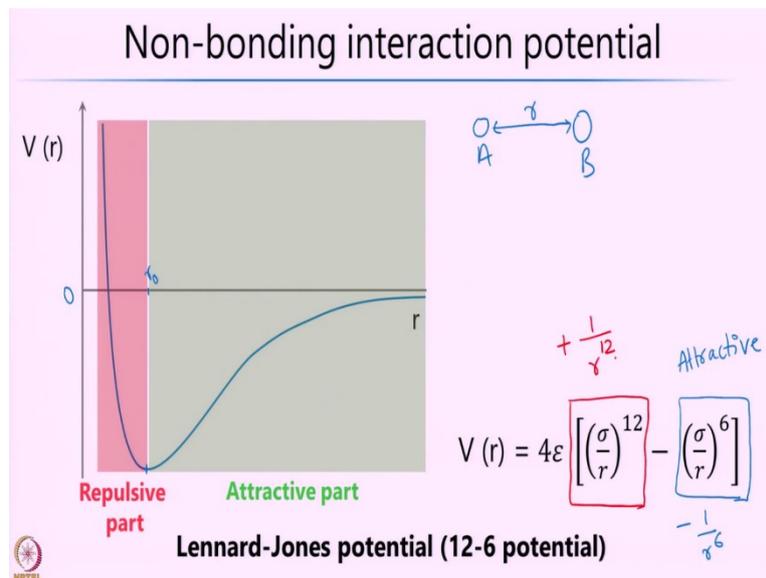
Finally, we had gone ahead and looked at water called as London dispersion or van der Waals interactions. Here, we had taken systems, which were neither charged nor polar in the ground state, that is molecules which are neutral and A polar, such as, methane, ethane, argon or these kinds of inert systems.

And the idea here was that because of the instantaneous fluctuation of the electron density, that would lead to a induced dipole in one of the molecule and that affects the way the neighboring molecules are arranged around it. And that leads to what people call as London dispersion or van der Waals interactions.

So, with this sort of an interaction, with an understanding on the various interactions between molecules, we shall now jump into seeing how that affects the properties of gases. Before we get there, let us first try to understand a bit of this van der Waals interaction a little more detail.

In the last class, we had looked at the interaction energy between the two molecules, that is, if I have a molecule of methane another molecule of methane, as they come close together, then they would interact with one another. And we had described this as  $1/r^6$  dependence.

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So, now let us go ahead and look at this a bit more detail and try to see what happens if we actually go further and try to bring the two molecules very close to one another. So, for that, what I have shown here is a potential energy diagram for interaction between two molecules and  $r$  is the distance between the molecules.

That is, if I have, let us say, the molecule A and molecule B, it could be either same molecule or different molecule, this is the  $r$  and  $V$  of  $r$  is the potential which describes the interaction between these two systems. And when they are completely apart and the potential is 0, that is the horizontal line.

So, as we bring the two molecules close together, A and B, then they would interact by either let us say induced dipole, induced dipole interaction that is a van der Waals interaction and that would lead to a stabilization or a lowering in energy. So, that is what you see here is this the blue trace goes down and you hit a minimum at a certain distance which is called as  $r_{\text{naught}}$ .

And if you now try to actually go further, what you would do is to actually bring both the molecules very close to one another. And because of Pauli's exclusion principle, you can only bring the molecules only so, close to one another thus, you see a huge repulsive interaction building up which is on the other side of this  $r_{\text{naught}}$ .

So, this can be actually broadly classified as shown here, that is going from the  $r$  at a larger distance, and as you come down or as you bring the two molecules together, they interact and

then the whole system gets stabilized and equilibrium  $r_{\text{naught}}$  is called as what is called  $r_{\text{naught}}$ .

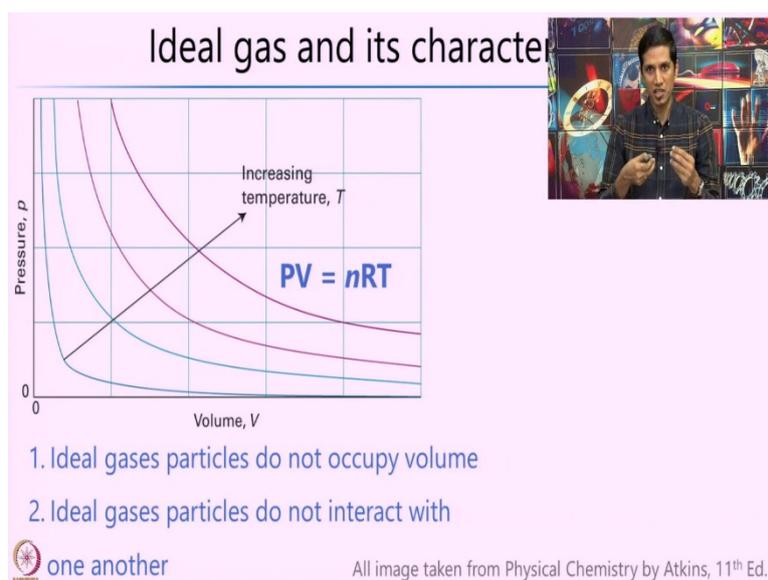
And if we now actually go ahead and try to get the molecules even further close to one another, you see that they actually repel one another, because of Pauli's exclusion principle and thus, you end up having the repulsive part which actually goes much sharper compared to the attractive part. So, this is what people typically call it as what is called as Lennard Jones potential or a 12-6 potential or sorry 12-6 potential. And the potential has the form as shown here, that is  $V$  of  $r$  is equal to  $4\epsilon \left(\frac{\sigma}{r}\right)^{12} - \epsilon \left(\frac{\sigma}{r}\right)^6$ .

So, if you actually look at this, this looks very similar to what we had seen in the van der Waals interaction, that is, this part of the Lennard-Jones potential is the attractive part. Because you have a  $1/r^6$ , you can think it is, this is similar to  $-1/r^6$  and that is the attractive part between two induced dipoles. This is what we had seen it as a van der Waals or London dispersion attractions.

However, the other part which actually did not look at in the last part is this repulsive part, which is the  $1/r^{12}$ . This goes as  $1/r^{12}$  and please note it is positive, that means it is repulsive and  $1/r^{12}$ . So, that is if you bring the two molecules beyond a certain distance, they actually instead of attracting they do repel, because of Pauli's exclusion principles.

So, this is a very important potential or principle to keep in mind that you can bring two molecules close together until an optimum distance till which the interaction energy is favorable. And beyond that, actually, the energy of the system actually rises rather than decreasing. So as a result, the total system becomes destabilized. So, with this sort of understanding on how two molecules interact with one another, now let us go ahead and first start to see, let us see about ideal gases and then, we can look at real gases.

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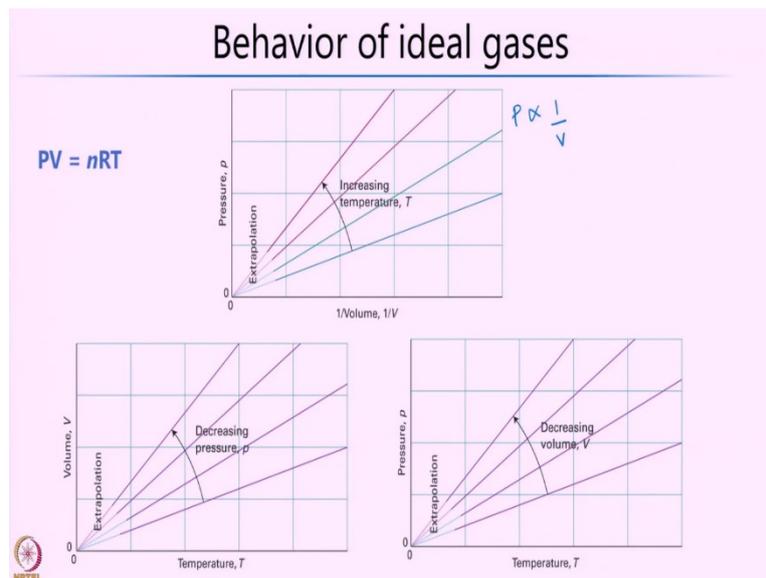
So, the moment I say ideal gas, I am sure, you all would be thinking of this equation, which is  $PV$  is equal to  $nRT$ , where  $P$  and  $V$  stands for pressure and volume respectively. And  $n$  stands for the number of moles,  $R$  is the universal gas constant,  $T$  is the temperature in Kelvin. So, once you have this equation, what one can do is, we can draw various different forms of it in terms of the graphically. And one, which we are going to use quite often in this lecture is this diagram of pressure versus volume.

And since you know that the product of the pressure and volume is a constant, if you look at how does the pressure change as you change the volume, you would see these kinds of hyperbolic graphs as seen here. And each of these curves represent at a given temperature. So, or in other words, each of this is an isotherm that is at a particular temperature.

In addition, the ideal gas laws also make some assumptions. And those are, and the two most important are that the ideal gas particles do not occupy any volume. That is, if I take a chamber and fill it with gas molecules, so each of the particles do not occupy any volume, this is one of the assumptions of the ideal gas theory.

And the second is that the ideal gas particles do not interact with one another. So, here, again, the point of interaction between the molecules of the atoms should again come into picture and we will see what is the influence of that. So, now this is what is a typical ideal gas law that is  $PV$  is equal to  $nRT$ . You would have all learned this, and these are the two most important assumptions of this theory.

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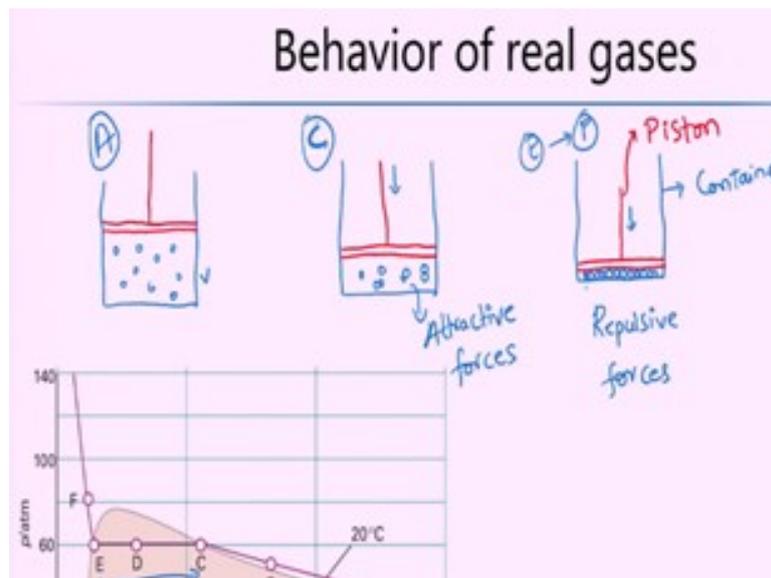
Before we get into the real gases, let us just quickly look at other forms in which one can write this, one can draw these graphs. So again, I have just written down  $PV$  is equal  $nRT$  for the sake of convenience, and then one can have pressure versus  $1$  by volume. And I hope you see that if I take a look at if I remodify this  $PV$  is equal to  $nRT$ , so then I can get  $P$  is proportional to  $1$  by  $V$ , with the constants.

So now if I draw  $P$  versus  $1$  by  $V$ , then it is very similar to drawing a  $Y$  equal to  $mx$  curve. And as a result, you have all these straight lines at different temperatures going through the center or going through  $0, 0$  point of pressure and volume. So, this is one form. And similarly, one can draw a volume versus temperature. And I hope this is pretty obvious because you have now volume, which is directly proportional to the temperature.

And similarly, one can also draw a pressure versus temperature graph, and this is again, a linear and goes through the center or the  $00$  point. And this is because again, the pressure is directly proportional to the temperature from the ideal gas law. So, this looks very straightforward and something which is very familiar to all of you. So now, let us see what happens if you go to actually real gases.

So, what do you mean by real gases, is that, in real gases, there could be the we will see, how does gases behave, as we apply temperature or pressure or changes in the volume? And with these changes, does the behavior what we looked at previously does it hold?

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So, for that, let us first take a simple example where what I have is, I have a container, I will just draw three containers here. Assume they are of the equal size and volume. And then, I would have a piston, which is shown in this red color. So, this is a piston. And the blue is the tank or the container in which we have the gas molecules.

So, now, if we actually start putting in gas molecules. Let us say putting in gas molecules like this, so they are all freely floating around, so they are not actually interacting with one another. And if I want to actually decrease the volume of this, let us say this has a particular volume  $V$ . If I want to decrease, I will just push this piston down and now I will decrease the volume of this or increase the pressure.

So now, what actually happens is that you will start seeing some of these gas molecules which are represented by the round beads, they actually start coming close to one another, instead of or sort of interacting with one another, rather than just being freely floating around. And if you now push it even further, the piston, then you would have a kind of almost a layer, monolayer of gas molecules or molecules which are actually stuck to one another.

So, this is the actual scenario which one would encounter with real molecules or gases such as, let us say methane, ethane, argon or others. So, now, you must be thinking, what is it of relevance? Why is these real cases more important than ideal gases? So, just to give you a feel, or a feel for the importance of this, so I am sure you all are aware of the importance of fertilizers in our day to day life, where the fertilizers do play an extremely important role in getting the crops across to everyone.

And in order to make the fertilizers ammonia is one of the key ingredients. And this ammonia was synthesized by Haber and Bosch in a process called as a Haber-Bosch nitrogen fixation where they were able to take hydrogen and nitrogen and compress them together at a high pressure and temperature to obtain ammonia in presence of a catalyst.

So, I just repeat, so they take hydrogen and nitrogen gases, and they put them together at a very high pressure and in presence of a catalyst, they were able to convert that into ammonia. So, this is a classic example where, when you take real molecules, such as nitrogen, and hydrogen and subject them to very high temperatures and pressures, it is very important to understand how do they behave?

Do they interact with one another? What happens to them? And what leads to the formation of the ammonia, which is a very important industrial fertilizer, which we currently use. So, I hope this gives you an at least a feel why one study these kinds of processes where we look at real gases at a higher temperatures and pressure, because they have real, actually technological applications. So, with this, now, let us see, how does an isotherm would look like PV isotherm would look like.

So, here on the left-hand side, what you see is a pressure versus volume isotherm. And if you start from this, that is at a higher volume, that is let us say I can, you can think of it as I am close to the leftmost figure, where I have the molecules which are freely floating around pretty much without any kind of interaction or very little interaction and I can actually come down along this line going from A to B to C.

So, if I come to C, here, what happens is, if it would have gone as we expected, it would have gone along the dotted line. But here you start seeing a deviation at C, that it goes via C, D, E, rather than going via the dotted line. So this is because once you come to C or once you compress the volume such that you are at around at a particular volume, like in this case about 0.22 or so, what happens is, the molecules actually come close together, and once they come close together, they start interacting with one another by van der Waals or London dispersion interactions.

As a result, you will have a condensation, that is, conversion from gas to a liquid. And this two that is the gas and the liquid actually exist in equilibrium with each other, or they are actually in coexist along this line that is C, D, E. And because of this once, the moment you have gas going to liquid, you have a compression.

So, as a result, you without any further actually applying the force, you can decrease the volume that is going from C to D to E. And this indicates the process where the gas gets liquefied or it undergoes liquefaction at least partially and both the gas and the liquid and coexist in this particular regime.

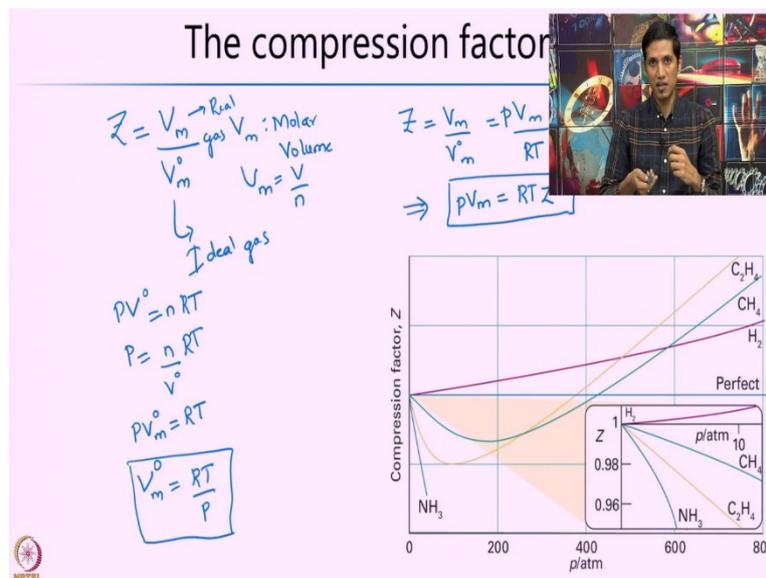
And now, if you actually want to hit the E, what happens is now we have found mostly liquids, or it is almost completely in the liquid state. And if you now even apply further, if you want to decrease the volume, then actually you cannot decrease the volume further because the molecules have a finite volume, so you cannot put or compress one into another.

As a result, they actually start repelling each other and you will have a significant increase in the pressure. That is what you see in this particular graph that is going from E to F with this small change in the volume, you see a significant increase in the pressure that is it goes from about 60 to about 80 atmospheric pressure with a very small change in the volume.

So, this actually is a consequence of the intermolecular interactions between real gas molecules. And also, because they do have a finite volume. So, just to put in perspective, I will just try to show you which of these phases belong to which of the three lines that is A is this. This is the point A where you are pretty much in the very close to the ideal gas behavior and this is C where the molecules are start attracting with each other that is attractive forces are coming into picture and that is from C to D this is the attractive part.

And once you are here that is E to F now we have the repulsive forces coming into picture. That is because you have already formed a kind of liquid or equilibrium in a liquid and a gas and that you cannot compress further. As a result, you have a significant increase in the pressure as you go from E to F. So, I hope, this gives you an idea of what happens if you try to compress a real gas compared to an ideal gas.

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So, having looked into this, now let us go ahead and see what is called as a compression factor. Since you are talking about compression, let us try and put that into a little more mathematical sense. So, here, I am going to write the compression factor  $Z$  as the following.

$Z$  is equal to  $V_m$  divided by  $V_{0m}$  and  $V_m$  is the molar volume or in other words,  $V_m$  is equal to volume divided by the number of molecules. So, that is the molar volume we are talking about. And then volume driven number of moles. So, once we know this, I am sure you will all agree that if we have an ideal gas, then the  $Z$  is equal to 1 because both  $V_m$  and  $V_0$  are the same at all different temperatures.

However, for the real gas that would be different. So, in order to see that, let us try and slightly modify this expression. And here the  $V_m$  is for a real gas or for a, and  $V_0$  is for the ideal gas. And if we now go back to the, our ideal gas equation that is  $PV$  is equal to  $nRT$  this can be rewritten as  $P$  is equal to  $RT$  divided by  $V_0$ . So, that is nothing but or in other words, we can write it as  $PV_0m$  is equal to  $RT$ .

Now, I can take this expression for  $V_0m$ , and put it inside. So, I am going to write this as  $V_0m$  is equal to  $RT$  by  $P$ . And I shall take that and put it in the expression for  $Z$ . So,  $Z$  is equal to  $V_m$  by  $V_0m$  is equal to  $V_m$  by  $RT$ , and then the  $P$  comes up so I am going to write it as  $P$  or in other words,  $PV_m$  is equal to  $RTZ$ .

So, this is an expression, which looks very similar to the ideal gas expression. And we will look into this in a bit more detail. But before we do that, let us first take a look at the what is the physical meaning of a compression factor and what does it tell us.

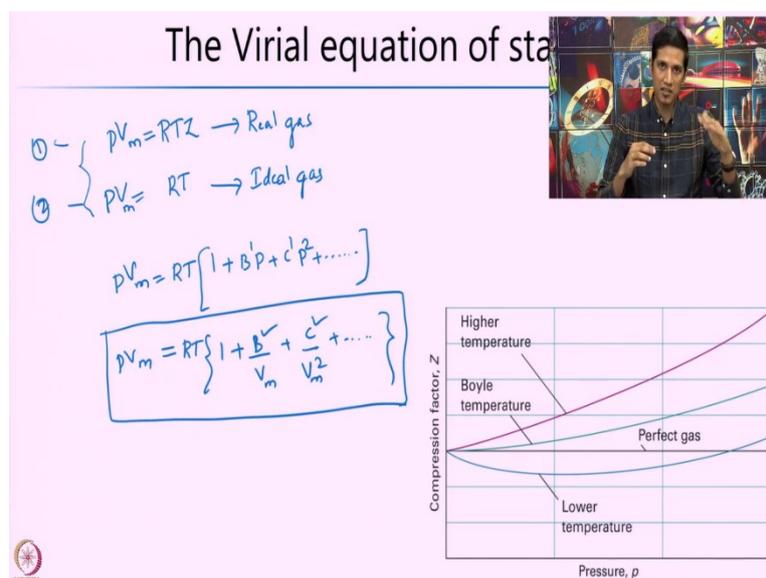
So, now, here, what I have shown on the right-hand bottom corner is a compression factor for various gases as a function of the applied pressure. So, like for example, here, what you see is that the four different gases have a completely different behavior. But if you zoom in on the lower pressure regime that is close to the zero atmosphere, you do see that they all start from a, they all have a Z value very close to 1, which is an ideal gas behavior.

In other words, at very, very low pressure, all gases or most gases actually behave like ideal gases. However, as you keep on increasing the pressure, then what happens is they deviate from the ideal behavior and you would get a very different nature of compression factor as a function of the applied pressure. And this again, comes back to the intermolecular interactions which are at play here.

For example, if you take the case of the methane and the ethane, what you see is that, you have a dip followed by a rise. And the dip, initial dip is because you have an attractive intermolecular interaction, which will reduce the effective volume or they will reduce the volume and thus compared to the ideal gas and thus you have a Z value which is lower. Whereas, if you now go to very high pressures then you can no longer compress it because otherwise you would run into repulsive zones.

So, as a result the  $V_m$  or the molar volume at very high pressures is higher for a real gas compared to that of our corresponding ideal gas, and thus you have a Z value which is higher than 1. So, this again the compression factor also gives you a feel for how does a given gas behave compared to an ideal gas.

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Now, to understand the real guesses in a little more detail, there are various kinds of expressions or theories which are invoked. In this lecture we shall look at one of them which is called as the virial equation of the state. And let us just start by writing out what is this equation means.

So, I will just write down what we wrote in the previous previous slide that is  $PV_m$  is equal to  $RTZ$ . And if you, now, this is for real gas is what we had seen. So, if I now take this as  $PV$  is equal to  $nRT$  or in other words or I can just put it as  $PV_m$  is equal to  $RT$ , this is for an ideal case.

So, if you actually look a bit close to these two equations, that is the 1 and the 2 you see that they are actually very, they are very close to one or they resemble one another. So, in order to understand this better, what we need to do is to let us see if we can expand this  $Z$  term, that is,  $PV_m$  is equal to  $RT$  1 plus let us say  $P$  dash times  $P$  plus  $C$  dash times  $P$  square plus so on and so forth, so forth.

So, if we now just take a look at this, and then the first term would be  $PV_m$  is equal to  $RT$  plus followed by all the higher order terms you have. However, if the  $P$  tends to  $P$  is very or the  $P$  is tending towards 0 then all these higher order terms gets cancelled, and you will be left with the ideal gas equation.

So, this is what is basically what we have done is, we have taken the  $Z$  and expanded it so that it can capture both the ideal as well as the real gas behavior. And this can be further written in another form that is  $RT$  1 plus  $B$  by  $V_m$  plus  $C$  by  $V_m$  square and so on and so forth.

And this is what typically people refer to as the virial equation of state this particular equation and these constants  $B$ ,  $C$  and the following ones are called as the virial coefficient or the virial constant and  $B$  is called as a second virial coefficient,  $C$  is called as a third and so on and so forth.

So, the significance of this equation is it actually tries to capture both the real gas behavior, as well as, an ideal behavior of a gas as  $P$  tends to 0 with some sort of an approximation. And these terms that is  $B$  and  $C$  in themselves are a function of temperature. And one can actually calculate this by experiments, the values of  $B$  and  $C$ .

So, having said this virial equation of state now just take a look, let us take a look at this compression factor and see how does it vary. So, if you take a look at this compression factor,

which we talked in the last slide, what you see is that, for perfect gas it is a horizontal it does not change as a function of pressure it remains constant that is one.

Whereas, at a higher temperature, it could probably go like this as shown here. At low temperature it could have a different behavior. And what is done is or what is what people call it is something called as a boil temperature or a boils temperature this is the temperature at which there is a temperature at which the virial coefficient becomes or tends to quarts the ideal gas equation and this happens usually as  $P$  tends towards 0. So, this is basically a kind of constant where your real gas tends towards an ideal gas and this the onset is what is called as a boil temperature.

So, with this, we shall stop here with our discussion on real gases. And in the next lecture, we shall look at another formalism to understand the real gases that is called as a van der Waals equation of state and the consequent properties. Thank you.