Chemical Principles 2
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Real Gas and Virial Equation

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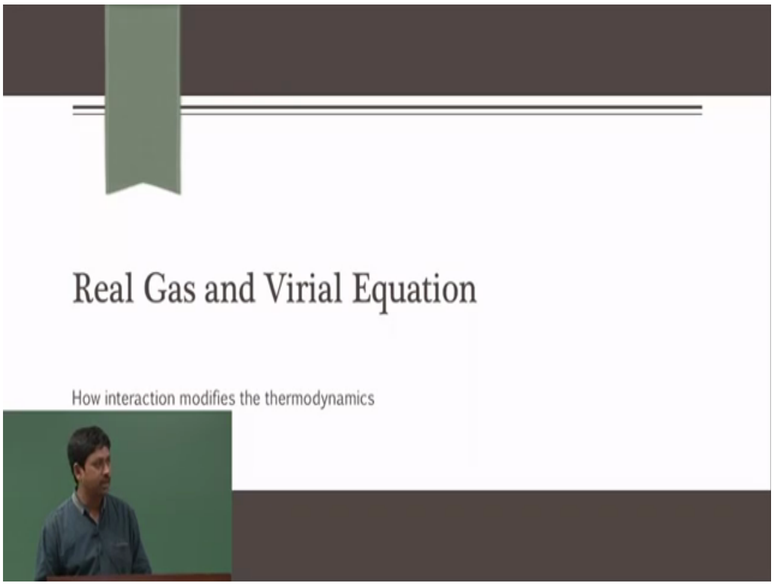

Real Gas and Virial Equation

How interaction modifies the thermodynamics

Welcome to our next lecture on chemical principles 2 and today we are going to talk about real gas and virial equation.

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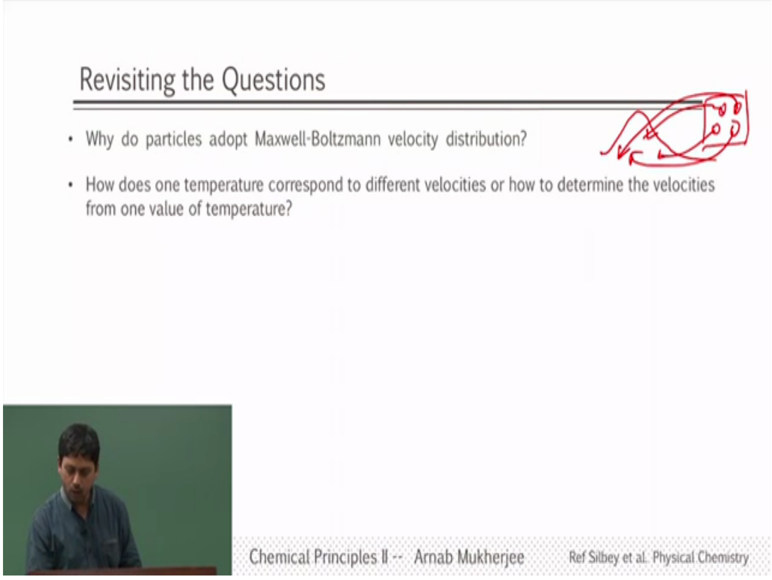

Revisiting the Questions

- Why do particles adopt Maxwell-Boltzmann velocity distribution?
- How does one temperature correspond to different velocities or how to determine the velocities from one value of temperature?

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So before we actually go there we are going to revisit the questions that we asked yesterday and also these are the questions that interesting ones so we will discuss that. So first question is that why does particle adopt Maxwell-Boltzmann velocity distribution? So you will learn later on that the fact that Maxwell-Boltzmann velocity distribution is attained at a given temperature is because the microscopic particles will interact with each other in such a way that the system will maximize its entropy.

So since we have not discussed that it will not be immediately clear that why the distribution is Maxwell-Boltzmann like, but it will become clear a later on. So now we will come back to the second one, so how does one temperature correspond to different velocities and how to determine velocities from one value of temperature? So that question was there with you and it is kind of intriguing to know that we give one temperature but we get multiple velocities.

Now how do we even understand this particular thing? We know that individually each particles since we know that kinetic energy is proportional to the temperature, individually every particle has different temperature. However, when you talk about system containing several atoms and molecules there what happens is that we are getting an average average essence of all those velocities and these averages are not simple averages they are not like you know v 1 plus v 2 plus v 3 and you know divided by 3, they are not simple averages they are kind of weighted averages we will come back to that later on.

So because of these weighted averages, we are going to get one particular value of temperature given all possible different velocities. However, if you want to think microscopically then the temperature associated with each particle is different, but for a microscopic system when you measure with a thermometer or any other devices that we talked about before, then we are going to get the average effect from all the particles involved in the system.

Now let us say I give you a temperature 300 kelvin and I ask you to find out the velocities of the particles, how do you do that? So for that what we normally do regularly in molecular dynamic simulations is that we select random velocities from the Maxwell-Boltzmann distribution, so let us say for every given temperature we can draw for every given temperature given the mass of the system we can draw a Maxwell-Boltzmann velocity distribution, right now we can pick random velocities from that.

Now if we do that for several atoms of the system then essentially when you calculate the average temperature of the system it will come out to be the temperature that we give as an input. So for example let us say I have this distribution and then I want to find out the velocity of and I have this system of particles, I want to find out velocity of this one so I draw that from here and this one I draw that from here randomly and draw that from here randomly, if I do that enough number of times then essentially I am sampling the full distributions and therefore we need to recalculate the temperature back again we are going to get 300 kelvin, is it clear?

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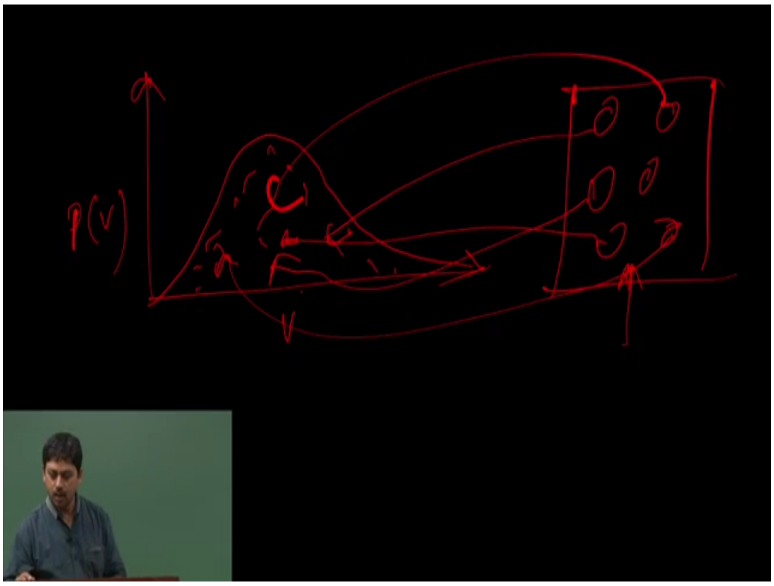

Once more, okay. So I will go here so let us say I give you a system of gas particles and I give you a temperature and you know the mass of the particles let us say, so it will have a particular Maxwell-Boltzmann velocity distribution. Now I will pick up random velocity so this is probability of velocity and this is the velocity, I will pick up random velocity from this distribution for that also I will pick up, for this also I will pick up all I am doing randomly assigning velocities.

Now if I have several thousand molecules here then essentially I am going to cover the entire distribution itself. So therefore I will recalculate the temperature of this particular box I am going to get the desired temperature that was that input. So therefore, you understand therefore even though I have one value of temperature I have several possible velocities of the particle and this is regularly done in molecular dynamic simulations where let us say we start a system box of water molecules at 300 kelvin, we draw the velocities initial velocities randomly from Maxwell-Boltzmann distribution, okay.

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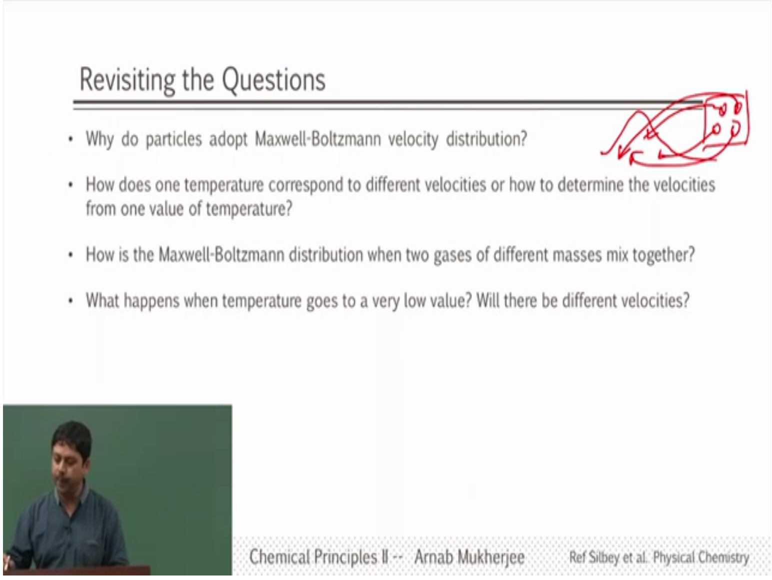

Revisiting the Questions

- Why do particles adopt Maxwell-Boltzmann velocity distribution?
- How does one temperature correspond to different velocities or how to determine the velocities from one value of temperature?
- How is the Maxwell-Boltzmann distribution when two gases of different masses mix together?
- What happens when temperature goes to a very low value? Will there be different velocities?

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How is the Maxwell-Boltzmann distribution of two gases of different masses mix together? That was another question very interesting so let us say I given a mass so for example if you mix two different temperature of same masses gaseous systems of same masses but two different temperature when you mixing them you know that it will come to a different equilibrium temperature and therefore the distribution will shift to a different value that is not a problem.

How about the mass? Let us say if you mix nitrogen and oxygen at a given temperature. Now you know that at one value of mass you have one distribution and another value of mass you have another distribution. Now what will be the overall distribution? So it turns out that if you do the calculation you will turn out that overall distribution is actually a product of both the distributions.

So you for let us say mass 2, you will draw from the distribution that is given by mass 2 for Maxwell-Boltzmann distribution and for mass 1 you will draw from the distribution given by mass 1. So therefore, let us say you are talking about initial velocities of proteins, proteins will have several different types of atoms, right. For each of the atom there is a corresponding Maxwell-Boltzmann distribution you are only going to change the mass and you are going to randomly pick up the velocities from them and eventually what will happen is that you are going to get velocities for all the atoms of the protein and you measure the temperature back again, you are going to get the temperature that you gave as an input.

What happens when temperature goes to very low value? So as you will see that temperature is in the temperature will modify the variance of the distribution, so therefore when that temperature goes lower and lower value the distribution is going to be more and more picked.

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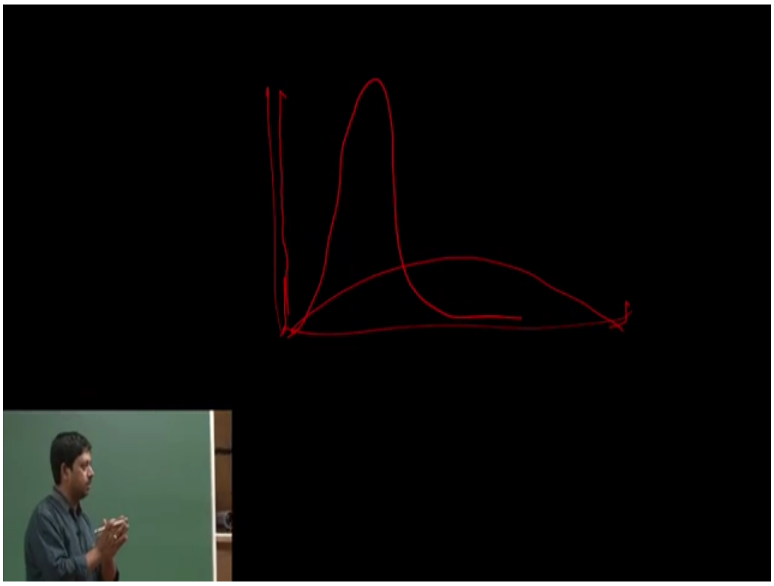

So let us say at a higher temperature if the distribution lies this, at a lower temperature the distribution is going to be picked. Now if you go to very very low temperature, you will have a very sharp pick like that, so of course it is still Maxwell-Boltzmann distribution however, it is so narrowly picked that you know depending on your error bar of calculations it will be that much.

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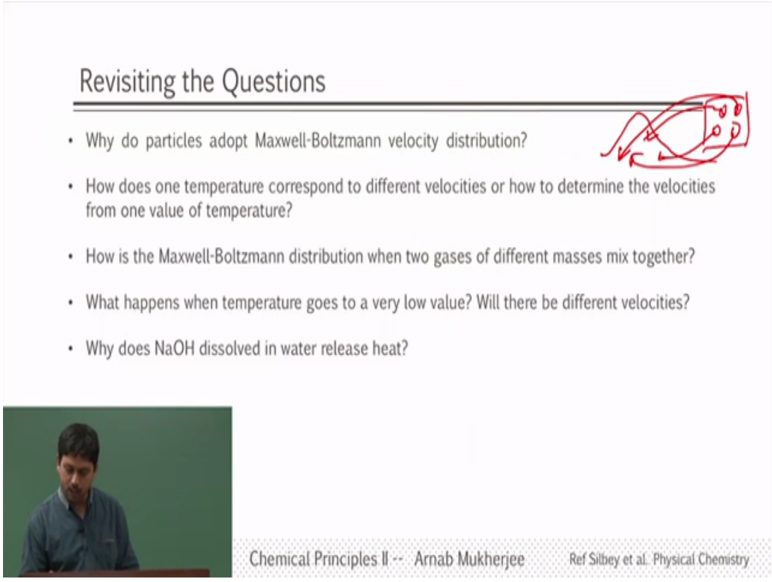

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Why does NaOH dissolved in water release heat?

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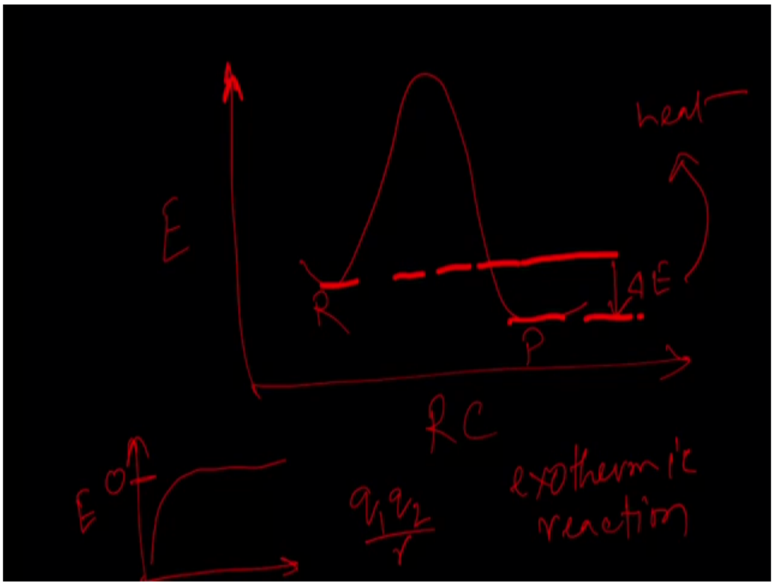

This is want to clarify back again, so we discussed about energy versus reaction coordinate and we discussed that when the product is less than a reactant in energy less than energy of the reactant then the system gets stabilized and this delta E amount of heat released to the environment as heat and that is how we call that as exothermic reaction, which means that when we drop NaOH in water and it got heated up we calculated the temperature, right it went to 60 degree from 40 degree, which means that it release the heat, which means it is an exothermic reaction.

That indicates that NaOH in water is more stable than NaOH alone, now how does that happen? Because when you put water Na plus and OH minus gets separated, once they get separated energy should increase because coulombic interaction goes by 1 by r, right coulombic interaction is 1 by r but here the energy is minus 1 by r, is it not? So therefore it is going to be like this, where this is 0 and this is a negative value remember it is q1 q 2 by r and since q 1 is positive, q 2 is negative overall value is negative and as r goes to infinity is going to go to 0 value.

So when Na and OH are separated by water it should have increase the energy for the product, but there is a decrease in energy therefore, the heat is being is released. Now do you know why there is decrease in energy? Correct, so sodium hydroxide sodium Na plus and OH minus gets dissolved in water which means that water molecules solvent them, they stabilized these ions in presence of water and due to this stabilizations ions overall energy of the system goes lower. So NaOH in water is more stable than NaOH alone, because it is more stable the extra energy is released as heat.

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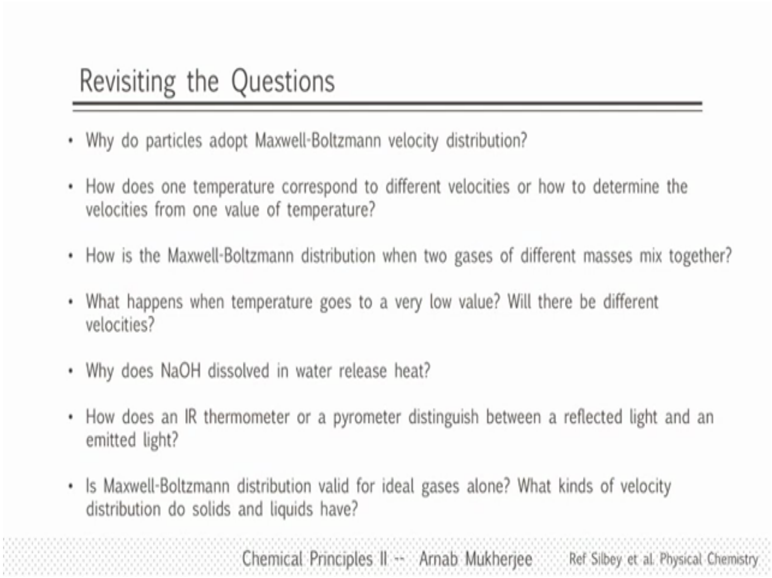

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- What happens when temperature goes to a very low value? Will there be different velocities?
- Why does NaOH dissolved in water release heat?
- How does an IR thermometer or a pyrometer distinguish between a reflected light and an emitted light?
- Is Maxwell-Boltzmann distribution valid for ideal gases alone? What kinds of velocity distribution do solids and liquids have?

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How does IR thermometer or pyrometer distinguish between reflected light and emitted light? That was a good question, so the thing is that we talked about blackbody radiation, blackbody radiation gives out all possible different frequencies it fit to that and therefore we get the temperature, right. However, (we) a machine will not know whether it is reflected light or which is emitted light due to its own thermal radiation.

So this pyrometer and infrared thermometer works on the principle of Stefan–Boltzmann law, where it calculates the energy density and the energy density is certainly will be different irrespective of the colour of the light, so therefore this white light temperature was 300 something that is much lower than the yellow light, but blackbody radiation wise a blue light should have hand much much higher temperature.

Is Maxwell-Boltzmann distribution valid for ideal gases alone? Because we have derived that or we have talked about that in case of ideal gases. Now how does it work for let us say liquids or solids? So it turns out that ideal gas does not have an interaction between the particles, but it turns out that even when there is interaction between the particles they are also Maxwell-Boltzmann velocity distribution be valid, even you know recent papers was that it is valid for solids also and liquids.

So therefore when we talk about proteins we actually take the velocities we can take velocities from Maxwell-Boltzmann velocity distribution that is the reason even when there is interaction present. So that clarifies all the questions, you have any extra? Okay, so we are going to go to the next topic of real gases, we talked about ideal gases and we talked about (interaction) internal energy of the system.

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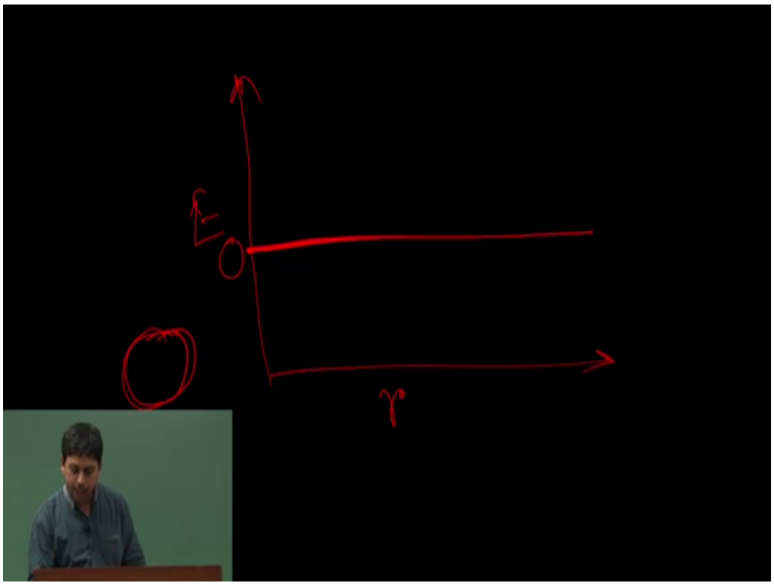

Now if you connect these two things you will see that ideal gas does not have potential energy it has internal energy but only kinetic energy and kinetic energy as you know that it is related to temperature therefore the energy of an ideal gas is nothing but that is coming from only the temperature and it does not have any potential energy interactions which means that if you know plot energy of an ideal gas with respect to distance, do you know how it will look like?

For two ideal gas particles as a function of their distance how the energy will look like? As a function of their distance how they will look like? Correct, constant but what is the value of the constant? 0, the value of the constant is 0. So irrespective of the distance you see even when r equal to 0, so that means that ideal gas particles they can actually be on top of each other without any problem because they are ideal gas, they have no interactions among itself, all of them can come in the same place because there is no interaction energy and it does not matter whether they are close or far away.

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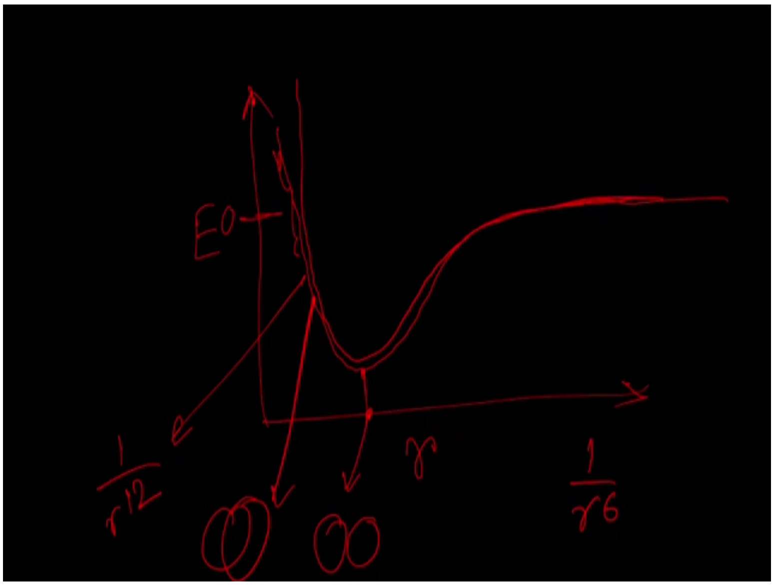

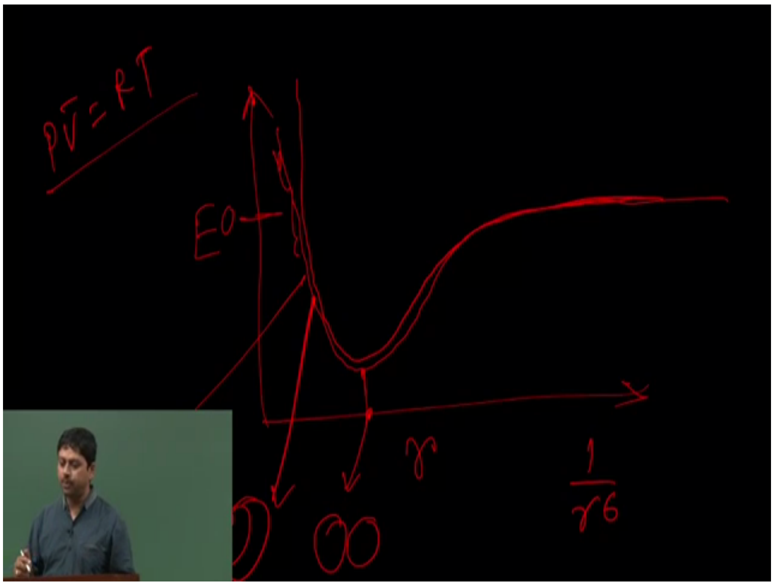

However, real gas systems will not be like that and as we have shown yesterday that a real gas typically will follow this kind of profile with respect to distance that means when it is very far away it will have 0 energy interaction energy, right let us say 1 kilometre apart, it does not have to go to 1 kilometre it can go to let us say few nanometres it will be 0 because there is no interaction between the particles, but as it comes closer and closer what will happen is that it will feel an attractive interaction and that attractive interaction happens due to dispersion type of interactions.

Dispersion is an induced dipole induced dipole interaction (())(13:59) density will induce a dipole on the other molecule which will again in turn will induce a dipole on this one and therefore you will get an interaction and that interaction typically goes as 1 by r to the power 6, very fast it goes very fast to 0, r to the power 6 means is really really fast 6th power, right.

Now if you bring them even closer even closer, what will happen? It will start feeling a repulsion because now the electron densities are trying to compress on each other without any bonding see it is very different case than bonding, in case of bonding electron density is overlap and they form a new type of systems, but here only thing that is happening is that the repulsion between the electron densities.

So therefore when they are very close then it rises extremely sharp, so my drawing is not accurate, it is very sharp rise and then decay and this sharp rise happens typically as r to the power 12. So you see now that unlike ideal gas, the real gas systems because of its interactions will not follow the ideal gas type of equation. So for ideal gas it was PV equal to RT, right equation of state PV bar meaning 1 mole of gas, but whenever there is an interaction with the particles we can expect that it will no longer be same, it is going to be different. Now how different it is going to be that is what we are going to talk about today.

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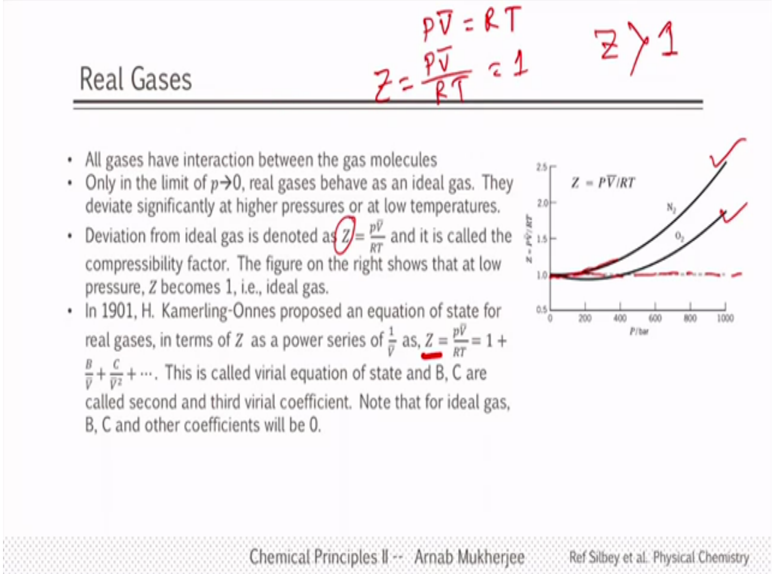

$p\bar{V} = RT$

$Z = \frac{p\bar{V}}{RT} \approx 1$

$Z > 1$

Real Gases

- All gases have interaction between the gas molecules
- Only in the limit of $p \rightarrow 0$, real gases behave as an ideal gas. They deviate significantly at higher pressures or at low temperatures.
- Deviation from ideal gas is denoted as $Z = \frac{p\bar{V}}{RT}$ and it is called the compressibility factor. The figure on the right shows that at low pressure, Z becomes 1, i.e., ideal gas.
- In 1901, H. Kamerling-Onnes proposed an equation of state for real gases, in terms of Z as a power series of $\frac{1}{\bar{V}}$ as, $Z = \frac{p\bar{V}}{RT} = 1 + \frac{B}{\bar{V}} + \frac{C}{\bar{V}^2} + \cdots$. This is called virial equation of state and B, C are called second and third virial coefficient. Note that for ideal gas, B, C and other coefficients will be 0.

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So all gases have interaction between the gas molecules, now only in the limit of p equal to 0, so what do we mean by p equal to 0? Is that when the pressure is really really less and the pressure will be less when the volume is much larger at a given temperature. So volume is larger means in the same volume let us say there are two particles in a small volume now there are two particles in very large volume and being gas molecules they will try to go everywhere and therefore effectively interactions will be extremely minimal because they will spend more time further apart from each other.

That will be the reason that at p equal to 0 the real gases will behave like an ideal gas because ideal gas has no interactions at p equal to 0 real gases spent time far apart from each other and therefore it will have 0 interactions most of the time and therefore it will have the property of just like an ideal gas. So they deviate significantly however at higher pressure, higher pressure means again volume will be less so particle spent close to each other and you have seen that when they spent close to each other they will have an interaction with each other and because they will have an interaction there will be some changes in the equation of set.

Now how do we understand that? Now deviation from ideal gas is denoted as Z a compressibility factor, compressibility factor is given by Z which is pV by RT and it is called, okay the figure on the right shows that at low pressure Z becomes 1 because at low pressure it forms like ideal gas, right like as I said that p tends to 0 it will become ideal gas. Now let us write that so we know that PV bar equal to RT, now if I divide by RT it will become PV by RT equal to 1, this is the equation of an ideal gas.

So at low pressure since it becomes a ideal gas, our Z which is defined as PV by RT will become 1 and you see in the graph at very low pressure it starts with 1. However, since a nitrogen and oxygen both are real gases they significantly deviate from the value of 1, 1 goes oxygen goes little bit lower than 1 you see and then goes upper. So at high pressure all of them will be higher than 1, but however at intermediate pressure it can go below 1 also and we have to understand why it goes below 1, right. So it is less than whatever would be PV, whatever would be for an ideal gas.

So in 1901, Kamerling-Onnes proposed an equation of state for real gas. Now this equation that this profile that you see in you know both these graphs they no longer represent a very nice looking profile, what I mean by that is that it is not a straight line or a parabola, a straight line is 1 order equation y equal to mx, a parabola will be second order you know x square and then third order and fourth order.

However, for any complicated function you may not fit the function with one or two orders. Therefore, you need a polynomial to fit any arbitrary curve. So Kamerling-Onnes proposed this particular equation of state as Z equal to PV by RT as 1 plus B by V C by V square and things like that, so have you heard about Taylor expansion?

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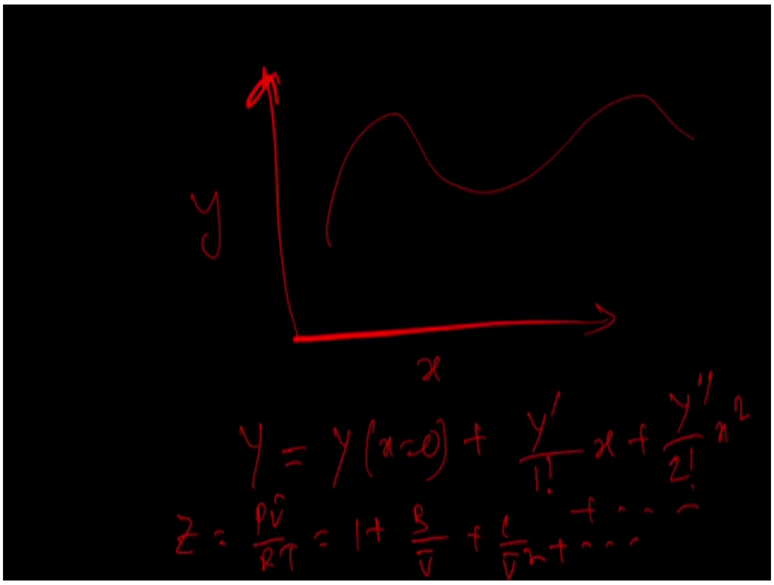

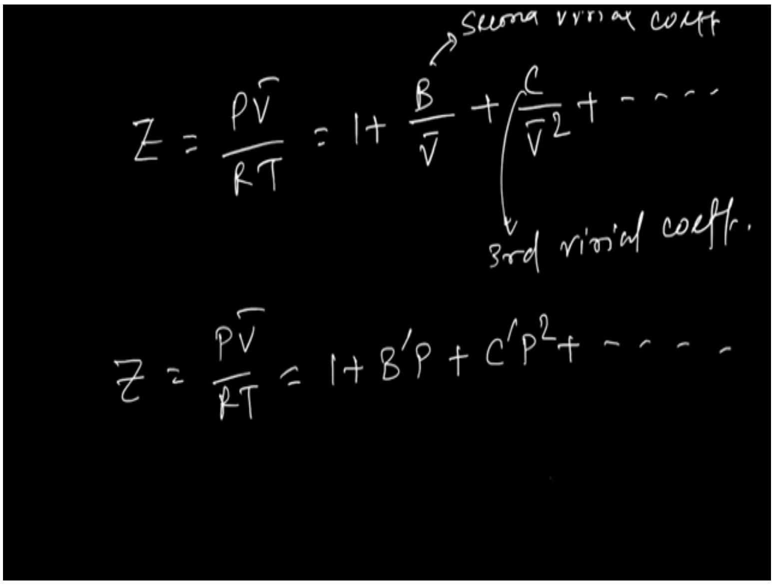

So Taylor expansion says that any graph that you take, so this is let us say y and x then you can expand that in terms of y x equal to 0 plus y prime y prime is the derivative by factorial 1 into x and then y prime prime by factorial 2 x square and things like that. So since it has an infinite number of infinite number of powers, one can fit any equations with that, right. So therefore Z which is PV by RT can be also written as a Taylor expansion of volumes (()) (20:12) by volumes PV by RT equal to 1 plus B by V C by V square and things like that.

So this is expanding the compressibility factor in terms of molar volumes V bar is a molar volume. Now what is B? B equals second virial coefficient, C is called third virial coefficient and things like that, second virial is basically the second term and third virial is third term. So by expressing Z in terms of all possible series powers of molar volumes one can fit any any real gas expression.

Alternatively you can also express this one in terms of pressure but there we will let us say use B prime P C prime P square and so on, okay. So this is how a real gas real expression is used. So you can this is just a fitting parameters, once you get the experimental value of this then you fit to this and you get your virial coefficients.

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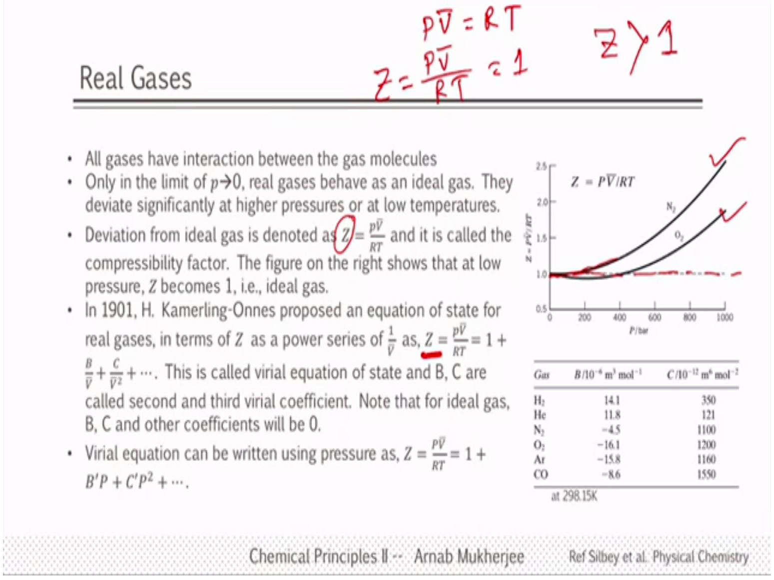

Real Gases

$p\bar{V} = RT$

$Z = \frac{p\bar{V}}{RT} \approx 1$

$Z > 1$

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- Virial equation can be written using pressure as, $Z = \frac{p\bar{V}}{RT} = 1 + B'P + C'P^2 + \cdots$.

Gas	$B/10^{-6}\ m^3\ mol^{-1}$	$C/10^{-12}\ m^6\ mol^{-2}$
H_2	14.1	350
He	11.8	121
N_2	−4.5	1100
O_2	−16.1	1200
Ar	−15.8	1160
CO	−8.6	1550

at 298.15K

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And typical values of this virial coefficients are given here. For example you can see hydrogen, helium has positive value of B and nitrogen, oxygen, argon and carbon have negative values of B. Now do you have any idea why in certain cases B is positive and certain cases B is negative? So think about only two terms Z equal to 1 plus B by V, because see what happens is that you also you will see in the Taylor series is that often your coefficients become smaller and smaller as you go along with the power because it will pretty much be fitted let us say with 3 order or 4th order, you do not need to go beyond that often, right. So but the first order is most important because the contribution of that is very important because that is what deviating the most.

Then you know the second term will be having lesser contributions and things like that, so now let us say we only talk about two order 1 plus B by V, now can you say that why certain cases B will be negative and what is the implications of having a negative value?

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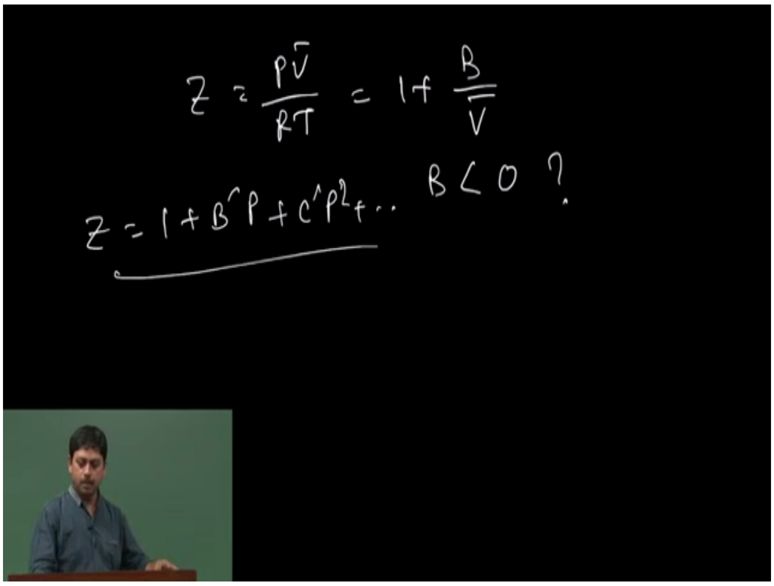

So let us say we go here and say Z which is PV by RT, let us say 1 plus we truncate it at the label of this stage and if B is negative what will happen? So Z will be less than 1 you see that is the reason your graph or certain cases are going down below 1 and then going up and certain cases it was not going up at all, if B is positive it will be more or less always positive however, if B is negative then it will go negative and then positive because finally at a large value of pressure you know that the higher terms will actually contribute because you can also think in terms of pressure, right.

So Z equal to 1 plus B prime P, so at a very large value it the higher powers will come. So now question is that why B is negative in certain cases? So we know that because B is negative it is actually dipping it and then going up so why B is negative, so we will have to in order to understand that we will have to think about a simpler picture than actual real gas, so we will do that in a moment.

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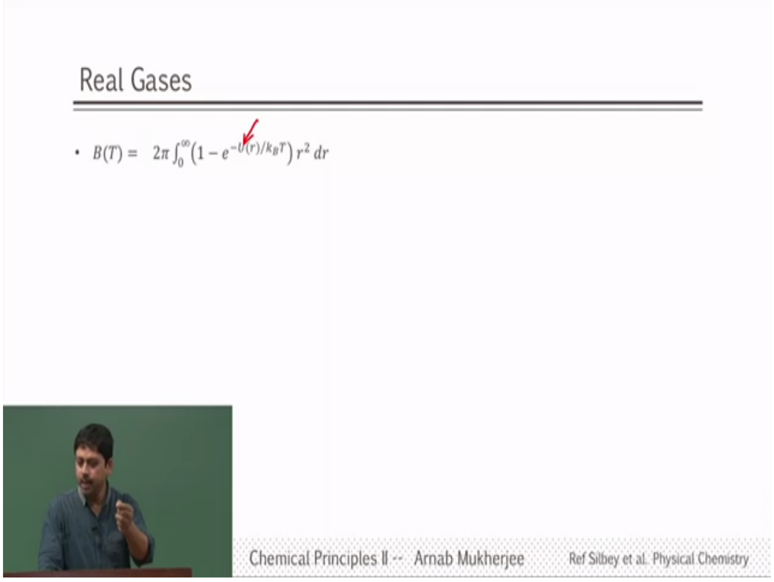

Real Gases

- $B(T) = 2\pi\int_0^\infty \left(1 - e^{-U(r)/k_BT}\right) r^2\, dr$

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But statistical mechanical derivations which of course we cannot discuss here fully, but one can show that the second virial coefficient B originates due to intermolecular interaction which I told you right. So here U r is a interaction energy between two particles and we have shown you how U r changes I mentioned that as e but you can take that as U, right.

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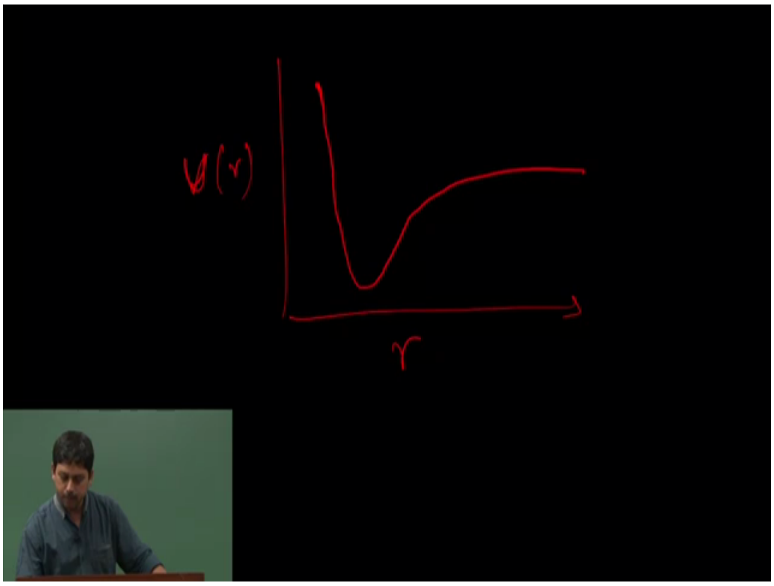

So U r, I showed you right that U r changes with this kind of expression with this kind of profile, right.

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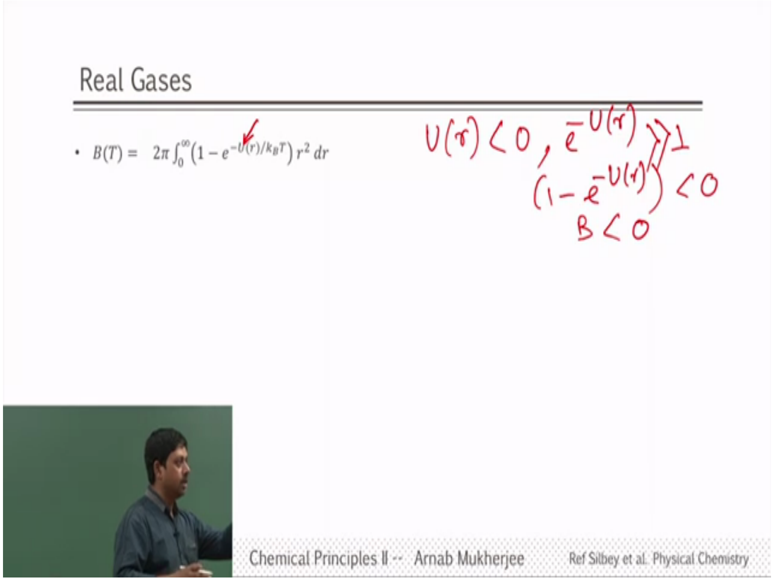

Real Gases

- $B(T) = 2\pi \int_0^{\infty} \left(1 - e^{-U(r)/k_B T}\right) r^2\, dr$

$U(r) < 0,\ e^{-U(r)} \gg 1$

$(1 - e^{-U(r)}) < 0$

$B < 0$

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So now B T is like this, now let us take one you know special case let us say U r equal to 0 for all r, what will happen? This quantity will become 1 minus 1, right so B will become 0 and it will reduce to ideal gas. Now let us say U r is negative, what will happen? If U r is negative then e to the power minus negative of negative will be positive, so therefore 1 minus this term if it is greater than 1 the overall B will be negative.

So stronger the interaction between the particles B will go to negative value, is it clear from that particular equation? Is it clear? So if U r is negative then e to the power minus U r will become a positive quantity or much greater than 1 and therefore 1 minus e to the power minus U r will become a negative quantity and B will become a negative quantity, okay. So that means the cases in which there is stronger interaction the B will be negative, okay.

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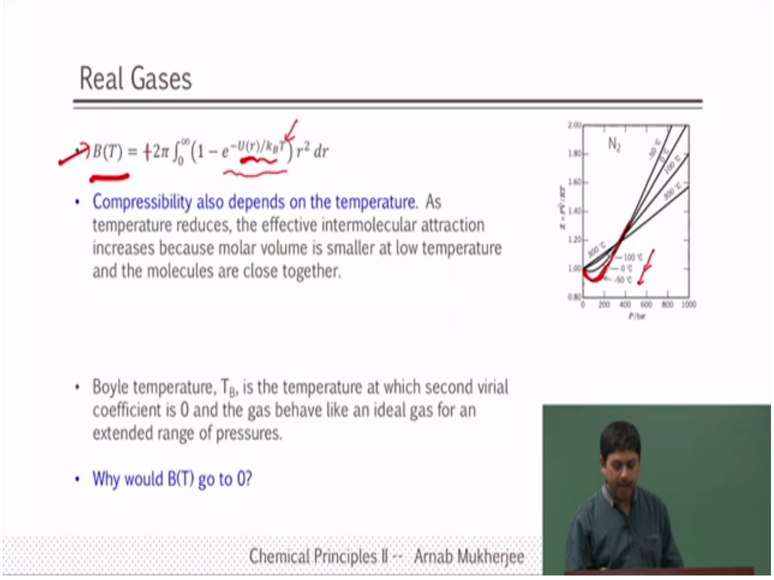

Real Gases

$B(T) = +2\pi \int_0^\infty \left(1 - e^{-U(r)/k_BT}\right) r^2\, dr$

- Compressibility also depends on the temperature. As temperature reduces, the effective intermolecular attraction increases because molar volume is smaller at low temperature and the molecules are close together.
- Boyle temperature, T_B, is the temperature at which second virial coefficient is 0 and the gas behave like an ideal gas for an extended range of pressures.
- Why would B(T) go to 0?

Chemical Principles II -- Arnab Mukherjee

So now compressibility depends also on temperature, so as temperature reduces because B is a function of T, so as you can see that as temperature reduces so T will become less, if T becomes less than U r by k B T becomes larger and when that becomes larger this overall quantity will become more negative and overall value of B T will become more negative.

So as temperature becomes lower what is going to happen is that interactions effective interactions between the particles will become stronger and therefore it will be more negative as you can see in this particular picture here that the nitrogen gas molecules are shown against pressure at different different temperatures and you can see that as the temperature goes lower values from 100 to 0 to 50 degree initially at low value of pressure it is becoming more negative and then it becomes positive that indicates that that effective B the B value with temperature lowering of temperature is also getting more and more negative and that is how you see the (())(27:28) if the U r interaction is stronger, okay.

And you will also see later on that why it is always it will minus U r by k B T because that is what the Boltzmann factor is. So lower the energy more probability of the system to be there, okay and at a particular temperature so as you see as you go down so the profile of Z is changing now at a given temperature this situation will come where this B will become B T will become 0 at a given temperature because it will be close to 1, right.

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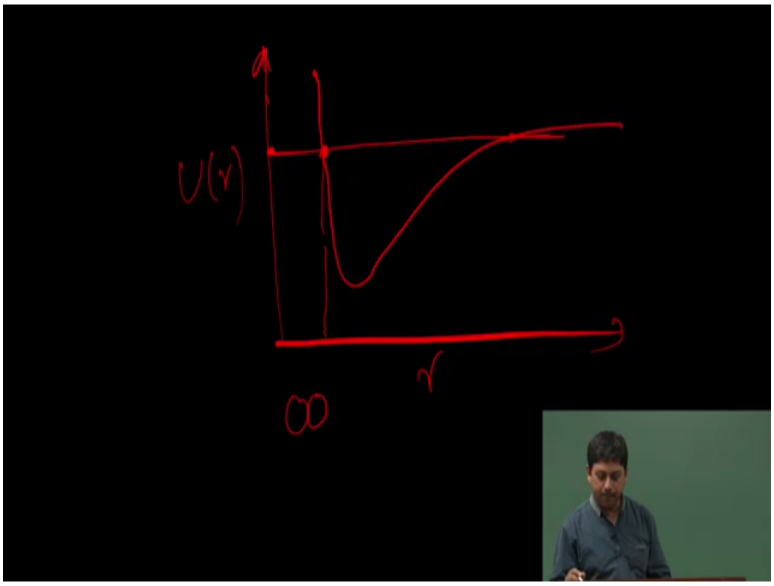

And that also you can see here that even for a real gas if you draw this profile again, so 0 is here right. So when it is far apart it is 0, but also when they are close together it is actually it turns out that this is a situation when they are actually touching each other at that position also it will become 0 the potential energy is 0 before it actually goes to repulsive mode.

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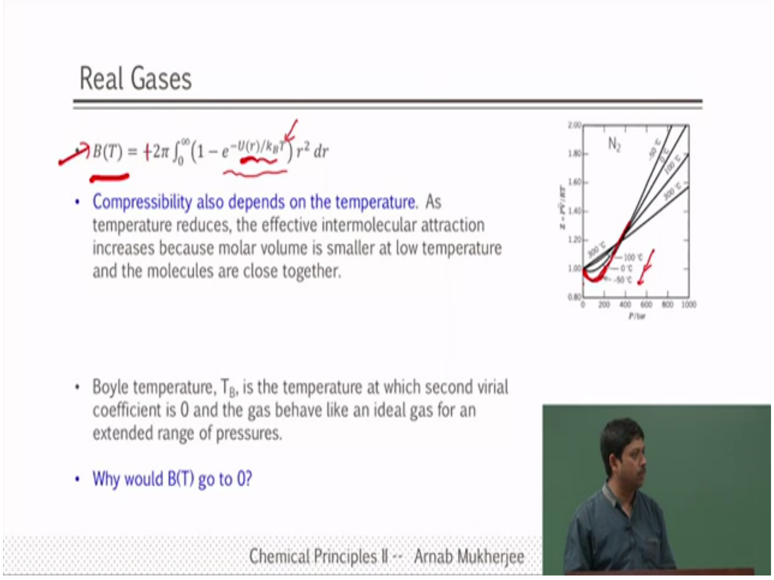

Real Gases

- $B(T) = +2\pi \int_0^\infty \left(1 - e^{-U(r)/k_B T}\right) r^2 \, dr$
- Compressibility also depends on the temperature. As temperature reduces, the effective intermolecular attraction increases because molar volume is smaller at low temperature and the molecules are close together.

- Boyle temperature, T_B, is the temperature at which second virial coefficient is 0 and the gas behave like an ideal gas for an extended range of pressures.
- Why would B(T) go to 0?

Chemical Principles II -- Arnab Mukherjee

So at a given temperature what will happen is that this quantity will become very close to 1 and therefore 1 minus 1 will be 0 and B T becomes 0.

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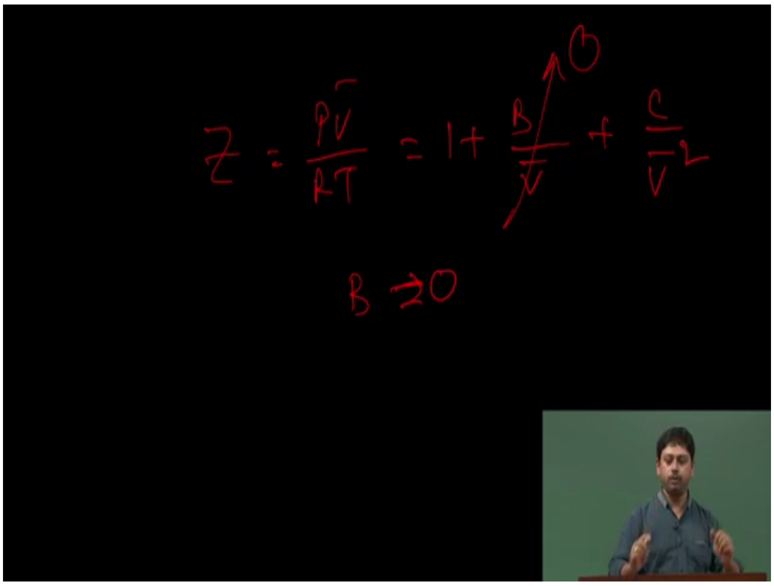

$$Z = \frac{P\bar{V}}{RT} = 1 + \frac{\cancel{B}}{\bar{V}} + \frac{C}{\bar{V}^2}$$

$B \rightarrow 0$

And if B T becomes 0 than in the expansion of Z which is PV by RT is 1 by B by V bar plus C by square, if this quantity goes to 0 then you can see that for a longer duration of volume it will behave like an ideal gas because the square terms typically pick up later on initially it will not pick up, in the first order it is not picking up, it is picking up only at the second order. So Boyle's temperature is the temperature in which B is equal to 0, the temperature corresponding to which the B is equal to 0 is called Boyle's temperature because for a longer range of volume it will behave like an ideal gas.

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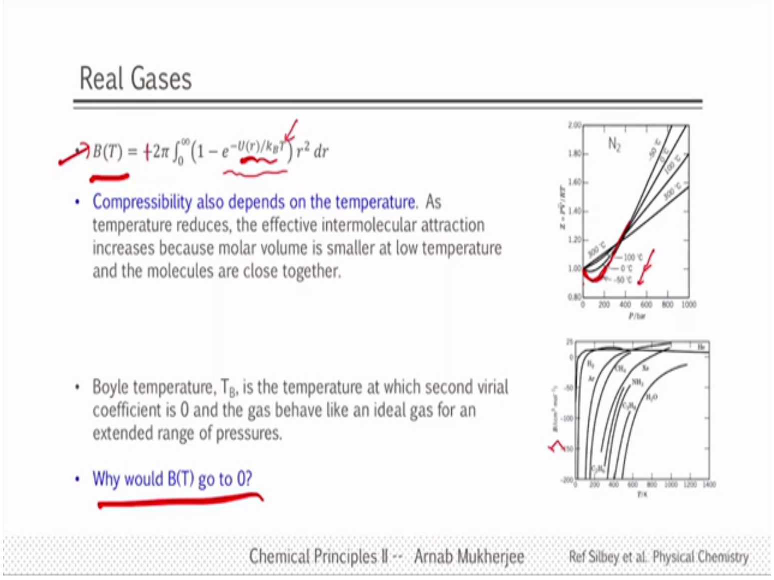

Real Gases

$B(T) = +2\pi \int_0^\infty \left(1 - e^{-U(r)/k_B T}\right) r^2\, dr$

- Compressibility also depends on the temperature. As temperature reduces, the effective intermolecular attraction increases because molar volume is smaller at low temperature and the molecules are close together.
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- Why would B(T) go to 0?

Chemical Principles II -- Arnab Mukherjee   Ref Silbey et al. Physical Chemistry

Now why would B T go to 0? Because we have discussed that there are situations where it will also even for a real gas it will come to a situation where the interaction energy can go to

0 because it is basically the balance between repulsion and attraction, there is a plot here that how the B changes with different different temperature for different gases and you can see that various gases at various different temperatures are going to 0.

For example hydrogen T B is lower than water and ammonia and things like that. Now you can you have to reason out that why ammonia will have T B higher than hydrogen and things like that. So if there are stronger interactions then you need higher temperature in order to make it 0, because it has to balance between U r by k B T, right.