Advanced Chemical Thermodynamics & Kinetics
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Lecture – 01
Review of Classical Thermodynamics 01

Hello everyone. So, welcome to this new course on Thermodynamics and Kinetics, which is offered through NPTEL. And this course is designed at an advanced level, compared with earlier course, which I offered in the last semester. And that was an at an introductory level course on the same subject. So, we will first give you an overview of the earlier course, in which we covered the general or the introductory level various aspects of thermodynamics and chemical kinetics. So, to begin with we will first discuss on the properties of gases. So, let us start with that topic

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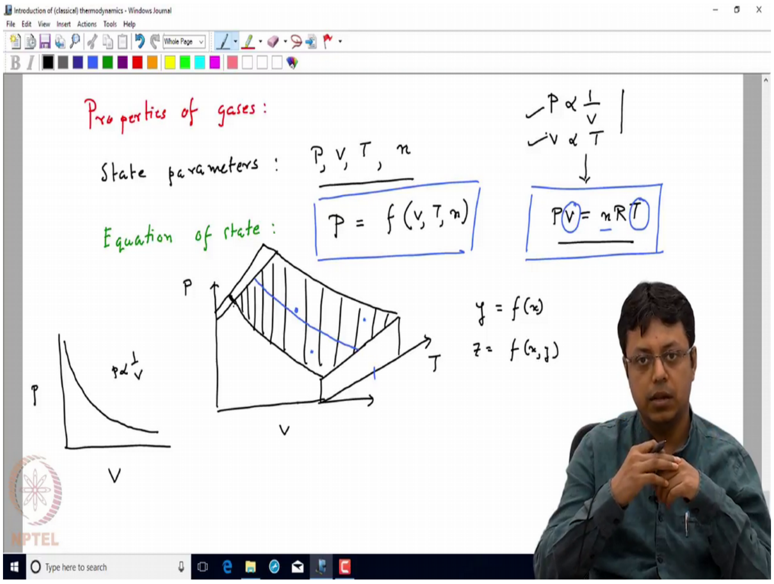
Properties of gases:

State parameters: P, V, T, n

Equation of state: $P = f(V, T, n)$

$P \propto \frac{1}{V}$

$V \propto T$

$PV = nRT$

$y = f(x)$

$z = f(x, y)$

The properties of gases; now, when I tell the properties of gases it means actually any so, we have to first define the phases of matter. As you know that in classical thermodynamics, we always talk about matter as a macroscopic system. Meaning we do not give any particular microscopic detail, how the matter is composed of like you know already that any matter is composed of molecules and molecules are composed of atoms.

So, this kind of detail is not necessary to describe classical thermodynamics. Similarly, the nature of energy is also not necessary in the sense that, like for example, the form of light, we you know that light is an electromagnetic wave. You can also explain it in terms of energy quanta which are known as photons. So, those descriptions are not necessary.

We just use this macroscopic or general description of matter and energy. And we will establish relation how matter and energy are basically interacts with each other. And there which lead to some physical chemical transformations. So, matter continuously exchanges energy with the surrounding a system. And then we actually see the effect of the system, of that process which the system is undergoing, on the surrounding. And that is how we make actually interesting experimental arrangement to formulate some laws in classical thermodynamics.

Now, to begin with as you know that matter can exist in 3 major forms. Solid, liquid and gas and we will start with the very the simplest form of matter which is the gaseous form. Now, whenever we talk about matter in a macroscopic sense we have to first define: what is the state of the system. Now, as we know that for a state of the system are defined by something which are known as state parameters. And the most common state parameters are pressure, volume, temperature. And of course, the sometimes we also write the number of moles of the gas molecule or something like that.

So, we have to establish a relationship between this pressure volume and temperature so, that we have a functional form. Say I ask you how the pressure is actually changing if I change temperature or volume or say number of moles. So, that functional relationship which connects all these macroscopic state parameters is called an equation of state. So, that equation will describe or completely describe the state of the macroscopic system. So, equation of state is nothing but suppose we are writing the equation as with respect to pressure. So, we write that pressure is a function of volume, temperature and the number of moles. We have to find out what is the equation of state for a particular gas.

Now, again so, we make some approximations. And those approximations for the gas molecules are will lead to something which is known as an ideal gas equation; already you know all these concept, but I am just restating all these basic concepts. So, that we are all on the same page. So, as you know that the ideal gas equation means, actually the molecules are in the gas behaves ideally in the sense, that there is no intermolecular force. And also this there is no explicit volume of the molecules. In the sense that they are just point masses; so, if we make that approximation, we see that this equation of state has a particular form. And already you know that particular form is something like PV is equal to nRT which is the ideal gas equation.

And which actually people observed on experimenting on gases, which are real gases; but, in a at a very low pressure regime and high temperature regime. As you know that initially this actually equation ideal gas equation came from something like the Boyle's law, which actually states that the pressure is inversely proportional to the volume as well as the Charle's law, which actually says that we will vary as the absolute temperature.

And by combining Boyle's law and Charle's law, along with the Avogadro's concept, we got the ideal gas equation which is PV equal to nRT. Now, if we want to plot how the functional form of P looks like following this equation PV equal to nRT. We will get basically 2 variables let us say that n is fixed. So, my variables are here temperature and volume. And the function that we are going to plot is the pressure.

So, it will be a 3 dimensional plot because, there is one function, which is the pressure. Suppose we are plotting the pressure along this axis and then I am plotting the volume along this axis, and temperature let us say along this axis. Now we will get think about it like if I have a just 2 function that y is equal to function of x. So, x is the variable and y is the dependent parameter.

So, then it will be a line, because it is a if it is not a multivalued function, it will be just like a line. Now, if we have actually z is a function of x and y. So, we will have a surface. So, we will have a surface plot in this case also. And let us try to draw how this surface plot will look like. So, I on these axis, I am plotting T I can equivalently say that I can plot the temperature axis along here.

And then let us draw the surface and what we can first draw is this isosurface. Let me get some part. So, this axis remember is the temperature axis. And this axis was the volume axis. And the vertical axis is the pressure axis. And this is the pressure how basically the pressure changes. That is basically a kind of 3 dimensional plot which we have tried to draw here and on this 3 d plot we see that there is a surface.

So, this surface tells me that this is basically equation of this surface P equal to nRT by v. Now, any point on this surface actually is represented by this equation PV equal to nRT. Now, if I actually fix temperature, which means I have to take a slice along a particular temperature, let us say I am talking about this temperature, which has a particular value. And if I actually take a slice then I will see that the curve will look like something like this. How the pressure is varying with volume?

So, if I plot it separately, it will be something like this, which is nothing but the Boyle's law. Similarly, I can actually recover the Charle's law the at a particular fixed pressure, how it basically the volume varies with temperature and this is known as isobar, and this is known as isotherm for because actually Boyle's law we kept the temperature constant and similarly you can also do isocode when the volume is kept constant.

So, this surface actually is represents again the equation of state. And the Boyle's law and the Charle's law or the isotherm isobar as well as the isocodes can be actually recovered from this generalized surface. Now moving on next we talked about how the pressure varies or the how the how can actually pressure will define pressure for not a single component system, but a multi component system.

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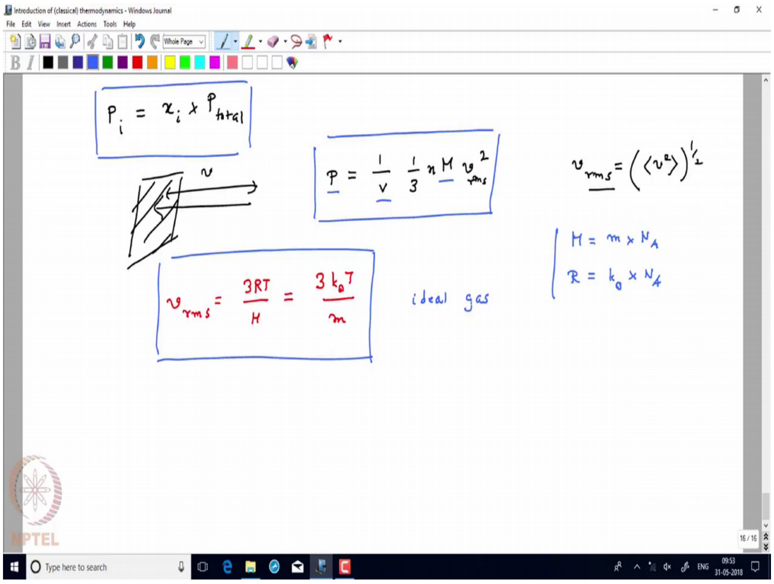

$$\boxed{P_i = x_i \times P_{total}}$$

$$\boxed{P = \frac{1}{V}\,\frac{1}{3}\,n M v_{rms}^2}$$

$$v_{rms} = \left(\langle v^2 \rangle\right)^{1/2}$$

$$\boxed{v_{rms} = \frac{3RT}{M} = \frac{3k_BT}{m}}$$

ideal gas

$$M = m \times N_A$$

$$R = k_B \times N_A$$

In the sense that I have few gases, let us say together and then I call it as mixture instead of a multi component system. So, next we talk about what is known as the pressure what are the expression for the pressure for a mixture. So, in that case, you know that we can always define some quantity which is known as the partial pressure, and which is related to the total pressure as it is the mole fraction of that ith gas times the total pressure.

Now, the partial pressure is defined suppose I have a container and I have 2 gases a and b. And now a has some pressure and b also has exert some pressure and so, that the total pressure will be the addition of these 2 pressures. Because it is basically related to the total force the molecules generate by bombarding on the wall. So, that has to be additive and pressure is just force per unit area. So, pressure is also additive. Now you can think that the partial pressure will be something like that if I if the one particular gas let us say the a gas if it occupied the entire volume in the absence of the other gas which is b that will be the partial pressure of a, and moment we insert the second gas b. Similarly, the b will also have a partial pressure if a is absent.

So, together when they are present in a mixture the total pressure will be the addition, and that is how we get the relationship from partial of partial pressure with the total pressure. Now this pressure has a molecular origin although we do not we said that we will not it is not necessary for us, to go back to a molecular picture. But, when we discuss the reaction dynamics in gas phase, they are actually we talked about how m other molecules are coming together they are colliding. And, what is a energy criteria that there is a threshold energy that you need to cross the for the reaction to happen and those things when you considered then you have to actually invoke a very much molecular level picture. And we will give a very simple description here, and here the atoms and molecules again are considered to behave ideally. In the sense again they do not have any intermolecular interaction.

There is no interaction potential between the 2 atoms or 2 molecules and. So, when I say 2 atoms or 2 molecules I am saying and I mean that the gas is either composed of atoms or molecules. For example, if I talk about helium gas. So, helium is mono atomic. So, it is between atoms only and when I talk about say methane gas, it is basically the interaction between methane molecules. But if the gases we have ideally. So, the point here is that the individual particles which are either atoms or molecules they do not interact with each other. And secondly, they are regarded as a point mass and since, they have still a mass. So, the pressure you can express as a rate of change of momentum divided by area. Because according to Newton's third law the rate of change of momentum is identical to force.

Now, how do you calculate the rate of change of momentum? You can actually calculate the how many molecules are striking the wall of the container. And then if you actually assume that there is some average velocity, with which the molecules are striking this wall. So, then actually you can derive a formula which is which you have seen definitely in your introductory level course on kinetic theory of gases. And there we finally, we get a expression for pressure as P is 1 over v, and then there will be a one third factor. So, this factor actually comes from the isotropic nature of the molecular speed, times n n is basically the number of moles times capital N, which is the molar mass and then I have v rms square.

Now, what is v rms? A v rms is basically the root mean square velocity. So, it is the square velocity and then I take the mean squared velocity, which is basically taking the average of the square velocities. And then I take the square root of that. So, that saw the name comes it is root mean square velocity. So, we get an expression for pressure and this expression and now we can actually further modify this expression. Because we know that the ideal gas equation that P times V is equal to nRT. And if we plug in all the things then we get an expression for the rms velocity or the root mean square velocity, and that will be 3 RT by m.

Sometimes we instead of R we actually express it in terms of the Boltzmann constant. Remember that m is the molar mass which is nothing but mass of an individual molecule times Avogadro number. Because, one mole contains Avogadro number of atoms or molecules; so, we can actually write it in that way. Similarly, R is nothing but the Boltzmann constant, which we write as k suffix B that the B denotes the Boltzmann constant and times it is the Avogadro number.

So, if we plug in these two conditions we get in terms of the Boltzmann condition Boltzmann constant, it is 3 k B T by small m where small m is the mass of the molecule or individual atoms. So, thus we get a expression for the rms. This is for of course, this is for an ideal gas or a gas that obeys the ideal gas law, which is PV equal to nRT.

Now, this much information from the kinetic theory of gases, as a sufficient and then what we discuss is that in collection of molecules, because a gas means it is a macroscopic system. And there are many molecules and all the molecules will not actually have the same velocity. There will be a distribution of molecular velocities and distribution of molecular speed. And by speed we mean that the only the magnitude of the velocity independent of any direction.

Now, the velocity distribution according to the Maxwell Boltzmann distribution law assumed it is not as entities also there are many arguments, how why the velocity distribution along a particular direction; If I talk, if I just write it as f of v x where f is nothing but a.

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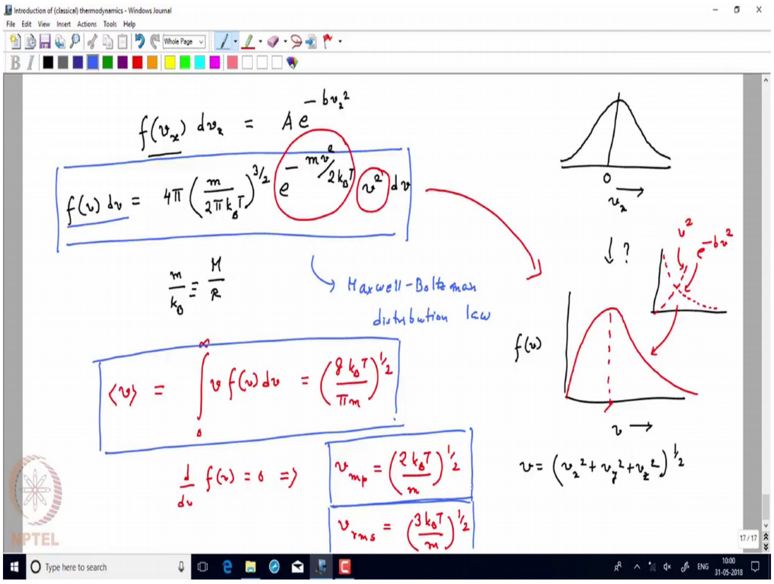

$$f(v_x)\,dv_x = A e^{-bv_x^2}$$

$$\boxed{f(v)\,dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_BT}\, v^2\, dv}$$

$$\frac{m}{k_B} = \frac{M}{R}$$

Maxwell-Boltzman distribution law

$$\boxed{\langle v\rangle = \int_0^\infty v\,f(v)\,dv = \left(\frac{8k_BT}{\pi m}\right)^{1/2}}$$

$$\frac{d}{dv}f(v) = 0 \Rightarrow \boxed{v_{mp} = \left(\frac{2k_BT}{m}\right)^{1/2}}$$

$$\boxed{v_{rms} = \left(\frac{3k_BT}{m}\right)^{1/2}}$$

$$v = (v_x^2 + v_y^2 + v_z^2)^{1/2}$$

Probability distribution of the fraction of molecules, which have say velocity from in the range v x to v x plus dv x; if I define it in that way. So, that will be something like some constant times e to the power minus PV x square. And that is a Gaussian function. So, in the sense that if I plot the velocity v x along this direction. So, the distribution will look like a Gaussian distribution. And remember that the velocity is when the velocity is 0 that actually picks up, in the sense that the velocity has both positive and negative direction. So, but from that actually we want to know how the speed distribution looks like, which means actually we will just talk about the magnitude of v independent of the direction and some probability.

So, this probability now actually tells you: what is the fraction of molecules having speed in the range v to v plus d x, and v plus d v. Where v is nothing but v x square plus v y square plus v j square and taking the square root of that and, if I want to derive that. So, then there are a few steps which we discussed in our earlier course. And finally, you will get an Maxwell Boltzmann distribution law in this form. So, it is 4 pi and then m by 2 pi k B t, raise to the power 3 by 2 instead of m by k B we could have written as capital m by R also. Into e to the power of minus m v square, by twice k B T. Into v square d v where v again is a molecular or atomic speed not the velocities.

So, this distribution law is known as Maxwell Boltzmann distribution law; which is already known to you Maxwell-Boltzmann distribution law. Now think about it this is a probability distribution as I said, because f v dv is basically the fraction of molecules or the probability of the molecules having speed in the range v to v plus d v. So, you can calculate any other quantity from this. For example, if I want to know what will be the value of the average velocity.

So, then all I have to do is that, I have to take the velocity multiplied with the probability distribution, and integrate over all possible distribution of speed. Now, in this case the speed distribution and go from 0 to infinity, it cannot go to negative because it is a speed distribution. And that you can easily work out using gamma function and you will figure out that the value will be 8 k B T by pi m square root of that. So, that is the average velocity and similarly we can talk about a velocity which is the most probable velocity, but before that let me just plot how this function looks like.

So, this function has basically 2 parts. As you can see there is a exponential part e to the power minus a b v square, and there is a v square part. So, the exponential part will actually be something like a decaying like this. And the v square part will actually dominate v square part actually will be something like this. So, let me redraw it once again. So, what I am saying here that this function is actually composed of 2 different functions are multiplication of two different function. One is e to the power minus v squared some constant into v square, that actually goes like this. And then there is e to the, it is just a v square term which is actually a quadratic function which will be something like this.

So, if I take a multiplication of these two these actually looks like this function. So, it actually goes to a maximum, as you can see. And if we want to calculate what is this speed which is a most probable, and then all we have to do is that you have to take that function and take the derivative of that function, and set it to be 0 to find the maxima and minima and that will give you the value of the most probable distribution. And that you will get as the most probable, is twice abt by m raised to the power half. And already we talked about the v rms in the previous section. I am writing it once again and that from ideal gas equation we got it as 3 RT by m, or let me actually use the similar notation k B T and small m.

So, we can write it as 3 k B T by m square root of that. So, we have actually definition of 3 different velocities. One is the root mean square velocity that is directly connected to the pressure of the system. And the second one is basically the average velocity which is 8 k B T by pi m. And then the third one is the most probable speed, which is basically the speed where actually the probability distribution is maximum or which is the most probable value of this speed distribution. Or, that or basically which is at the speed at which the probability distribution maximizes.

Now, having all these things in mind, next thing what do we try to calculate is basically what is the number of collision within the gas molecules; because, that will be very important in calculating the reaction rates. Because any reactions in the gas phase or liquid phase any common space is actually promoted initially by collision.

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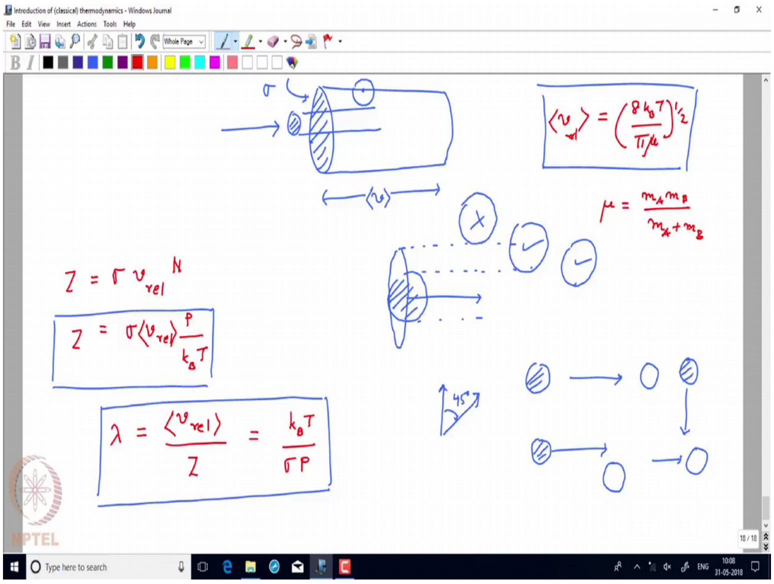

And for that actually you try to calculate that the number of collision that one particular gas molecule mates with many other gas molecules. And then you think that fine you let us consider a cylinder, of length say v. Because this is the time this is basically the length or I mean which this particular molecule will traverse per unit time. Because that is identical to it is speed. And then you talk about that whatever molecules are suppose this molecule is going inside, and it is this trajectory and other molecules which for which the center is actually lying within this cylinder, will collide because it is very easy to understand that if a molecule has a diameter like this, and it is moving in a straight trajectory and if a molecule actually lies out it will not collide.

The collisions will happen if the center of the molecule lie in such a way, that they just touch or they are inside. So, all these molecules actually will collide with this particular molecule, but this molecule on collide. So, in a sense what we are saying here we are talking about, some cross sectional area which is important and which basically is the cross sectional area of the cylinder. And all the molecules which for which the center of the molecules are within this cylinder, will actually collide with this particular molecule. And that we can actually calculate it very easily.

And you can actually just calculate the volume of the cylinder, you take the number density multiplied with the volume you get the total number of molecules. And from that you can actually calculate the collision frequency in terms of this cross section, if I call this cross section as sigma. So, then we get a an expression for the collision frequency. And that collision frequency expression will be something like if I call at call it as a z, and z will be nothing but sigma times v.

It is actually not v it will be actually v relative and because it is a relative velocity. Because we said that one molecule is moving all other molecules are static. This is perfectly fine because we are actually considering everything in a relative velocity frame, not in the absolute frame of the laboratory frame and then, multiplied by the volume. And then we can actually not volume it will be the number density. Which we denote as say capital N and then that actually we can rewrite as sigma into v relative, into P by k B t.

If P is the pressure so, this is the expression for collision frequency that is that number of collisions a particular gas molecule mix per unit time per unit volume. And now the interesting thing is what is interesting quantity to look at is the mean free path, meaning actually it is the distance of particular gas molecule travels between two successive collisions. And that you can again very easily understand how to calculate. So, per unit time actually it travels the v relative distance and then we also know that per unit time it is making so many collisions z collisions.

So, by logic actually this mean free path which is basically the distance traversed between collisions will be basically the total distance traversed per unit time, divided by the number of collisions per unit time. And which will be nothing but if I plug in all the relations all the expression. So, it will be nothing but k B T by sigma into p. Now, one thing we have written here we have written here as sigma P relative, but in reality it will be the average of the v relative. Now the question is what is average of v relative and. So, as you can see that it is basically the average speed, but it is the relative average speed. Now, you can think that: what is the relative speed between 2 molecules, at suppose one molecule is static and the second molecule is moving.

So, it can have actually a head on collision. That is one probability. It can also have something which is known as a grazing coalition, meaning the molecule just touches the other one the surface is just touch. And it can also have pollution like with respect to the other molecule in a 90 degree. So, considering all these possibilities, you can think that we can have a 0-degree collision, we have a one 80-degree collision something like that, but one 80 degree collisions we are not considering because it is a relative velocity.

So, you can have a 0 degree I mean collision it can have a 90-degree collision and if you take that average of this. So, you can think that one molecule is moving like this. The other molecule is basically moving like this at a angle which is 45 degree. So, if you take that. So, you have to take the projection of the velocities and the v relative will be nothing but just by from vector relation square root of 2 of the average velocity.

So, if you plug in all this relation, you will find that just like we had expression for average velocity, that v average was 8 cavity by pi m. So, you can easily figure out the relative velocity will be 8 k B T by pi mu where mu is the reduced mass of the 2 particle system. And it is defined as if I have, if I am considering actually the relative velocity between 2 molecules which are a and b. So, then mu is nothing but ma mb by ma plus ma, which is a reduced mass of the 2 particle system.

So, up to this point we actually we have discussed, what are the what are the basic concepts of the kinetic theory of gases. What are the properties of gases taking into account of the fact these gases are behaving ideally or basically we are following ideal gas law? So, the obvious question is what happens if the gases do not behave ideally or the or there is a deviation from ideal behavior. And which is what we observe in reality because, gases must be real gases. And all real gases behave ideally under certain condition which is like at very low pressure and a very high temperature

So, what is the equation for actual reality? Because the PV equal to nRT does not hold other than at a very low pressure and very high temperature. So, in order to do that we have to device or find some model, that can successfully explain the behavior of gases at other temperature at say normal temperature and pressure. So, then we actually talk about real gases. But again all gases are actually real gases. Real gases a show ideal behavior in the limiting case; so, we will now talk about the properties of those I mean properties of real gases or in terms of the properties of gases actually. In any condition not only at a limiting condition where; only the ideal behavior is shown.

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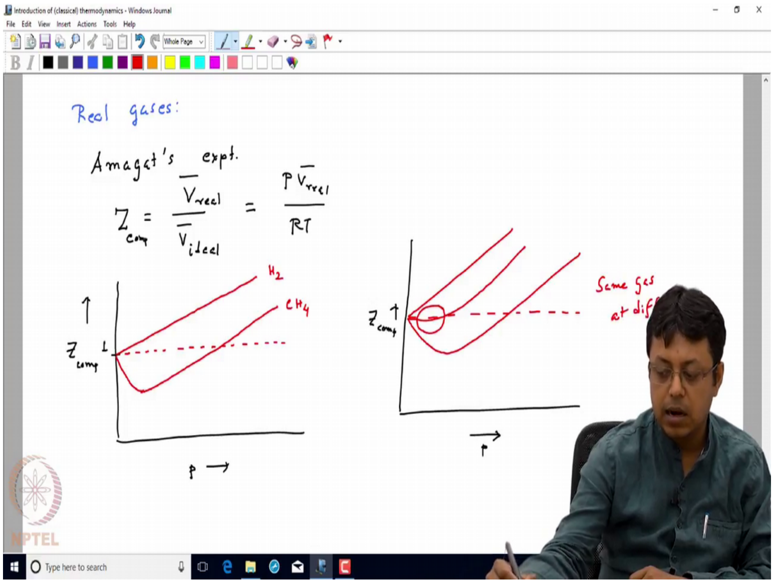

Real gases:

Amagat's expt.

$$Z_{comp} = \frac{\bar{V}_{real}}{\bar{V}_{ideal}} = \frac{P\bar{V}_{real}}{RT}$$

So, let us now start our discussion on the properties of gases or properties of real gases. So, the first thing we discussed when we discuss the properties of real gases is: what are the deviations from the ideal behavior, from real gases. And then we talk about two important experimental observation. And one is known as Amaget scarf, or which are actually based on the experiments by Amaget. And what Amaget plotted is basically a quantity, which is known as the compressibility factor. And which is defined as Z, but do not get confused with the Z, this Z and the collision frequency Z.

So, maybe we can actually write it as Z comp and that is defined as the molar volume of a gas and it is ratio to the ideal molar volume, or the molar volume of an ideal gas which, means if the gas behaves ideally the compressibility factor will be 1. If the gases volume is actually more than the ideal volume at a particular pressure and temperature; so, which means actually now the gas occupies more volume than the ideal problem or the gas is actually less compressible.

Similarly, you can think that if the actual volume or the you can actually put a suffix like a real volume, is less than the ideal problem which means the compressibility factor is less than 1, then the gas is more compressible. So, what all we want to do is get an expression for the compressibility factor and we know that P bar, again the bar notation is for 1 mole and P bar ideal is nothing but active I P following ideal gas equation.

So, this is nothing but P into V real divided by R T and this is the expression for compressibility factor and when Amaget plotted this compressibility factor, Z versus pressure. And remember that for ideal gas it will just be some curve, which is around at 1; because the compressibility factor is always one for ideal gas. And for some gases he observed that this is always increasing.

In the sense that the gases are less compressible, and the example is hydrogen at again room temperature. And which means actually it is a temperature dependent. And we will come back to it and that for other gases let us say for methane he observed, but there is an initial dip and then there is a rise. And when he did repeated the same experiment, for different gases at different temperature. He observed an interesting observation; again the Z equal to 1 line corresponds to the ideal gas behavior. And he found that for a particular gas, if we just keep on changing the temperature we will see curves like this.

So, and for a particular intermediate temperature, he found that this curve actually more or less lies on the ideal gas or the gas actually behaves more or less ideally. Because, as you can see that the slope is actually flat with the with respect to the x axis, where we are plotting the pressure, but this happens only in the low pressure region. So, that is something important which we will come back. And then the other experiment. So, this is for the same gas at different temperature. So, this was discussed in the earlier I mean earlier course.

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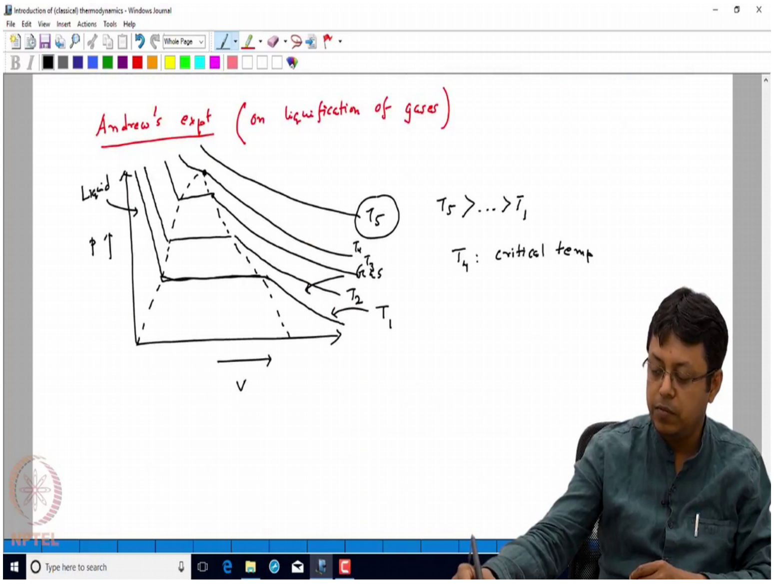

Or you can also get it from any standard textbook, which have been recommended to you. And then the second thing is the Andrews experiment. So, these are also experimental observation on liquification of gases liquification of gases. Now, liquification means actually, if I increase the pressure and decrease the temperature any gas actually condenses to form liquid. And the existence of liquid phase are basically these phase existence of this phase transition, clearly tells that there must be some attractive force between these gas molecules, which actually forces them to form liquid. Because, we know that due to the intermolecular interaction the attractive potential the molecules are forming liquid

So, which means actually this assumption in the kinetic theory of gases, that there is no intermolecular interaction is not correct. And let us try to plot the a (Refer Time: 38:02) Andrews a experiment what he actually observed. So, Andrews was trying to plot the pressure volume plots, which had nothing but isotherms at different temperatures. And he found that a typical curve actually looks like this.

So, this region is basically the vapor region or the gas region. So, it happens at a very, very low pressure regime, as you can see it is at a bottom of this pressure axis and, the below to very low value of the pressure. And at a very high value of the pressure this is basically the liquid origin. So, the gas is already liquefied and in between he observed a flat region where actually even if we were up changing the volume at a particular pressure and temperature. So, this is for a particular temperature, let us say T let us say T 1 and for that particular temperature and the pressure basically the condensation happens.

So, a phase transition is happening at a particular pressure and temperature and then the volume actually is shrinking. And this volume when it shrinks the pressure or temperature is kept fixed. And similarly if you what he did is that he repeated these experiments for higher temperatures. And here what he found that this particular region actually shrinks, this the region over which the phase transition happens.

And ultimately it reduces to a very particular point above which. So, these are at very various temperatures. Let us say T 2, T 3, this is T 4, this is T 5. What we have that T 5 is the highest temperature. And then he basically showed that we have a region comprising something like that liquid vapor equilibrium. And that region basically vanishes above at a particular temperature and that temperature he called as a critical temperature.

So, the above critical temperature always, the substance actually behaves as if it is a gaseous substance. So, that is why we made a comment that at a very high temperature, the ideal gas law is ovid. Although we are telling that at this temperature which is T 5 in this case, which is higher than the critical temperature we are calling it as if it behaves as an ideal gas, but the substance is not actually gaseous anymore. It is called a new state of the system which is known as the super critical phase or new phase of the system.

Now, in order to explain all this behavior, which is the Amagets curve which actually talks about the compressibility factor, and the Andrews curve which talks about the liquification of gases then many theoretical models came up.

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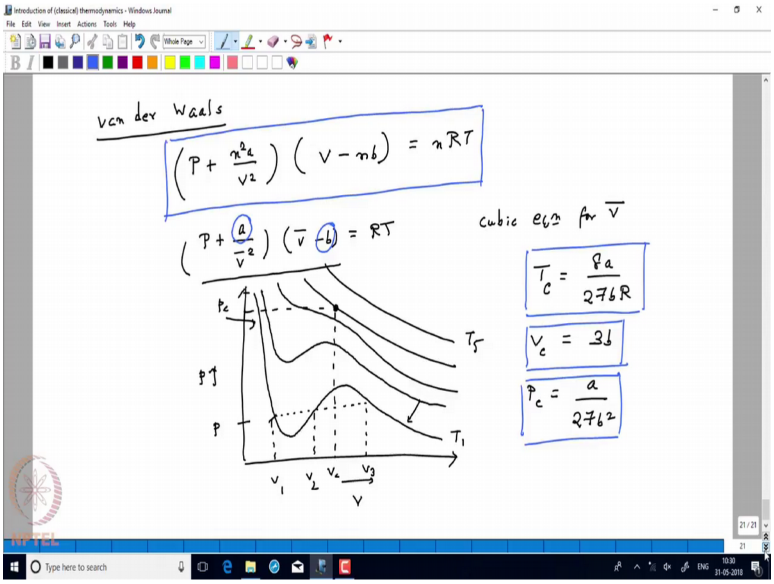

van der Waals

$$\boxed{\left(P + \frac{n^2 a}{V^2}\right)\left(V - nb\right) = nRT}$$

$$\left(P + \frac{a}{\bar{V}^2}\right)\left(\bar{V} - b\right) = RT$$

cubic eqn for $\bar{V}$

$$\boxed{T_c = \frac{8a}{27bR}}$$

$$\boxed{V_c = 3b}$$

$$\boxed{P_c = \frac{a}{27b^2}}$$

And one of the very simple, but yet very elegant model is that one which is which is put forward by Van der Waals. And the Van der Waals equation of state is something like this. P plus n square a by v square, where a is a constant, into v minus n b and b is also an constant is equal to nRT. Or we could write it in the molar volume notation, in the sense that for one mole it will be something like P plus a by v bar square into v bar minus b is equal to RT.

So, this is the Van der Waals equation of state because again this actually explains the state of the system. And if we want to plot this equation, how the pressure volume of the how the isotherms look like, we will see that this actually has a typical behavior like this.

And, if you remember that Andrews curve this region was kind of flat, when the liquification was happening, but Van der Waals equation of state actually shows that there is an interesting deep and rice behavior as we increase the volume or lower the pressure.

Now, it actually successfully explains the gaseous region as the liquid region, as well as this change in the phase. And if we actually keep on increasing the temperature, it also shows that there is an existence of a critical point. At some particular temperature, again we are using the similar type of notation. And then from that equation you can actually solve for the critical temperature.

What are the values of the critical temperature? You can actually analytically get an equation from the Van der Waals equation of state. And how do you do it ah? You see here that when we have a particular pressure let us say this pressure I have actually 3 volumes as you can see here this is just coming from the nature of the curve, and if you look at it carefully it is actually P plus a by v square into v minus v is equal to R T, and which means actually it is a cubic equation in v cube.

So, it is a cubic equation for v bar. So, for any cubic equation you will have 3 roots. And these are the basically 3 roots which are which I can write it as a v 1 v 2 and v 3. So, when you solve this equation it should get 3 roots, but at the critical point all these 3 roots actually merge together to a single point. So, that all the roots become degenerate and that way you can actually easily solve this equation. And basically talk about the maxima and the minima or actually you can say that all these you can actually factorize it into different terms, like we actually solve a cubic equation. And that way you can actually figure out what is the value of this critical temperature. And this value of this critical temperature is 8 a by 27 b R

Similarly, if you call that at that critical temperature if I call the corresponding volume as critical problem, and the corresponding pressure as critical pressure you can also figured those out. So, the corresponding volume will be 3 b and corresponding pressure will be a by 27 b square. So, using the Van der Waals equation of state one can actually get an expression for the critical temperature, as well as critical volume and critical pressure, which is great. Because this is a model which shows that look I can analytically find an expression for and also explain the existence of this critical state. And also explain the liquification of gases.

Similarly, one can also explain the compressibility factor. I am coming to that, but before that of what a little comment on this constant a and b. So, the a actually comes from the inter molecular interactions, which you already know when you study the Van der Waals equation of state. And that basically tells that the actual pressure will be always less than the real ideal pressure. Because when the gas molecule is going to strike the wall, it actually experiences a pool of the other molecules which are behind it, which is at the bulk and. So, it speed is actually slowed down and. Secondly, the volume occupied by the gas is actually there will be some excluded volume, in the sense that every gas molecule actually possesses some finite volume.

So, these two things actually leads to conceptual development of this in the equation, but again a and b here are empirical parameters. Which means actually you have to you have to figure it out for or you have to experimentally determine these parameters for various gases. Because, the attraction force intermolecular attraction force or the molecule volume from methane and the for hydrogen will be very different.

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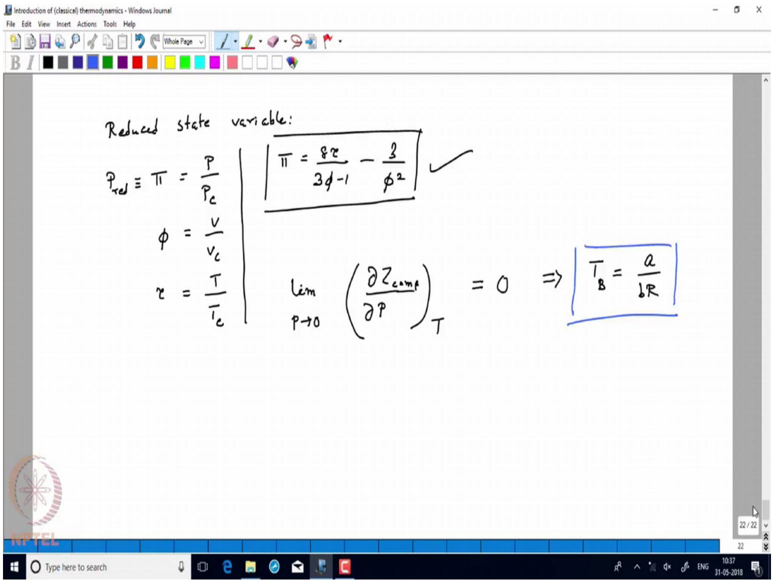

Reduced state variable:

$$P_{red} \equiv \pi = \frac{P}{P_c}$$

$$\phi = \frac{V}{V_c}$$

$$\tau = \frac{T}{T_c}$$

$$\boxed{\pi = \frac{8\tau}{3\phi - 1} - \frac{3}{\phi^2}} \checkmark$$

$$\lim_{P \to 0} \left(\frac{\partial Z_{comp}}{\partial P} \right)_T = 0 \Rightarrow \boxed{T_B = \frac{a}{bR}}$$

So, a and b are actually dependent on the gas molecules. Now, the question is this a limitation of Van der Waals equation. Which is not true because actually you can always define some quantity which is which are known as the reduced parameters or reduced state variables. In the sense that I can always write some suppose I have a pressure, and I can always take a ratio of the pressure to the critical pressure, we can call it as a pi.

Similarly, sometimes we actually write it as a P R or P reduced. Similarly, the volume we can actually define as the volume by the reduced volume. And some reduced temperature we can also define as the temperature divided by the critical temperature and if we actually plug in this relationship, into the Van der Waals equation after some algebraic like with manipulation. We can show that everything actually reduces to a very nice equation, which is pi is equal to 8 tau divided by 3 phi minus 1 minus 3 by phi square.

So, this equation is obtained after you start from the Van der Waals equation of state. Which is P plus n square a by P square, on all this thing and then you use the values of a b and R in terms of P c v c and dc. And then you actually write the P by P c as the reduced pressure, and this way and now you see that we actually get a very fantastic equation which is basically the Van der Waals equation is reduced form.

In the sense that now this equation does not contain any a or P, which means now I have actually removed the dependents of the Van der Waals equation of state on a particular gas. Because, it is not it is now independent of a and b, and now I can actually plot it and then if I plot phi versus pi that equation will be same for all the gases because it is all already the critical pressures as being divided.

So, all these explicit dependence on the constants a and b which are actually some kind of molecular parameters, can be removed if I express the equation of state in this particular form. Now, the next thing which we discuss in Van der Waals equation of state is that you can actually calculate: what is the compressibility factor which actually Andrews described. And remember that the compressibility factor is like the idea is that at what temperature this compressibility factor is more or less equal to I mean behaves like a ideal gas.

And, if you see this condition that which I have circled here and at some intermediate temperature; any gas actually behaves and ideally in the low pressure region; of course, because at a very high pressure region as you can see this part it is again deviating. So, what you can do actually using the Van der Waals equation you can actually evaluate this quantity. How this, what is the slope of this z, or the compressibility factor curve with respect to pressure. And that keeping the temperature constant that actually can set to be 0, but you have to remember that this is in the limit of P tends to 0.

Now, if you do it, then you will see that there is a temperature which is known as the boiling temperature. And this temperature I mean it will be basically at that temperature this will be 0. And then you can see that the expression for the ball temperature is very simple. And it actually depends on the ratio of a and b which are those molecular parameters. So, this ratio will basically tell you, that what is the boiling temperature for a particular gas or which means actually at that temperature at a very low pressure region the gas will behave ideal. And above the ball temperature you will have an or below the ball temperature the gas will have deviations as we have shown here. So,. So, those and at a particular at if the temperature is equal to the ball temperature, then the gas will behave ideally.

So, thus actually the Van der Waals gas also the Van der Waals gas equation or a Van der Waals equation of state, also explains the nature of the compressibility factor for a particularly gas. For a different gas the reason that a particular temperature they were very different is that, for one particular gas may be actually the particular temperature is higher than it is ball temperature and for the other gas actually it is lower than a tennis ball temperature.

So, they will behave very differently. And thus the Van der Waals gas equation satisfactorily explains the existence of critical state as well as the compressibility factor. However, it does not fully actually explain the nature of the curve because as you can see, we have it is a cubic equation and we have basically 3 roots as we have shown here. If you want v 2 and v so, but what do we saw actually at a particular pressure and temperature, we have a when the first transition happens the volume actually changes volume into the strains.

So, it cannot correctly explain the equation of state or correctly explain the ideal real gas behavior; so, for that there are many other equation of states also. For example, Barceló equation of state, that is the equation of state there are many other equation of states, I have been and in formulated. Which gives actually sometimes better agreement with the experiment, but we always restrict our discussion within the Van der Waals equation of state. Because, it is easy to use first of all and it is it is very elegant model in the sense that conceptually it just depends on the on the thinking that the main 2 assumptions that actually give rise to the ideal gas law.

One is the gases are behaving as a point must they do not have any volume. So, that is wrong and the second thing is that the gas molecules do not have an intermolecular attraction and that is also wrong. So, once you actually invoke this idea that the gas molecules have a finite volume, as well as there is an intermolecular interaction. Then actually you can very easily by introducing some empirical constants a and b, you can actually arrive at the Van der Waals equation. So, let us summarize what we have discussed under this topic.

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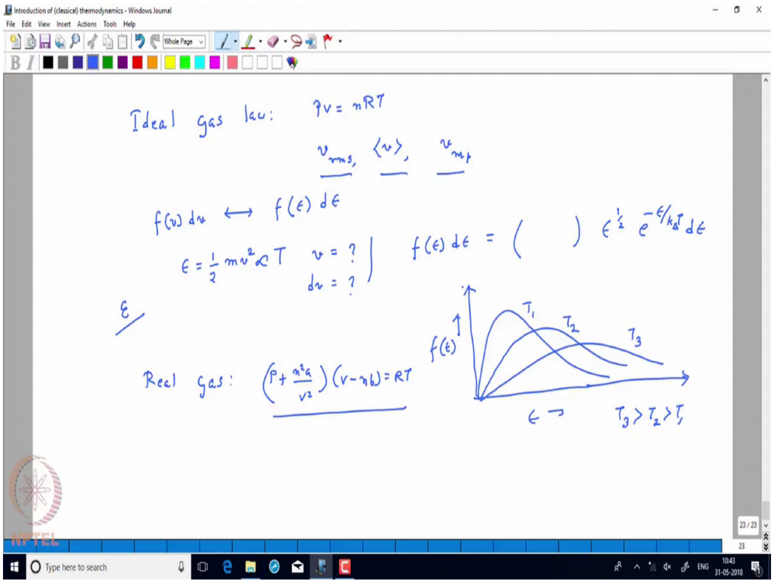

Ideal gas law: $pv = nRT$

$\underline{v_{rms}}$, $\underline{\langle v \rangle}$, $\underline{v_{mp}}$

$f(v)\,dv \longleftrightarrow f(\epsilon)\,d\epsilon$

$\epsilon = \frac{1}{2} m v^2 \propto T$ $v = ?$ $dv = ?$

$f(\epsilon)\,d\epsilon = (\quad)\,\epsilon^{\frac{1}{2}}\,e^{-\epsilon/k_BT}\,d\epsilon$

$\underline{\epsilon}$

Real gas: $\underline{\left(P + \frac{n^2 a}{V^2}\right)(V - nb) = RT}$

So, we first started with the property properties of a gases. And we talked about first the ideal gas law. And there we talked about water basically the various what are the basically concepts of the equation of state. And then we talked about the various parameters, like I mean we talked about Maxwell Boltzmann distribution. And under the Maxwell Boltzmann distribution we talked about what are the expressions for various velocities that you can think about like rms, velocity or the average velocity or the most probable velocities.

What we did not discuss is that that velocity distribution you can easily also convert to speed distribution, in the sense that you can always ask this question and that was it is a fraction of molecules that have energy in the range e to e plus T. And that is very easy to understand, because all you have to use is this relation the average kinetic energy is nothing but, half m v square. And then from that you can actually plug in whatever you have to write v in terms of epsilon and also d v in terms of d epsilon.

And then actually you can write the distribution function in energy. So, it will be f epsilon d epsilon. And you will have some functional form where actually you see that it will have some constant times epsilon to the power half, e to the power minus epsilon by k B T, d epsilon. And you will have a similar curve like the Maxwell Boltzmann distribution if I plot f of epsilon versus epsilon.

So, this is a notation like this epsilon notation for energy. So, sometimes you write it like this sometimes you write it like this. So, it is just a notational thing. And then we would found the expression for after calculating that various expression for various speeds, we actually are the velocities we talked about the real gases and where we talked about first the deviation of the real gases, from the ideal behavior. And then we talked about a particular law or equation of state which is the Van der Waals equation of state. Which is P plus n square a by v square into v minus nb is equal to RT

Now, again this is a model, the reality is something like which is always cannot be truly explained by any model. So, there will be always some deficiencies in every model. Now you refine your older model to get a better model and to, so, that actually it can explain the reality other experimental observations much more in a much more better way. But always you have to keep in mind, that this is just a model. And one particular thing that we did not discuss here is that if we increase the temperature how the Maxwell Boltzmann distribution actually looked like. So, we plotted it for a particular temperature, if we had increased the temperature.

So, the curves actually gets more and more flattened, but always keep in mind that the area under the curve will be always equal to 1; because this is a probability distribution. So, as you can see the most probable speed actually shifts towards right which is obvious because if I increase the temperature we will have more and more speed of the gas molecules or the average speed at the most probable speed everything will increase.

Because, everything as you can see is proportional to square root of temperature; each of these velocities like the average velocity of the most probable velocity of the root mean square velocity. So, actually if I increase the temperature, the curves will actually shift towards right. And they actually flattens out more. And similar observation is also seen for the energy curves, because energy is nothing but proportional to the square of velocities and then since v squared is proportional to absolute temperature. So, energy is proportional to the absolute temperature, which makes sense because k B T is or act is a unit of energy.

So, the curves will gets similarly flattened out for different temperatures. So, this is plotted for T 1 T 2 and T 3, where basically T 3 is higher than T 2 is higher than T 1. So, we will stop our discussion on the properties of gases right now. And, then we will first give you an overview on the laws of thermodynamics where; we will again give you a very brief overview. But we will give you a sufficient amount of homework, as well as we will give you some handouts which will actually summarize all the things which we are covering in the lecture.

So, that you can first have a look at the summary of the lecture notes and looking at the equations and also the formulas and some worked out problems also will provide. And, then after having I mean after actually watching the videos and going through all these the notes of or the handouts, then you can actually attempt at the problems which will be given to you. And then after certain time the solutions will be released which you can always look at and check your answers with that. So, this is the overall plan of this course, and I hope you have already started enjoying it.

Thank you.