Engineering Thermodynamics

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Week-02
Lecture-12
Properties

Welcome to the last and fifth part of the property lecture. In this lecture, we will discuss the equation of state. Then we will introduce compressibility, which is a parameter that is different from the ideal. and the different gas equations. This is normally in the form of a graph. We will discuss this later. We will discuss the usual equation of state for real gas. Let's start with the ideal gas equation of state. You must have read this in the previous video. It starts on the 10th of November. Any equation of state represents the P-T relation in an empirical form. The most basic and easy to understand equation of state is called the ideal gas equation of state. Basically, it comes out that when there is very low pressure, the gas molecules are very far away and assume that they do not interact. There is no attraction or repulsion in it. And in the same way, its relation is found in the experiment that in such a situation, your pressure is temperature.
The ratio of pressure is inversely proportional to the volume of the sound. So that is why the ratio of PV is equal to RT. So, this equation is very simple, but it works very well in many situations. But the temperature and pressure should be correct. Like low pressure or high temperature. It works very well. Because in such cases, your particles are very far away. So, if the gas is low pressure or dense, then it can be applied with the alarm. So, this pressure into specific volume and this is your RT. So, this R that you can see is basically a constant. And this constant is called a gas constant. The unit of this is kilo joule per kg per Kelvin. We can write this in many ways. PV is equal to RT and R is your universal gas law or universal gas constant which is 8.3147 kJ per kg Kelvin. This R is connected to R is equal to Ru divided by M. You can write it as follows or write it as follows PV specific volume V by M Mass is equal to, RT So this is your PV where V means volume and M RT This is your equation of state, the ideal gas equation of state. And this R, as I said, this normal gas constant is your universal gas constant divided by molar mass, which depends on this. molar mass kg per kilo mole. That is why R can change, if you change the substance, then R will keep changing. As we have seen in the example. Helium, Argon, Nitrogen, and so on but the universal gas constant does not change Like this unit has 8.314 kJ per kmol So PV is equal to MRT or if you want you can write it in moles form then you will have to use universal gas constant. As we can write it in this form also. PV is equal to small specific volume, RT you said. And we can write this as P and V divided by mass. So, PV is equal to MRT And if you want you can write this in universal gas constant This is your MRU divided by modular mass PV is equal to M by M RUT and PV is equal to RUT so this is PV is equal to NRT this is your number of moles so PV is equal to NRT or PV is equal to MRT both are We do the work depending on the information we have. Suppose for example, you say that if the mass of any system is fixed, we take a gas and assume that it is an ideal gas. Then we can use this ideal gas equation of state. temperature P1 T1 to change to P2 T2 okay so its volume will

also change but mass is constant so if PV is equal to RT if M is constant then P1 V1 and R is also constant so P1 V1 RT1, P2 V2 RT2 can be written because M will be cancelled M is constant and when it is constant then naturally if the condition changes then M by M are will be same in every situation such relations are used a lot in problem solving in the relations of ideal gas For example, if you want to extract V1 you can do it like this. You can solve such problems. Sometimes it is written that if you want to write per unit more, you can write it as V bar, and this is your RUT. So, it is written in many books. You can see the symbol that this small v has a specific volume. and this is your Molar Volume which means volume per unit mole. So, you can present it like this. Okay, just like this, you can also represent units in per unit mole. Like internal energy per unit mole, you are calling it U bar, H bar. Anyway, we will discuss this further. Usually, per mole or per kg is interchangeable. You can change it according to the problem statement. And you know that mass is molar mass into mole. basic definition of commissary add on a j m is equal to capital M multiplied by n is going on a we discussed here, or you do form of equation of state we discussed here a PV is equal to m mass RT So as we discussed earlier, real gas behaves like an ideal gas when the density is very low. Usually, the density is low when the temperature is high or low. This is how real gas behaves like an ideal gas. But in other situations, the relation between real and ideal gas is not good. So, we should use it very carefully. We should not use it under any conditions. So, we will discuss this in detail.

If you understand the phase diagram or the property diagram, then in which region we can use the idle gas. But first, let's give an example. This is an example of your gauge tire. Before starting any trip, the initial pressure of the tire in the car was 210 kPa. P gauge 1 And P gauge 2 after your trip is 200 kPa. But where it was 220 kPa, the atmospheric pressure was 95 kPa. So, we assume that when we started, it was 100 kPa. So, the question is, if the volume of the tire is the same, the tire has an air temperature of 25 degree Celsius So what will be the final temperature of the tire after the trip? First of all, we have to assume that this is an ideal gas. So, the idle gas and its mass and volume are also same. So, if we say that PV is equal to MRT, then it means that P1V1T1 is equal to P2V2T2 because the volume is same, so P1T1 is equal to P2T2 and we have to find out T2, so what will be T2? P2 by P1 multiplied by T1 so this is your relation now you have to find out P2 so what will be P2? P2 is the final pressure which will be P gauge plus atmospheric pressure means 220 plus 95 kPa and P1 will be your 210 plus 100 kilo pascal So this is your P1 which is P1 is 310 kPa P2 is 315 kPa But you can calculate it by using calculator, so let's move ahead We have said that ideal gas can be used at low pressure or high temperature But the question is what is low or high?

So, before addressing it Before answering it First of all we ask this question Can we consider water vapor as ideal gas? This is a water phase diagram Temperature vs specific volume We have written isobars on different pressures If you have paid attention This is a critical point These are all pressure lines This is 30 MPa and this is 0.8 kPa 0.10 kPa So, this experiment has analyzed that if the pressure is less than 10 kPa, then we can treat water vapor as an ideal gas. We can consider the superheated part of the water vapor region as an ideal gas. And this region that has been highlighted, we can consider it as an ideal gas. But as the pressure increases, we cannot consider this region as it is not an ideal gas. And the errors of the ideal gas increase a lot. And the larger the error, the more critical point it will be, the more the error of the ideal gas increases. That is why the use of the ideal gas, like steam power plant, does not occur in all these places. So, you should use idle class very carefully. If you see here percentage error in this region is almost 0% if you calculate the error of the table on the table which you have used before and if you calculate the error of the table then you will see that it is almost 0% and as you go to the pressure, the error is the percentage of the area is quite high as you can see here, it is around 170% or 150% percentage this much variation is there so but in that region where the error is less than 1% so we can use idle gas as we have already highlighted.

So, we introduce a term for the deviation of the ideal gas. And we call it compressibility factor. So, compressibility factor is like PVRT is your ideal gas. So, if we introduce Z, it means Z is equal to PV by RT. And this is because if the actual data is and the ideal gas is We can also write the ratio of the specific volume of actual value and the ratio of the ideal value by assuming it. So, it represents that if it is same, it will approach 1. It means that if it is an I.G., it will be z equal to 1. If it is real, it can be less than 1 or greater than 1. So, it represents deviation. And deviation means how much it runs away from Ideal gas behavior. system behavior. It is very useful in thermodynamic plots. As mentioned earlier, the more the gas is separated from the unit, the more it will be different from the idle gas behavior. So, as we discussed in the previous session, that the ideal gas behaves at low density and low density usually happens at low pressure and high pressure. So, the question is, what is the meaning of low pressure and high temperature? What is the relation? What is the condition? For example, 100 degree Celsius is low for metal That's why it will remain metal But water will boil at atmospheric pressure But similarly 2000 Kelvin will melt some metals So relatively which one you will call low or high It depends on what substance you are taking If there is air, water or metal, then it will have different meanings. So, the answer to this is that we always talk about critical temperature and pressure. So, it means that if you have Considered a gas or substance or fluid which has this phase diagram or property diagram so the higher temperature will come out because it is relative and below it will be low temperature right? So, in a way we critical temperature or pressure. It has been experimented that when the pressure is very low, P goes to zero. So, every real gas behaves like an ideal gas. So, this is a universal truth that when the pressure is low, every gas will start. This means that your particles are so far away that they do not affect each other because they do not have attraction or repulsion. So, they contribute to the properties like an ideal gas.

Now we will introduce a principle of corresponding state. Now gases behave differently. If you take methane or propane, then every temperature and pressure behave differently. For example, if you take temperature versus volume. It is a specific volume, it is 1 by rho, so it will be 1 by density. So, as you considered different, as we take hydrocarbon, methane, ethane, so its critical temperature keeps increasing and its phase envelope will also be different. So, I am just giving you a rough idea of how it works. It cannot be numerically correct. But it is noted that T by Tc, if everyone does Tc, then you get reduce temperature and V by Vc, reduce volume or you do P by Pc so these plots these plots are superimposed on one plot means they come on top of each other what I mean to say is that when you In Reduce, you can see the units, because it doesn't have any units.

So, these three come. So, in this, your CH_4 comes, C_2H_6 comes, and other data comes. So different, this is known that in this, suppose this is a circle, this is a square. Because this is T by Tc, this will be 1. And this is V by Vc, so this will be 1. So, this type of behavior, which is on the reduced plot, all the other phase envelopes come on each other, we call this type of principle, principle of corresponding state. And this is remarkable, this has been said that all the gases in it behave in the same way, which are similar gases. For example, if you take the hydrocarbon series, you can take any number of carbons in it. And the number of carbons in which there are 24, they also behave in such a way that they come on top of each other. And it is very beneficial because if you have a graph that is in a reduced plot, then you can basically take any condition and you can get the properties from there. So, we will talk about this, that specific compressibility charge is the same from where the data is in the reduced plot and you extract information from that plot. So, let's summarize this ideal gas behavior. If you see the ideal gas behavior in the TV diagram, then this is the TV diagram, so this is your typical phase plot. Here your ideal gas behavior is usually found in this range and here your non-ideal gas behavior is found. This is liquid so we don't assume here So, the ideal gas behavior is at a distance from critical point and at a high pressure.

Now, let's talk about compressibility of charge. We talked about the compressibility factor of Z. And this is what we represent as Z as a function of TR, PR. All these are reduced plots. So, this is the comparison of Z factors for various gases. Here Z has been plotted for various gases. Z is also a non-dimensional gas. So as a function of this, it is reduced. So, note that methane, ethylene, ethane, propane, n-butane, isopentane, n-heptane, nitrogen, carbon dioxide, water. like this line is TR equal to 1, this line is TR equal to 1.1 and this line is TR equal to 1.2 different symbols are representing different gases and you can see how it is falling if you fix this and this then you will get this specific point and on this, whether it is methane or ethylene If you have fixed the PR and TR, then there will be a specific z at this point. z is independent. Whether it is ethane or methanol, when your tr and pr are fixed, then z is also fixed. After that, you can extract the rest of the information from other properties. But this is the corresponding state principle that on every reduced line, no matter what the gas, which represents 10 gases, all fall on the same line. On TR1.5, all are falling. This is very interesting, and this is what we call the corresponding state principle. It has a different meaning. how to explain it fundamentally but mainly when you have TR and critical point represents a nature of any substance so when you divide it you reduce it so you have scaled its characteristic features its key properties and when you have scaled it then the rest is similar behavior you can understand of other gases which falls in one line and one curve. Generalized Compressibility Chart is usually available in books. It is available at low pressure and high pressure. Usually, it will be Z versus PR. The data you see here are on different TRs and VRs. You can use it in problem solving sessions. If you have any problem, you can use it from the table. or use the chart for information. So, you can get information from these three. Which data will be useful for you. Usually, the table is the best information. Compressible chart is also very good if you have this chart in that range. So sometimes reading the chart is difficult because if you see it manually, there are chances of error. So, the table is more accurate. but nevertheless, FIDI is a very useful thing but the special thing is that all the information is not in the compressibility chart so many times the equation of state is used so if you know all three then depending on which problem statement you can pick what data will be found and according to that you can solve the problem Equation state is only used under certain conditions and pressure. That is why it has been modified.

Many equations have been introduced. Van der walls introduced it in the beginning. After that you will get many more equations. Van der walls basically corrected the pressure and volume.

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

the ideal equation and state and here is the correction term. And this represents to a large extent in real form. But of course, there is a limitation and a disadvantage. We have already read that if you take the PV diagram, then here is the critical point and usually this is the temperature. So saturation curve and when critical point will come here,

$$\left(\frac{\partial p}{\partial v}\right)_{T=Tcr=constant} = 0$$

$$\left(\frac{\partial^2}{\partial v^2}p\right)_{T=Tcr=constant} = 0$$

There are two types of term used in this equation One is Intermolecular attractive force which comes from here and due to this, pressure is collected and the second is volume which is collected by the molecule In I.G, we consider forces as zero and we consider volume as negligible In addition, you will get a more complicated equation of state with many parameters. In this case, there are only two parameters A and B. In this case, there are other parameters of B-tailed Bridgman. And it is quite accurate. It is reasonable to accurate up to 0.8 times rho critical, i.e. critical density, for some particular substance. Bennett-Webb-Robin equation of state has 8 constants and it represents the real state to a large extent 2.5 times, it can capture you to a large extent in super-heated regions A, B, C are temperature dependent only and this is called Virial coefficient the more you add, the more valuable your information is or information collection is done but it is a little difficult because it is taken out of molecular nature so A, B, C, D information is not available so it is not that popular but this is such a question state that you can be connected to the molecular nature A for example is the contribution of two molecules and B is the contribution of three molecules C is the contribution of four molecules So in this way the state represents the molecular nature and the rest is more of an empirical relation and parameter fitting So this equation state is of different accuracy If you look at nitrogen and if you calculate the error of the equations of the relative volume of nitrogen The plot given on this plot is temperature vs molar volume This is the two phase region and this is the saturated vapor line These are the isobars and whatever is represented in this is the error of this You can see that it is performing very well van der walls, Betel, and so on But as you move towards the critical point You can see that this range is near the critical point And this is showing van der walls at 0.5.7 Betel is at 59.3 and 18.7 But its behavior is different For example, van der walls shows bad behavior here So this varies according to your range and you can make this equation of state more complex by which you can get more parameters by which accuracy is better but the equation of state used by today's youth is the Peng Robinson and 2-3 other equation of state so this We will not go into detail in the course, mainly we will use the IE STT. But it will be good to know that different forms exist. And Chemical Engineering Thermodynamics is a second usual course in your second year. You can understand it better in the second year and third year. The equations can be stated in different ways and the accuracy can be different. In this advanced course, we will explain more about this. Particularly, the Peng-Robinson Equational State and other advanced equational states are more popular and are used.

In this series of lectures, we have studied pure substance, its phases and its changes. how to define compressed liquid, saturated liquid, saturated vapor and superheated vapor how to identify two phase region and what conditions will be the compressed liquid and superheated vapor we represented the changes in the property diagram finally we saw the property tables We have also introduced enthalpy which is the internal energy plus PV term. We have also defined different kinds of tables which can be used. In this lecture, we have understood the IG state and particularly what conditions can IG be used in or whether gases behave or IG. Compressibility factor has been introduced which is the deviation from IG. and we have also introduced the graph of the compatibility factor Finally, there are very few possible different kind of equation of state which we have introduced, but there is a lot of possibility which will be taught in the advanced courses I hope you understood this property and its use will be used in the future lectures This is a very important lecture See you in the next video