Engineering Thermodynamics
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Lecture – 20
Properties of a Pure Substance: Thermodynamic behaviour of a pure substance.

Very good afternoon; we start our next set of three module, three lectures on module 3 which is Properties of a Pure Substance. In an module 1, we looked at conception definitions, module 2 we looked at what are the laws of thermodynamics and how we applied those two problems. We got to a point where we could take the system, show thus system boundary, decide which equation to put and what assumptions to make that gave us a relation between heat work and properties, for either a closed system or an open system.

So, now, if we know any two of those, the third one can be calculated and that becomes the starting point for analyzing any problem or looking at the performance of any real application. So, that is what we will look at.

Today we will revisit visit what are the properties of a pure substance; what is a pure substance and in particular we will look at thermodynamic properties of a pure substance ok. So, we begin with by seeing that properties of a pure substance could mean a lot of things.
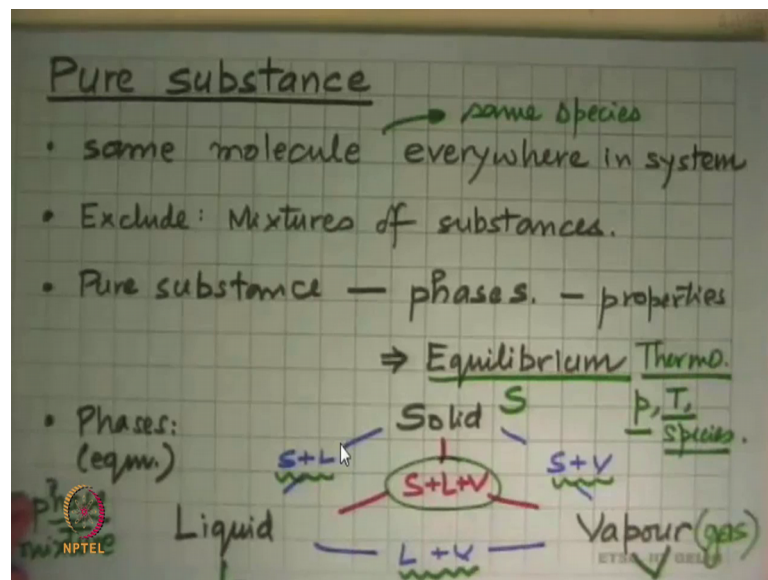
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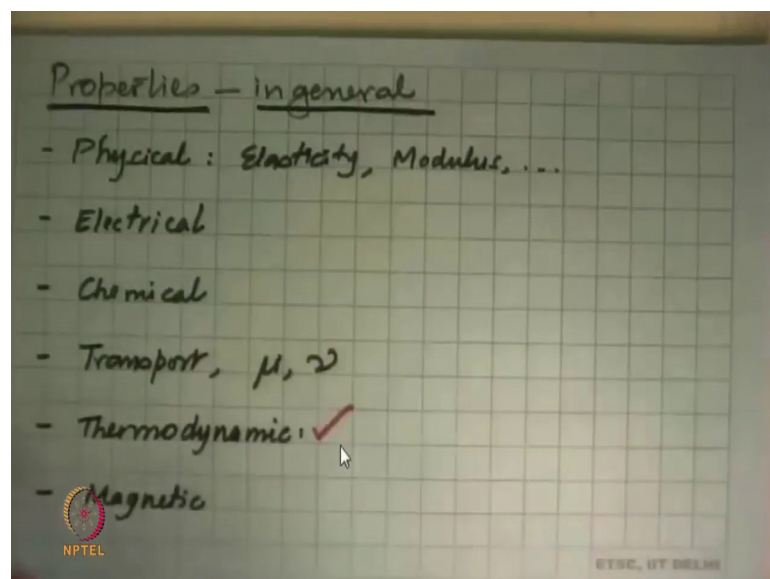
They could have physical properties like what we would have come across in solid mechanics or in strength of materials things like elasticity, modulus those types or there could be electrical properties resistivity like that; chemical properties that is a reactivity, transport properties that one comes across in fluid mechanics. Main ones there being the viscosity and then we have thermodynamic properties and also same magnetic property.

So, all in all the material when we say what is the properties of a material we look at about 30 to 40 properties of a material and many application we decide what properties we want and accordingly we come across a set of materials that satisfy our requirement. In this course on classical thermodynamics, we are going to be concentrating on the thermodynamic property.

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Pure substance
- same molecule everywhere in system → same species
- Exclude: Mixtures of substances.
- Pure substance — phases. — properties
  ⇒ Equilibrium Thermo.
- Phases: (eqm.)   Solid S   P, T, species.
  S+L   S+L+V   S+V
  Liquid   L+V   Vapour (gas)

So, first before we come to the properties, let us ask what is a pure substance and what are its general behaviour. So, pure substance is something we defined as something where these same molecule everywhere in the system.

That means at any point anywhere in the system whether it is a flow system or open system say what is the molecule there, we say where it is this particular molecule and it is a same everywhere. So, what we exclude by this definition are mixtures of surfaces, no substances. So, a mixture of say water and sand or salt and water or air and butane, we are excluding these. Technically even air is a mixture major components being oxygen nitrogen and then small quantities of carbon dioxide and other. So, those would be

classified as mixtures, but for the first analysis we will see how certain mixtures can be converted into a pseudo pure substance whose properties are very easy to know and that helps us in solving a lot of problems.

So, we are look at that later on. The pure substance itself can exist in many different phases, say by that we mean that we can get properties which are varying now and in all cases we can talk of property only when the substance is in equilibrium. So, the phase that we are talking of is an equilibrium phase and there we have three major categories solid phase, liquid phase and vapour. So, those are the three major phases that we have; solid, liquid and vapour. On this diagram, I have shown something more where a equilibrium state is possible.

The word equilibrium is very important here what it means is that we can have a situation where we have a liquid and vapour in equilibrium. We could have a situation where vapour and solid could exist in equilibrium. So, in the first case we get liquid vapour mixtures. So, these are now mixtures of a phase. So, when we talk of mixture here in classical thermodynamics in this part when we say mixture we will mean its a mixture of two phases. Later on in a more advanced courses, we look at mixtures of pure substances.

So, we have liquid plus vapour mixture possible, solid plus vapour mixtures are possible and solid plus liquid mixtures are possible. All individually in equilibrium and yet one more is possible where all three phases solid, liquid and vapour; all three exist together in thermodynamic equilibrium.

What that means, is that when there is equilibrium it means that they are in thermodynamic equilibrium. It means that pressure everywhere is the same, temperature everywhere is the same and species concentration in our case it is only a one species that is the same so. That means, these mixtures satisfy this property that everywhere in the mixture whether you look at a small element in the liquid or a small element in the vapour or in this case solid and vapour or in this case in any of the three, in all cases the pressure will be the same, temperature will be the same and of course, it is the same species because you are looking at a pure substance.

So, exists a same molecule everywhere essentially we are saying is the same species. So, this is something new that is coming up and it has a very far reaching implication as far

as lot of applications were. So, what is that is what we that is why we need to study this part. So, let us look at the few examples where we see this ok.

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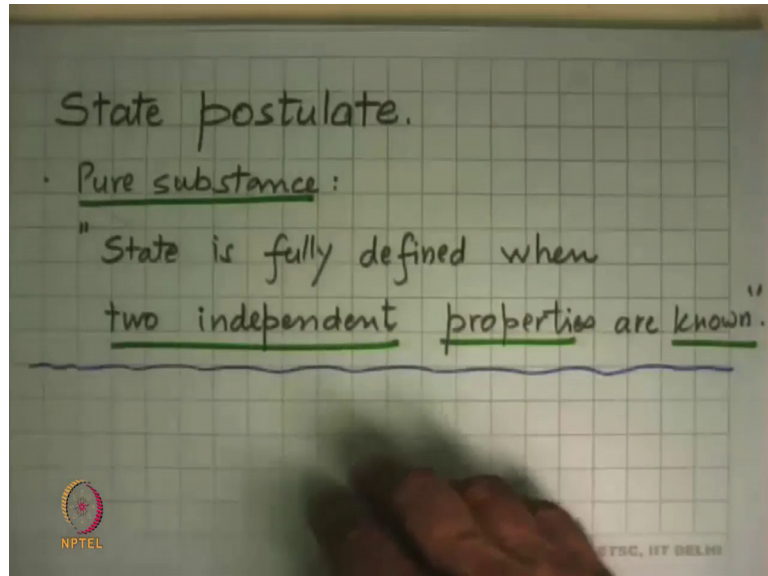
Before that we let us look at what we know as the state postulate. The full details we will not go into it, but suffice to say that for our purpose for a pure substance a state is fully defined when two independent properties are known. Any two independent properties are known which means that the pure substance the state of that substance is fully different and that is what we will look at.

That solving any problem if we need to do some calculations based on the state, we always have to see why do I have two properties here are the two independent properties there is not, do I have any more information in the problem by which I can get these property that are not known.

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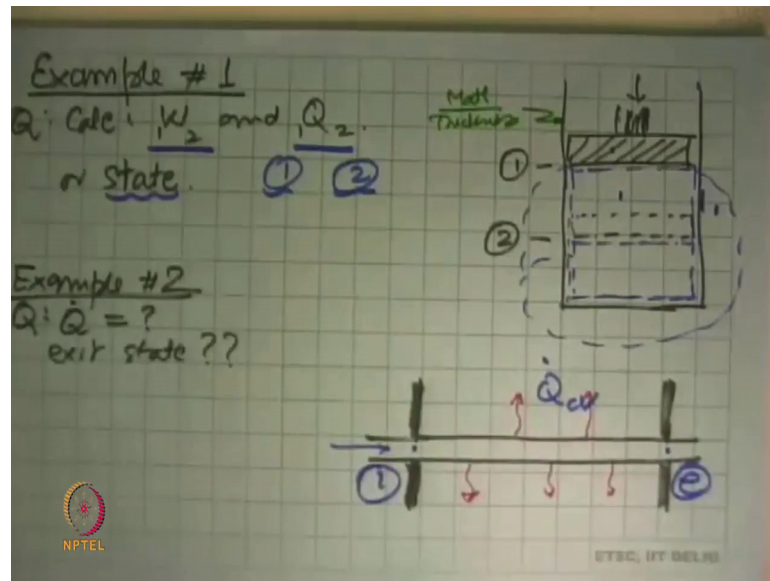
So, here two examples: this is the case of a cylinder in a piston arrangement in which there is a piston there and this is the working substance inside this. So, we call this as our system boundary. It includes everything except the walls of the system. Now remember this definition was very important because if we said that my system is like this, then this boundary which is the wall of the cylinder is now part of the system and when we talk of properties we would have to talk of the properties of the substance inside here as well as the substance here and also maybe even any other substance over there.

That makes lets very complicated and so, we have to be very specific as I have said all wrong that we must define the system very carefully so, that it includes that substance that is of interest towards and it is the pure substance. So, this we call state 1 and is this comes now here this is state 2. So, in that case the system boundary now becomes like this. So, we know that this is a closed system and we would apply the laws of the first law and second law of thermodynamics and we will say look what is the relation between the work, the heat and the states; the state at 1 and the state 2; that means, the properties at state 1 and 2.

So, if these three, any two are known, the third can be calculated and that is what the entire exercise of problem solving in thermodynamics becomes. So, that is what we need to know let to get the states, we need the properties and this information is important for some this thing need start doing the engineering of this device. For example, if in this

process you know that this is the maximum pressure that this substance will take, we know what we can then design, what material should be have here, what material should be there for the cylinder, how thick should it be, how it should be made' all those decisions get taken based on this thermodynamic considerations.

This is our second example of a flow system that we have a tube through which a substance is flowing and this is giving away its heat to the surroundings, then there is a change in the property of this and we want to know that what is the relation between the properties at the inlet and the exit state and how is that related to heat transfer from this. So, what is the same story that we first decide what are the of these things what is independent and what is known, what is unknown and then we calculate the unknown and then do the rest of the design.

So, like here also we get the same thing. If we know the state that is it is going to be, here these are look this is the inlet pressure and temperature this is the outlet pressure and temperature we have to select the tube which will not rupture at the highest possible pressure or the temperature. And so, let us see what materials we can take, what are those materials which are compatible with this substance with this substance and not within that substance, how should thick should it be. Now those decisions start to come in, what I am trying to say is that the basic thermodynamic calculation in the starting point for the entire mechanical design of the applications.

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So, let us see a few pictures of these. It is the picture of a now ship that was launched this week or the navy and this ship has so, reach the details of it. It is of the four gastromines which (Refer Time: 11:30) the ship. We do not see those here, but inside they are somewhere we have four gastromines, we are taking in here; it burns the fuel, it generates power, that power dries the propeller of the ship. Like this there are four of those. So, that is another example are given instead of the aircraft engine, a ship where the proportion is done by a gastrovent.

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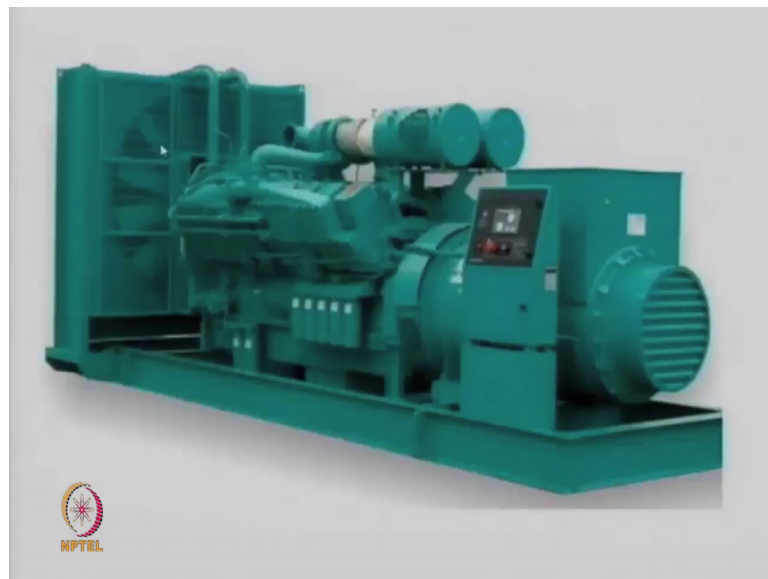
This is the photograph for such diesel generator set. What you are seeing here is at this part is the diesel engine behind that is the generator which converts mechanical energy into electrical energy this is the control panel and the front this pics where thing, this is the radiator which cools the hot water cool and coming from the engine cools it and sends it back.

So, if you want to do the thermodynamic analysis of an engine like this and predict you know what is the power it will give things like that or what is the heat transfer rate in the radiator then we assume that rotni substance here is something. In this case we assume that it is air, we treat air as a pure substance and start doing a set of calculations and we will get various numbers are there.

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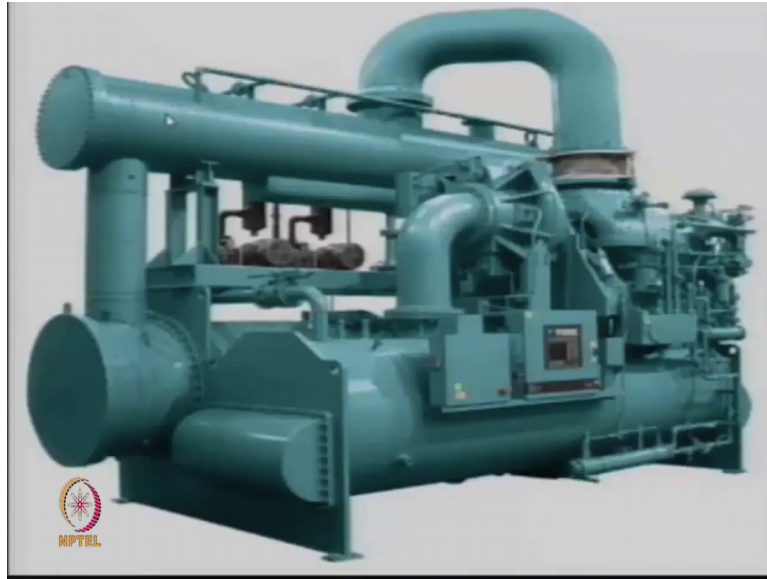
This is a vapour compression system in the chiller of a central AC plant. So, what this thing does is right here in this part, there is a compressor which is operated by a motor. Further behind this we cannot see that it compresses the gas, sends it out into this big thing where here water going through this which condenses it and this becomes a liquid refrigerant here, then it comes down here; it is shortened. And here we have another set of pipes bringing warm water in its gets cold and goes out as chilled water.

This chilled water is piped to different floors in a building or which then you blow air and we get the air conditioning here. This is at the heart of all central air conditioning plants. So, how do you analyze this system? It is basically the same refrigeration system that we have seen earlier except so much bigger scale and everything is lot bigger than what we see in a window AC or in a split AC it.

The last picture here is again something that we saw very recently India launched a GSLV vehicle and this is we can see here, it is on the launch track just been ignited and just now taking off. What you see here are on the site is four little things which are stepped on boosters which have a solid fuel which burns and comes out with that gives a momentum there and in the centre are cryogenic engines.

So, this thing contains two big tanks, one having liquid oxygen, the other having liquid hydrogen. The two are pumped and allowed to burn, they produce a higher temperature water which comes out and them gives thrust and that pushes the spacecraft ahead. So, we would not go into the analysis of this where a solid fuel is being burnt, but the idea of what is the hydrogen and oxygen how do you get liquid hydrogen liquid oxygen, why not gas, how does it burn; all those questions requires the knowledge of thermodynamics that we are going to be using that.

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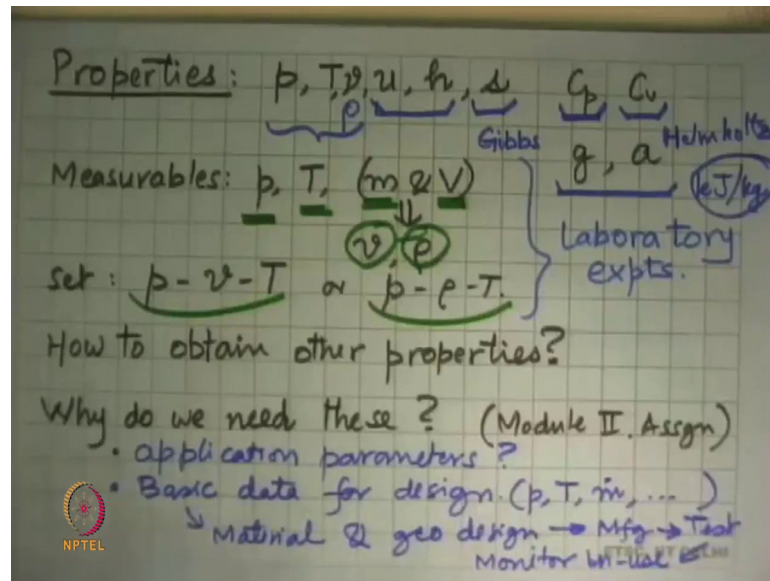
And here we have a whole series of properties that I have listed we have come across these pressure, temperature and specific volume is something we came across right in the beginning. Specific volume is same as the reciprocal of density. So, either we can say v or rho that is.

So, these three somehow came very basic in which we got some idea of some school days also. Then we looked at the first law of thermodynamics and came up with these two properties; specific internal energy, specific enthalpy. Then from the second law analysis, we came across specific entropy. Now we will define some more properties. The one is specific heat at constant pressure, the other is specific heat at constant volume and we will briefly introduce two more properties. One is small g which is called Gibbs energy and small a gives specific Gibbs energy and it is a specific Helmholtz energy.

So, this will complete all the properties that we require and the reason for introducing these two is that properties relations that way they evolve, they actually start up from here in one sense from in a mathematical way and give us equations by which we can calculate all of these. So, that is the reason for introducing that Helmholtz energy. So, a is called Helmholtz energy, Helmholtz free energy or Helmholtz function and you might have come across these in a course in physics or in chemistry and g is the Gibbs energy or the Gibbs free energy. So, this four properties u, h, g and a all of which are energy.

Now the specific energy is or we have being using kilojoules per kg. They all represent certain different types of properties of a substance or the properties of a reaction.

For example we know that h was u plus T v that T v we do not know is the flow work. Now in a laboratory, we cannot measure all of these. This is a big problem. What we can measure is pressure temperature and we can independently measure mass and volume from which we can get specific volume or the density. So, those are only real world data that we have from which we need to get the properties all of these that we need for this analysis. So, what we end up having is a set which is known as the p-v-T set or the p rho T set and what we do is we try to fit a mathematical equation to this and it is not a simple equation like a polynomial or things like that; the purely complex equation.

We try to make sure that it satisfies the property relations and Helmholtz equation and then we differentiate it and do various operations on that to calculate u, h, s and then you can even get C p C v from there. After doing that 50 years back when computers and calculators were not there, all these properties were tabulated in a table and table cannot have continuous data for every pressure, every temperature. They work pressure temperature data for very distinct points and if one wanted to do a calculation with a property in between, one needed to do interpolation.

Gradually that has given way and now we have all these equations here programmed into a software package. They give a graphics user interface and you can input two properties and it will tell you all the other properties that you want. So, we have reached that point. Some of these packages are available on the web also. So, others are there as open source some are there with books. So, we use any of these that is fine, it makes life a little more easier than using tables where you often have to do interpolation. So, we have tables, we have software packages and we also have graph or charts or diagrams.

Throughout we will try to depict every process on the property chart. So, that helps us to quickly visualize what is the process and what is it that we are looking at, what is possible, what is not possible. Some very quick answers come out of that. These charts are nothing, but taking all the data that we got from these property equations and we plotted them of the two axis one two, one two axis and the others as running parameters. We will look at those also yeah. So, this is how we what big plan is that how come these

data, first how do we get this data, what do we understand about the behaviour of the substance and from this data, how can we get this data.

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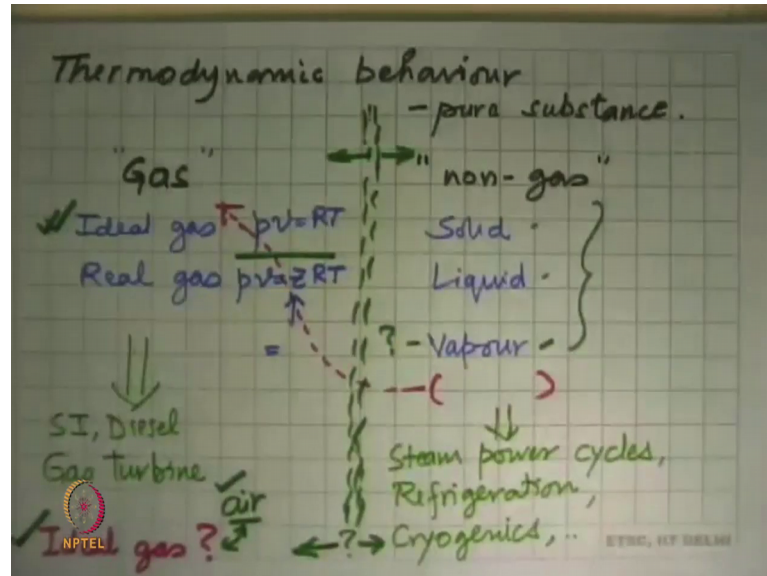
So, now, we come to asking what is the thermodynamic behaviour of a pure substance and broadly we can say that substances behave either as a gas or what I put in quotes it is non gas or not a gas; you can call it any of that. When in gases, we can say there could be ideal gas or a real gas. In non gases we of course, include solids and liquids though these are phases also that come in our discussion and what we call as vapour. We do not call vapour as a gas, although quite often engineers do speak of a particular substance and a vapour state, they call it a gas.

Sometimes we justify, sometimes the error could be large if we assumed to be a gas, but we will continue with saying that it is a vapour and differentiated that under certain circumstances, this vapour can be treated as a gas which in some cut situations can be treated as a ideal gas or else as a real gas.

If a substance cannot be treated either as an ideal or a real gas, then we have to say that it is in this real either because it a vapour states or the liquid vapour states or just say that it is a non gas behviour and we go back to our property data. The big difference here is that gases are very have nice and easy to work with; an ideal gas is something you learnt in school p v is equal to RT. The equation of state is very nice very elegant very simple.

Real gas is say when the room this is not the best thing if you calculate the specific volume based on this equation and you actually see what is there in the real world there could be a difference. That difference could be several percentage points and that should not good enough.

So, we start making modifications to this equation. The simplest one being that we introduce the compressibility factor z and then we get even more complex equations where we say that I will add many more terms to this equation to make it more and more realistic about the real gas behaviour. So, it is still not a vapour, but somewhat of a vapour in some cases and, but not an ideal gas the deviation from ideal gas is large and so we do real gas analysis.

We make this distinction although I have put this to a very different things. There is no hard and fast rule which says that this has to be treated as a gas, this has to be treated as a vapour liquids and solids; obviously, are not vapours or gases. So, they do issue of thinking about those as gases at all. The question then arises is which vapours can be considered to be a gas and then which gas can be considered to be an ideal gas. This boundary as to where we see make this differentiation this we will come across maybe in tomorrow's lecture or little later after that.

But for the point tell the lets say that there is no hard and first to we say look if this number is met, then it is a gas. If it is not if it is like that then it is this. So, there is a sort of a fuzzy boundary here and sometimes we have to make our own judgment call in saying well ok, I will accept so much uncertainty and isometric behaviour of gas my analysis going to be somewhat different than what I have here, but it is good enough to begin with.

So, this also we did not see what is the way by which we can say is a substance lies in this side or substance lies in that side. The practical reason why we make this differentiation is that we can broadly classify most of our work to energy devices via gas based devices or vapour cycle devices. Gas based device means that the substance all throughout the cycle or the process is always a gas or an ideal gas.

In this course we will assume it to be an ideal gas, we would not worry about real gas. So, we are stick with this and examples are the spark ignition engine the diesel engine, the gas turbines aircraft engines and (Refer Time: 24:42) the process that we will say that

this is an ideal gas. Now let us look at the analysis apply the laws and see how much work it produces, how much heat going to give. The unless it becomes very very elegant and simple because the equation of state pv equal to RT is very nice to deal with. So, now, onwards life becomes very much more easier, but it is true only as long as the working substance is our ideal gas which in our case we assumed that it is air which we assume to be an ideal gas and so we can do all the analysis here.

In more advanced analysis we start relaxing the fact that the air is not a pure substance. It is a mixture is not an ideal gas. Let us start modeling it as a real gas and then you start getting more and more the data that is in better agreement with what you see in practice. But in the beginning course we do this, we take air as a pure substance treat it an ideal gas and that gives us the handle to understand these substance these devices.

The behaviour of vapour and in many cases vapour plus liquid states has applications like all steam power cycles. So, coal fired power plant, oil fired power plants, nuclear power plants all of which will account for like 89 percent of our electricity generation. There we come across the substance in our case it is water which is sometimes is a vapour sometimes is a liquid.

And we need to understand how do I get properties when it is vapour and what happens when it is a liquid. All over refrigeration systems like the one I showed you just now also, that has some processes where you can treat it is a vapour, some processes where it is a mixture of liquid and vapour and somewhere where it is only a liquid. So, that is why this thing comes in and example that I gave was the cryogenic region liquid oxygen liquid hydrogen that is a liquid phase, but then it become a vapour phase and then burnt and it be some (Refer Time: 26:51).

So, all these applications require us to understand the behaviour of a substance when it is not an ideal gas and that is where we will start our discussion today. Before that let us quickly go through what you probably have learnt in about an ideal gas in school days or in a physics course and then we move on to the behaviour of substance in vapour state.

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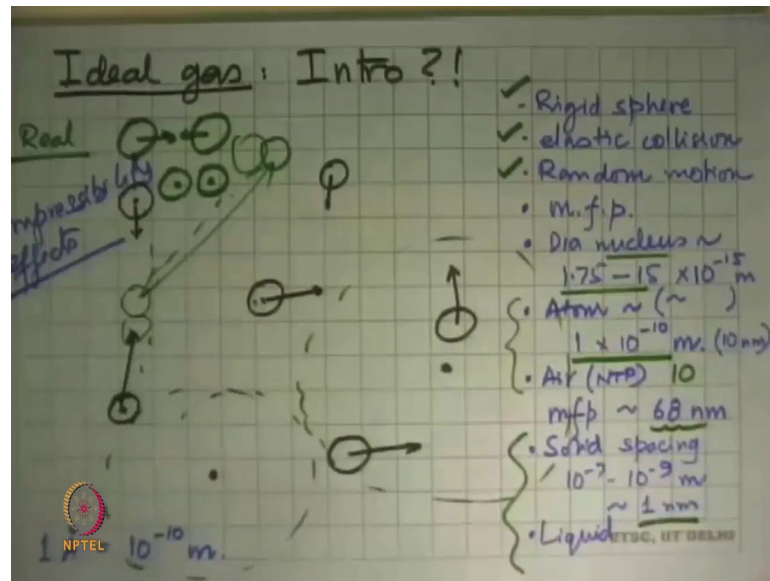
So, what we have as an ideal gas is that we assumed that it is consists of molecules which are considered to be a rigid sphere, each one of them is a rigid sphere. They are moving randomly in space, quite often they keep hitting each other and we say that those collisions are elastic; that means, is like two rigid balls hitting each other momentum and energy get conserved. And as they keep moving around, we say that look this is called an ideal gas because there molecule will travel a certain distance say this one went here, this came here and somewhere here; they had a collision and after that this molecule went there and had a collision with another molecule over there here.

So, this is a sort of a distance it was covering between two collisions and if we know this distance for every collision that happens and we take the average of that, that is called the mean free path. And the mean free path is much much bigger than the size of the molecule, then we can quite happily you say that this is a ideal this is a gas like behaiour.

To put some numbers for you diameter of a nucleus is of the order of 1.75 to 15 depending on the size of the nucleus into 10 to the power minus 15 meters, that diameter of the molecule itself including the electron cloud is of the order of 10 to the power 10 meters which means that if this is a nucleus then the electron cloud occupies a space whose diameter is 10000 times the diameter of this and that is a huge space. And the next molecules the closest that it will be is one whose electron cloud touches this one. And

when it touches this could either be a solid or a liquid this does not happen in a gas, these two are very far apart they are hating each other.

So, this gives an idea about the typical sizes of the nucleus and the size of the atom 10000 gives that number. The average distance travelled between two collisions in air at 1 bar and say 300 Kelvin is of the order of like 68 nanometers.

So, remember this was of the order of 10 nanometers this is 68 nanometers. So, mean free path is many many times bigger than the size of the molecules so; that means, that what we are saying here as a rigid molecule, there is a rigid nucleus in this, this is the cloud, this is a nucleus, this is the cloud and the distance between them is much larger compared to their own diameters; 10 times 100 times more. And as you go for greater and greater vacuums, this distance keeps increasing. If you look at the satellite, the orbiting is low attitudes that distance between two molecules that you see there is of the order of several kilometers.

So, that is at the low pressure side. At the high pressure side, as you start pressing these three together these molecules all start coming closer to closer to one another, the intermolecular distance becomes less that distance between collision becomes less and gradually you start deviating from ideal gas behaviour to a real gas behaviour and then finally, it is not gas at all. So, in liquids and solids the spacing is of the order of one nanometer. In gases it is 10000 times that distance.

The difference is that in gases these are all free molecules, they can roam around randomly where they want. In solids they are vibrating about their mean position and in liquids they are sleeping passed one another and they take the shape of the material in which they are there. Especially in a gravity environment, in a 0 gravity environment that property does not exist ok.

So, the ideal gas behaviour starts to get become a real gas behaviour when the distance between two molecules have become such that gravitational attraction between them becomes significant and it keep guess the molecules a little more closer than what we would have expected them to do. If they come even more closer, the nuclei begin to repel one another and from that actual thing will be in less dense then what the ideal gas equation will tell us. So, these are what we will we have called the compressibility effects.

We would have a full discussion on this later on. For right now I just introduce you to this fact that from an ideal gas, let me started compressing it or maybe reducing its temperature. These are all getting closer and closer and at some point we say look I can treat it as a real gas by not using pv equal to RT, but using something else, and even after sometime after that we said look you are using that is not good enough; there is too much error in it. Forget about it, it cannot be treated as an ideal gas, it cannot be treated as a real gas and we start looking at the concept of vapours and liquids. I come back to the questions little later because we will come to those questions in this module certainly.