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# Module - 1 Lecture - 2 Thermodynamics

Hello everyone welcome back, this is a second class. So, we just continue with our review of thermodynamics and probably get into mechanics, review of mechanics, and from probably two more classes after we will be going into required gas dynamics. First thing will be one dimensional gas dynamics that will be two more classes from now probably. I think in next class, we will talk about something physical about the gas. How it talks to each other? Enough, we will talk about that next time if we have time, we will see that.

So, last time we ended with the laws of thermodynamics, zero th law, first law and second law and we said that zero th law was needed for talking about something called equilibrium. And we said that if we say thermal equilibrium exists, then we need some property called temperature to be defined for the system, which I will say are equal for the 2 systems, if they are 2 of them, are in equilibrium with each other.

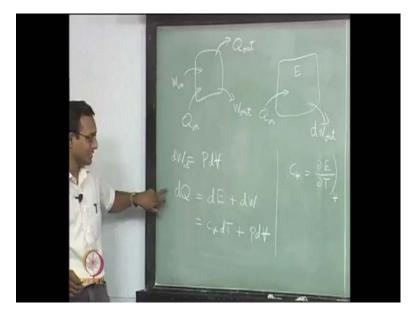
Similarly, if I say mechanical equilibrium, then forces at the surfaces that is pressure must be equal between the two systems, for me to call them to be a mechanical equilibrium across that. And then we said chemical equilibrium is a case where the composition of the gases inside the system does not change. We are interested in only gases. But this can be extended to liquids, solids, everything if you want we are in gas dynamics so, we will just talk about gases. In our case, if there is a system which is one thing that I missed last time. If there is a system which is in thermal mechanical and chemical equilibrium, that system is overall called as thermodynamic equilibrium with another system.

If there are system a and system b which are in thermal equilibrium, mechanical equilibrium and chemical equilibrium with each other, then they are supposedly called as in thermodynamic equilibrium with each other. There is nothing that changes as per as thermodynamics is concerned.

And then we went into first law where we said we needed some quantity called energy and then we said that that property is conserved always, if there is some amount of energy given to the system when it can use it to do some work or it can give out some energy or it can store it within itself. These are the various things possible. We did not put any mathematical expression for it yet, we will do it now.

The next one we said was second law of thermodynamics, where we said we needed some quantity called entropy and then we said that quantity entropy will always be increasing in the direction of naturally occurring process. If we go the opposite path in that process entropy will decrease and that will not be a naturally occurring process. So, now we have to put some mathematical expressions for them.

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So, if I think about the first law, I can easily say that I have some box, some system a and then some amount of heat is going in and let us say it is giving out some amount of heat and say there is some kind of work in, we will talk about next and then probably there is some kind of work out. Any other possible interactions currently for our systems, currently nothing, why we are assuming simple compressible substance? Where we can do only heat or cool the gas or we can do p d v work on it that is a only thing that is possible we said so, only this much is possible. Now, we will look at this, what do you mean by W in the surroundings are doing work on the system that is, let us say I am compressing the gas.

What am I doing? Surroundings are expanding, this is compressing. What is going to happen finally? Surroundings are doing work on the system. What should happen to the energy of a system? Surroundings let us go to work out, what happens if say work is done by the system on the surroundings. What should be the case now? The system that will be negative or positive work and the surroundings it will be negative.

For the surroundings it should be negative work. If I say that work is done by the system to the surroundings. It is just convention I guess. If I say W equal to P d V, I will go back and write it as molar volume, If needed currently let us keep it as volume as such if I write it like this what do I mean by this of course, when I write this I had to have a delta W or d W somewhere once I cannot be d w on other side nothing right cannot be there so when I write this I am considering I will follow this convention where my system is having a pressure P and it is expanding by a volume d V, and this is the work done by the system. And I am calling this positive work it means my work done by the system is positive. That is the way I am considering, what will happen if work is done by surroundings on the system, automatically if work is done by outside on to the system it is like some piston pressing from outside and the system get compressed.

So, that will automatically give you a negative volume and that will work if I pick this convention. Of course, I could pick completely opposite convention as long as I know the convention is the opposite it will still work I will just have to take care of that minus sign somewhere and it will completely work, we will follow this convention we will consider this as W out d W out is equal to P d V, we will just consider that way.

So, now of course, I can consider a W in and the W out and then find out the net or I will simply say I will take the summation of all this and I will go to a equivalent system where there is net d W out, net work done outward. If overall the volume of the system decreased I will automatically get this value to be negative. We will keep it that way, it just comes out to be negative which means outside external surroundings are doing work on the system, that will automatically happen. Similarly, now I can write this Q in and Q out in a similar fashion and I will just tell Q in, Q is the amount of heat that is sent in is what I will call as s Q n. Now, I will just tell if net energy is going from inside to outside this will be negative, that will automatically take care of the direction. Now I can write overall, what should be my energy balance if I think about these 2 things, these are the 2

interactions that are possible, heat transfers across the surface and P d V work across the surface only 2 things are possible.

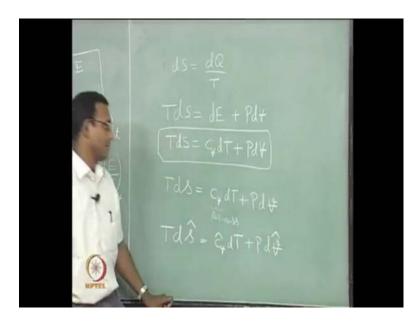
Now the net interaction will be in these 2 together. Anything else missing in my energy balance, maybe there is energy stored inside. This is the energy E inside my system. May be, think of this system as myself and energy can be money right now, easy thing to think about. Somebody gives me money I could use it to do some work that is pay somebody get something done or I can just keep it in my pocket. So, the system could just take the money from outside keep it inside in its pocket or do some work outside that is the only way you can think about. Money cannot be turn away that is the rule. Similarly, that is a first law of the thermodynamics. It says energy cannot be just vanishing somewhere, it has to be presence somewhere, it has to be conserved that is a simple logic. So, I am going to write, I will just put d Q from now on. It actually means Q into the system as positive.

That discussion went through up to here, after that I will just call it Q from now. Net Q in is positive and I am going to call this the d W out is positive. I will not put that out symbol anymore, I will just assumed you keep that convention. That is why we spend that 5 minutes in here. So, this is the way we will write, this is your first law from mathematical point of view, what is happening the net amount of energy taken into the system how much is stored verses how much is used for doing some work on the surroundings, that is what it says. Now of course, we can write it as a more common form C v times d T plus P d V is a more common form. What is C v here? Specific heat at a constant volume. How do we define this C v as differential change in energy for change in temperature? Keeping volume of the system constant that is your specific heat capacity of the gas. That is what is here and then of course d W. We already said this only simple compressible substance only pressure volume work is considered, yes to be more correct it should be partial differential we will keep it as partial differential.

I could change the internal energy keeping temperature constant and changing its volume internal energy, by the way I have to go back and talk about that next any state should depend on 2 other properties. So, it should always be partial derivative that is more correct. We will look that next. I will go back and explain that one more. Now if I go and talk about second law of thermodynamics, we said entropy is a quantity which always increases but, when we write it mathematically, we think of it as there was some net

energy interaction with the outside world and then that energy interaction if it is irreversible process, then if it is P d V work it can be reversed, if it is a heat interaction it cannot be easily reversed. So, we have thinking about heat interaction with the outside world and then, we will say for such an interaction, entropy is given by d cube by temperature of the system, actually it should be temperature at the interface.

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If you go and look at serious thermodynamics books, they will call at it is atleast this and then they will say for simplicity we will keep it to be temperature at the interface, all that is serious mathematically clear, mathematically correct books. We will talk more about this temperature; it should actually be the reservoir temperature which is not happening in our any of the gas dynamics problems really. If there is flow going there is no reservoir next to it. But, you will imagine that there was a reservoir next to it, that fluid element. Then we just consider that particular case, imagine a reservoir next to it and see what it would have done and then get to this calculations, That what should be happen but, as of now we want to get to the mathematical expression final form which I want so, we will just start from here and then we will say ideally it should be assuming a reversible transfer and all.

We would not go into too much mathematical details of this reversibility because it is not so important for our gas dynamics, as long as we assume that this max is not wrong. We will say thermodynamics have already talked through with this and they are clear about it, we will follow them as of now. So, I can rewrite this along with this other expression or I would like this one first, then I will go to this one. So, I will rewrite this as, I have written this expression, is it in terms of intensive property or extensive property? Why? So, I got both the answers only one of them is right really.

Contains volume, easy way to think about it I have 1 box with 1 volume say I take exactly replica of that put on more volume next to it, total volume will be double, that means it is an extensive quantity. Same thing with energy say I have a box with 1 joule energy gas take exact replica of it, 1 more joule of energy put them together the net gas has 2 joules of energy, intensive, extensive entropy also same case extensive. The whole equation is written in terms of extensive properties. As of now we will keep that way for now. So, of course, I can rewrite this as, this is the form we will use a lot in gas dynamics we will see now why, in today's class itself we will see why.

This form is very useful for us. So, I will just put this rectangular on this. Now, let us say in case I want to think about intensive quantities only for this expression, what should I do? To get an intensive quantity from an extensive quantity all I have to do is, divide it by another any extensive quantity. This is an extensive quantity I divide by say mass, which is another extensive quantity. So, will get per unit mass entropy I have to give a symbol for it, I will use small s. Ideally, I am changing to small c here, not very clear in my fonts at that is change. Now, I just call this per mass, this will have units of per mass. What is it actual unit? Joules per kilo gram Kelvin. What is the unit of this? One it is just joules per kelvin this is become intensive quantity because I change the units. I used this symbol already, last class at the beginning I used this that said volume per mass. It is an intensive quantity inverse of density if you want to think about it.

So, this is the typical way we will write if I want this expression to be change to intensive quantities. It will just become this simple. Now of course, I can have per mass basis or per mole basis, number of moles or number of molecules is another way of I can call it, another extensive quantity which I can divide this expression with and I will get another form of intensive equation. This is one intensive equation I can get another intensive equation if I want.

So, let us call that I am putting a cap on top saying this is per mole basis; this is molar volume 1 mole. How much volume will at occupy differential of that. And if I think

about c v, this is joules per mole per Kelvin. This will have a different unit, joules per mole kelvin and this is of course, entropy what is unit, Joules per kelvin per mole.

Now, your entropy units, here is joules per Kelvin. So, here it will be joules per kelvin per mole here it will be joules per kelvin per kilogram. It is typically mole, if you want you can think about kilo mole we will come to that, when we take numbers, we will do numbers soon. So, this is a very common form which we will use a lot but, I may choose to use one of these forms also in case, sometimes I may choose this.

Now, there are lots of other properties, which thermodynamics created which are useful in analyzing situations, special situations, like say a flowing gas. Now, I need to think about some more extra quantities, it is not close system, it is an open system. Mass is exchanging across with the surroundings, then I have to think about some extra properties what quantity did I introduced thermodynamics? Enthalpy, I introduce enthalpy for open systems, while they will use E internal energy for close systems. They will go and use enthalpy for open systems and that is defined by a simple expression.

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This is the relation and of course, I can still define more things. Gibbs was the father of modern thermodynamics and then he used this quantity and it became Gibbs energy, Gibbs free energy. He called that only free energy; it became Gibbs free energy afterwards. Gibbs free energy has this form and this is related to how much if I talk about change from state 1 to state 2, this will be G 1, this will be G 2. I am going from G 1 to G

2 that delta G, G 2 minus G 1 is the net possible work you can extract from the system, if the system goes through this process from 1 to 2, that is the usefulness of this G.

Thermodynamics what is the use of doing all this, we want to finally find, if I take my gas from one temperature to another temperature. How much energy should I give and how much will I get out of it? How much work will I get out of it? That is what engineers are all thinking about all the time. Yeah, I give some energy; I give some whatever heat to it. How much will I get out of it? To think about that thermodynamics gives you this quantity, it will be very helpful for you. This is also called available energy, if you go and talk to mechanical engineering thermodynamics people.

We would not talk about it so much; we will still call at Gibbs free energy. And in case I am doing control volume approach and I want to find sorry closed system not control volume, closed system. This is for open system. These 2 will be predominantly used for open systems. This will be for close system, if it is a close system, then this is your helm holes free energy, helm holes free energy, we will use this symbol. Of course, different books uses the different symbols, this is just E instead of H there. This is enthalpy this is internal energy that will be the only change, if you think about it in a physical sense what is really happening is, if I go from state 1 to state 2, I need to supply this energy plus I have to also supply some amount of energy to increase its entropy so that, the process naturally occurs from 1 to 2, this is in a way the bribe I have to pay nature to get whatever I want happening.

So, if I give the gas say 100 joules of energy that will be here, it will not give out 100 joules of energy as the work out finally, some amount of energy will be lost in increasing entropy of the gas. Yes, that is the best you can get out of it. You will never get this full amount typically. You will have more loses but, if at all you think about how much can I get for a process, then I have to think about G 1 and G 2 find the delta G, this is the best I can get from the system, I have to of course, think about H 1, H 2 minus H 1 minus T 2 S 2 minus T 1 S 1 and all that, where do the whole thing. So, that is use of these variables. Of course, I can always think about the same convention as I used in this case, capital S becomes small s if I think about intensive quantities. So, I will go and write intensive quantities here.

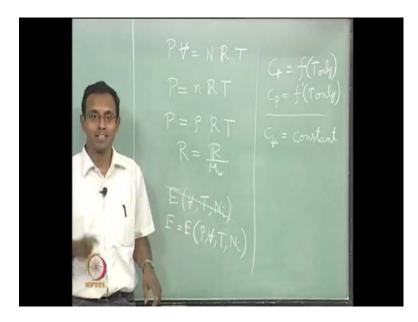
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So, if I think I will use mainly this system I would not worry about F. So, if I want intensive properties, this is per mass basis. If I want it per mole basis, I will put a cap on top of all these quantities, simple enough. And similarly, I have g this is again per mass basis, we will keep this and we will use this h equal to e plus P V predominantly in gas dynamics. It is a flowing gas open system always needs to be used. So, now we have come to point where we have used of all the thermodynamics laws, the next thing we need to talk about is about the gas itself.

Perfect gas, what is a perfect gas is the next question. What is a perfect gas? No inter molecular forces in a way, we can think about it that way, anything else. Specific heat capacity does not change with temperature possibly, any other explanation, any other ways of thinking about it, there is one more what is it? It follows the ideal gas law or ideal gas equation. So, what is the ideal gas equation?

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P V equal to N R u T, we will think of it that way. But, the way I am going to use it, I will remove this u because I want to write less on the board. I will put this double line R for universal gas constant. This is a constant for all gases, any gas you take in nature. It should be following this number of what is N? What number of moles of small particles sitting there?

Volume has total volume, it is extensive. The whole expression is the extensive. What is the extensive quantity here? N is the extensive quantity. Of course, remember both sides should have the same type of quantities. This is extensive so this should be extensive. So, this equation should be valid. It has other forms. This is another form where this N is mole density. N by V is your mole density. It can be written like this, if you want number of moles per unit volume, it can be written like this or I want write things in terms of per mass not per mole, this is per mole. I want it per mass basis. I can rewrite things in terms of that, then I will go and do this.

Remember this R is slightly different from the other R, this is your universal gas constant, this is called specific gas constant. It depends on which gas we are talking about. It is not all gases, this specific gas we are talking about. So, what is the relation between these two R's, this is universal gas constant divided by molecular weight of that particular gas. That will be this R and rho is my density of the gas. So, this is the link between pressure, temperature and density. If my gas is obeying this, then I will call this gas an ideal gas. But, of course that is not completely enough. I can call this as a perfect gas equation or ideal gas equation. Now I have to talk about the remaining things somebody guessed here that c V or c P, the specific heat capacity must be constant.

So, we will think about it. Typically, if I think about any property or we have to go back to that, ya this is a correct moment to go back to it. If I think about any quantity thermodynamic state of a system to define it, how many properties do I need, 2, why 2? Say I give you pressure and temperature, can you tell me number of moles. Look at this expression, can you tell me number of moles if I give you pressure and temperature of the system, you cannot. But, can you give me density? Yes, you can give me density, if you know the gas yes, you can give me density.

Let us say, I give you pressure and volume, can you tell me number of moles for my system? I still cannot. So, it looks like I need three quantities of which at least one of them should be extensive, for me to get the complete system. If I am interested in extensive quantities, if I am interested in only intensive quantities, then 2 intensive properties are enough that is what we saw here. If I give you pressure and temperature, both are intensive quantities. If I give you 2 intensive quantities, that is enough to give me all intensive quantities of my system.

I cannot tell you the size of the system but, I can tell you what it will be per kilogram of the system, that kind of information I can give you that is the idea of this. So, we are thinking about how many properties should I give for defining a system completely? Of course, you have to give its composition we started with zero th law, where we said we need pressure, temperature and composition.

So, we have to give all that to define things of course, I need composition of course, I can give you pressure and temperature, if I give pressure and temperature, then I am giving you 2 intensive quantities only in which case I can give you all intensive properties very easily. But, no extensive quantity, if I want to think about extensive properties also, I need to give you somewhere some extensive quantity, say mass of the system or volume of the system, number of particles inside the system, number of molecules, number of moles something.

I have to give you something that relates to the size of the system. But, can I give you a state of the system by giving you volume, total number of moles and temperature. Yes, I

can look at this expression, if I give you V, N and T, you know R. So, only P, if I get P, I have P and T, two intensive quantities. I can find any intensive property. If I want to find extensive quantity, then I just take this and multiply with that, I will get all the extensive quantities, it is simpler. So, you have to think about this.

Now, I will go back and look at my energy. If I want to define energy, I have to define it somehow in terms of 2 properties and composition. So, if I am thinking about a constant volume kind of systems, I want to think about volume as a key parameter. Temperature of course, is another key parameter for energy and then remaining things you need, will be concentrations, it could be intensive or extensive. I could give you number of moles of each gas in my air, say air is having so many moles of oxygen, so many moles of nitrogen.

I can give or I can just tell you 21 percent of molecules are oxygen, 79 percent of molecules are nitrogen. I can tell you that way also mole fraction or number of moles, I can give that also as long as I have another extensive quantity sitting here. This is another way of looking at it. So, you have to think about it in this specific way. Let us say composition is fixed, am I giving enough number of variables here, 1 intensive and 1 extensive. So, if I give you volume and temperature, you will tell me pressure, you cannot. So, ideally I need to give you three quantities, irrespective of composition.

Composition has to be known, other than that I need three quantities of which at least one should be extensive. Because I am writing extensive, I am interested in extensive quantities. So, I would say I will typically give you pressure. So, I will write this instead of this, I will write it like this. But, now we will go back and simplify the problem. We will tell that for my gas, internal energy is not a function of pressure. I am going to tell it is a function of temperature, main function is only function of temperature. Of course, it depends on volume but, that is related to, it is an extensive quantity that is the idea there.

So, we are going to say, I will keep pressure but, I will say my gas does not care about pressure, whatever be the pressure my gas does not depends on temperature the same way irrespective of pressure. That is what we are going to say, if a gas does this I am going to call this gas as thermally perfect gas. Thermally perfect gas that is I am going to write it differently, I will call this C v, the specific heat capacity per constant volume is a function of temperature only. Of course, we know the composition exists and the

extensive quantity volume also exists, we would not deal with all that right now. It just till this quantity is a function of temperature only. If this is the case, then my gas is thermally perfect gas. If this is the case, then I also can write specific heat at constant pressure will also be a function of temperature only but, a different function that is why I have put a prime there. Some question?

Student: It is depending with temperature and volume. So, why it pressure and temperature and all?

I am writing a generalized case, here I am saying to define a state of my system, I need 3 quantities irrespective of, I need composition plus 3 quantities. So, I am picking P V and T that is what I have done here. Now of course, I could have written this N i as X i, the mole fraction also, mole fraction of all the species also that will still work. Now, I am going to say volume. Yes, it is there that is what is my extensiveness of this quantity, we will keep it that way, only thing is pressure I do not want it to be thing dependent on pressure currently. I am going to consider gases which are typically independent of pressure either internal energies relation with temperature is independent of pressure that is all I am going to say. So, only those kinds of gases are called thermally perfect gases.

Now, we will go one more step further. We will say, if C v or C p the specific heat at constant pressure, if they are constants as a function of temperature. Now, it is not any general function, it is a constant with temperature. If I say that then the gas is called a calorically perfect gas, previous was called a thermally perfect gas. Now, it is calorically perfect gas.

Now, I have to define things very clearly. When I say calorically perfect gas, C p and C v are constant along with that I would also call this P equal to rho R T or P V equal to N R T is also obeyed by that gas. If I say my gas is calorically perfect. If I say my gas is thermally perfect, then I am saying P equal to rho R T or P V equal to N R T along with C p and C v are functions of temperature, only that is what we will have. Now, why are we talking about C p, C v so much in gas dynamics? Why? It so happens that for common gases, you had an answer tell me.

Student: flows. So, we need a parameter to define flow like enthalpy and also for enthalpy defining the enthalpy, we need the C p, C p for that.

Ok. Enthalpy is given as C p times T. When is enthalpy given as C p times T, for which gas for calorically perfect gas? In simple gas dynamics, if you go look at most of the books on gas dynamics, they will deal with H enthalpy is equal to C p times T. They are always assuming calorically perfect gas. But, in real life no gas is calorically perfect, for all range of temperatures. Every gas can be told that for some particular range say 100 kelvin to 400 kelvin, C p is constant. That kind of thing will happen for most gases. There will be a particular range where it will be a constant C p but, after that C p changes. Why?

Typically, all this time let us say for low temperatures, the molecules are not vibrating the bonds. But, at higher temperatures let us say I pick oxygen, oxygen connected with a double bond alright and the bonds get extended or contracted. If I go to very high temperatures till that time that particular vibration is not significant. There is not much energy stored in it we neglect it. But, when you go to very high temperatures of the order of 2000 kelvin for oxygen it matters. There is significant amount of energy given to oxygen will be taken for vibration of this bond. So, then it matters, at that time we cannot neglect this C p variation. So, I will go back to thermally perfect. I will not use calorically perfect gas in such situations. Typically, when we go from regular gas dynamics to high temperature gas dynamics, we will switch from calorically perfect gas to thermally perfect gas. Now, you just have to go give some relations between various variables.

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What is the value of universal gas constant R? If I write a number, I need units for this unless it is non-dimensional parameter. I will write whatever I hear first, this is a possible unit which is correct or I will just say remove this 1000 and 1000, I can equivalently write the unit could be joules per mole kelvin that is also possible units. I remember it does this simple enough. Now, specific gas constant but of course, now I have to know what gas it is?

Let us pick air, what is the molecular weight of air that is what I want to correct in this course? Many people will think it is 29. I do not want to use 29, use 28.8 if you want to be more accurate use 28.83 or 8 4, that is closer to a correct answer. Do not use 29, 29 will through you off and C p and C v values much more, we will keep this. What units is this? Grams that is it grams per mole, grams per mole but this is not s i unit. So, what will I do, I will make this into 10 power minus 3 kilograms per mole, I will write it like this. This answer comes out to be this 288.7, you should check the units also, per mole divided by per mole goes away k g is in the denominator, it just sticks to the denominator that is what you should get, use this, this is better than if you use 29 here, we will get 286.6 that will throw you off already a little bit.

When you want to do extensive variable calculations you will be thrown off much more. We do not want that, this is closer to the correct answer for air. Next variable will be C v. Let us say I want per mole C v, we use the symbol cap for it per mole C v how will I get that universal gas constant divided by gamma minus 1, this is the first time I am using gamma here, gamma is this C p by C v intensive or extensive what C p should I use here, they should both be same but, they can be extensive or intensive, as long as units gets cancelled I do not have to worry about it. I can have per mole C p, per mole C v divide them or per mass C v, per mass C p and per mass C v divide them that should all be fine, think about it that way for gas air.

What is it for air? 1.4 that is the number for this. So, of course I can calculate this number. I have to find out the number is I do not remember that number. 721.75. I am sorry, I made a mistake here, we will correct it right now this is kilogram kelvin which means, I should not put equal to sign here, I have used 288.7 divided by gamma minus 1 to get to this answer, 288.7 divided by 0.4 will give you this. I did it per mass basis, per mole basis will be a different number. You want me to write it again, I will write it.

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This will give you this number 721, if I do C p, this should be gamma by gamma minus 1 times R. This number is 1010.4. If you use 29 as your molecular weight, you will get numbers that are very different from this, you will get close to 987, 1000 that kind of numbers you will get, 1003.7 or something is the closest you will get I think. So, think about that use this number that is better for you.

The next thing we need to talk about is if I have a process, how will this process occur on a state diagram that is the main idea of using thermodynamics in gas dynamics. We want to review this thermodynamics so that, I can go for any particular flow situation and then look at how my gas is going from one state to other, is it a particular process. Typically, we deal with isotropic process. Of course, I can have some other processes constant temperature process, constant volume process, I can have different processes. So, I want to go and look at it on the state diagram that is what we will do the next time.

And then figure out, what kind of processes will give what kind of curves on that on the state diagram with different axis. We will try different axis that we will start with next time and after we are comfortable with different plots, we will go into loss of mechanics and derivation of mass momentum and energy equation that is what we will do next time. See you guys next time. Any other questions you guys have? See you guys next time.