

Applied Thermodynamics for Engineers
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Lecture – 01
Review of Thermodynamic Principles

Hello everyone, welcome to this new NOCC's course on the topic of applied thermodynamics for engineers, this is start of a new season, the first lecture so, I am really excited about what we are going to have in the following 12 weeks. I am sure that I can make this course interesting to each of you and it is your participation that is going to make it a fun affair instead of being a hard though subject like thermodynamics.

Now, to start with I should introduce myself first, I am Dipankar Basu, an Associate Professor in the Department of Mechanical Engineering, IIT Guwahati. I received my formal education firstly from the Jadavpur University, Kolkata and then doctoral research from IIT Kharagpur. I am here in this lush green campus of ours from 2012 onwards now, here in the Department of Mechanical Engineering, I belong to the fluid and thermal specialization.

Accordingly, I am associated with teaching fundamental courses like thermodynamics, fluid mechanics, heat transfer, applied thermodynamics also master's level courses like two phase flow or nuclear power generations and this is actually, not the first NOCC's course that I am doing. I have done NOCC's course earlier also but this is my first attempt to the applied thermodynamics.

I am really happy to be here because thermodynamics is a subject that is my all-time favourite, right from my college days I have always been a big fan of thermodynamics, the basic thermodynamics and also the application of that to different engineering fields. I have also taught this subject several times here at IIT Guwahati to the second year B.Tech students.

Therefore, I am very much confident about what I am going to offer to you. Before I start any discussion regarding the course, there are a few things that I have to mention. Firstly, the course is on applied thermodynamics so, basic thermodynamics is a prerequisite to this

particular course and thermodynamics is generally taught in the first or second year of any mechanical engineering course.

Because without thermodynamics, you cannot learn courses like fluid mechanics or heat transfer. Therefore, if you belong to the second year or third year of your mechanical engineering, you must have already done the basic thermodynamics. That background of basic thermodynamics is very important because what are the laws of thermodynamics, how to apply those laws in different engineering applications, you must have proper grip on that.

Only then we can go for the analysis of different kind of thermodynamic systems or engineering systems from thermodynamic point of view which is going to be the scope of this particular course. Also, a word of caution, as I have done NOCC's course earlier from there, I can say that while the idea of NOCC's is very encouraging and very interesting.

But the biggest hurdle that the students in early phases and not only students in fact as being an instructor for me is the lack of direct communication. Here I am not able to teach in a live classroom rather what I have is only this monitor and the camera in front of you. And all of you are on the other side of the camera and therefore, only communication that I can have with you is just whatever I am saying here.

Accordingly whatever feedback I am going to get from you, had it been a live class, I can immediately understand after explaining a particular topic if I want to or if I need to go a bit further on that if I need to repeat the discussion or I can continue. But here I don't have that option whether a particular topic has reached you or not, I can understand that only after getting the feedback from your side.

Therefore, your feedback is very important please regularly use the portal of this particular course. Whatever you are gaining from this course, whether you are getting the concepts or not, if you have any query whatever you have in your mind please write to the portal, so that I can immediately communicate to you. Also, in order to have a better communication and for the sake of better understanding for on your side, I think we can follow two things.

The first part is yours i.e., as I have just mentioned you need to give the feedback immediately to me if you have understood a topic, please let me know that. If you have not

understood anything please write that doubt to me, so that I can clarify that. It is only after getting your responses, I can think about repeating any particular topic or giving some more examples or maybe approaching a topic in a different way.

I am also planning to have a few live sessions where I can directly interact with you through hangout but of course that depends upon the logistics. And the second point that falls on me, I would try to go systematically and slowly through this course in fact, it is quite difficult to teach any fundamental subject like thermodynamics or fluid mechanics through slides and not at all a big fan of that.

Therefore, I am going to treat this one more like a classroom lecture with just plain blackboard, so that I can derive everything here, every small concept I can discuss in detail, every bit of mathematics I can work out here. Therefore, you may not get too many slides here rather there will be more number of empty slides where I am going to write the things I am going to discuss from very scratch, only big pictures which are absolutely essential or some big points which with which I have to start the discussion that probably will be available on the slides.

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Course outline		
Week	Module	Topics
1	Review of Thermodynamic Principles	Thermodynamic state & properties, Heat & work; First & second law of thermodynamics; Entropy, Exergy analysis.
2	Thermodynamic Property Relations	Maxwell relations; Generalized relations for changes in internal energy, enthalpy & entropy for ideal & real gases; Clapeyron relations, Joule-Thomson coefficient.
3	Properties of Pure Substances	Review of the phase-change process, T-s & h-s diagrams; Ideal-gas equation of state, Compressibility, Real-gas equation of state.
4	Air Standard Cycles	Discussion on reciprocating engines, Air standard assumptions, Carnot cycle, Otto, Diesel & Dual cycles; Stirling & Ericsson cycle.
5	Real Cycles for Reciprocating Engines	Fuel air cycles; Losses in actual cycles.
6	Gas Turbine Cycles	Ideal Brayton cycle; Intercooling, reheating & regeneration; Improvements & modifications in Brayton cycle.
7	Vapor Power Cycles	Rankine cycle; Reheat & regeneration; Improvements & modifications in vapor power cycles.
8	Cogeneration & Combined Cycles	Principles of cogeneration; Various combined cycles.
9	Refrigeration Cycles	Ideal vapor compression & absorption refrigeration cycles; Selection of refrigerants.
10	Gas Mixtures	Properties of ideal & real gas mixtures; Reversible mixing process & second-law efficiency.
11	Gas-vapor Mixtures	Properties of moist air, Psychrometry & Psychrometric chart; Analysis of different airconditioning processes, Concept of comfort; Components of airconditioner.
12	Chemical Reactions	Ideal & real combustion process, Enthalpy of formation & enthalpy of combustion, Adiabatic flame temperature; First & second law analysis of reacting systems.

I would like to go systematically, slowly and in detail to every bit of concepts. So, now let us begin our discussion. Firstly, we have the course outline, by now you must be knowing that it is a 30 week course or I should say 30 lecture course.

The entire content of this course has been divided into 12 modules, each of the module will be covered in a separate week, so we are planning to have 12 weeks of series of lectures.

This is how I am planning to go; the first module i.e., right from this lecture and following two-three lectures, we are going to talk about the review of thermodynamic principles. This is more like a review of what you have done in basic thermodynamics. I have already mentioned that thermodynamics is a prerequisite for this course, so you may be thinking what is the need for this one.

But issue is that, before telling the issue, I would like to thank you because of the large number of responses, I am getting in terms of the registration to the course and that also shows a good variety among the registered students. Now, when there are such variety among the registered students, I feel it is important to have a review of the basic thermodynamics.

Because in different places, thermodynamic concepts are explained following different standards, different approaches, different textbooks. Therefore, it is important to assimilate all of them into a common basic platform, so that you can understand exactly what kind of conventions I am going to follow here, what kind of symbols I am going to follow here and exactly what kind of interpretation of thermodynamic laws I am going to make use of.

In this first week I am going to review the basic thermodynamics where we are going to discuss basically everything starting right from thermodynamic states and properties, defining the thermodynamic system, the concepts of energy interaction in the form of heat and work, then the first and second law of thermodynamics and very important the concept of entropy and exergy.

Then next week, I am going to talk about the thermodynamic property relations as you will be seeing shortly, from the thermodynamic state postulate that if we know two independent intensive properties, we can calculate any other property. But how to calculate that? That you will be learning in this second week, where we shall be starting in the Maxwell's relation.

Then developing generalized relations for changes in internal energy, enthalpy and entropy for ideal and real gases, then Clapeyron relations and Joule-Thomson coefficient. Then properties of pure substances; it is also generally followed or covered in most of the basic

thermodynamics course but still I shall be reviewing the phase change process corresponding $T - s$ and $h - s$ diagrams.

Then, ideal gas equation of state, concept of compressibility and real gas equation of state which you may not have already learned. Then, the more relevant topics to applied thermodynamics like the air standard cycles which is the ideal cycle for the reciprocating engines. So, we shall be analysing the Carnot, Otto, Diesel, Dual cycle; and also, Stirling and Ericsson cycles.

Then, the application of this air standard cycles to real engines. So, we shall be talking about the real cycles for experimenting engines in terms of failure cycles and following different kinds of losses in actual cycles. Then, moving on to the gas turbines; the ideal Brayton cycle, intercooling, reheating and regeneration, possible improvements and modification in the Brayton cycle.

Then, moving on to the vapour power cycles, where you must be knowing about the Rankine cycle. So, we shall be starting with the Rankine cycle and then incorporating the reheat and regeneration concepts on that possible improvements in vapour power cycles. Then the combination of gas turbine and vapour power cycles in cogeneration and combined cycles. In week number 9, we shall be talking about the refrigeration cycles, where ideal vapour compression and absorption refrigeration cycles will be coming.

We shall be talking about different kind of refrigerants then, the gas mixtures; properties of ideal and real gas mixtures, reversible mixing process and second law efficiency. Finally, the gas vapour mixtures which is associated with air conditioning. So, we shall be talking about the properties of moisture, psychrometry and psychrometric chart, analysis of different air conditioning processes, the concept of comfort.

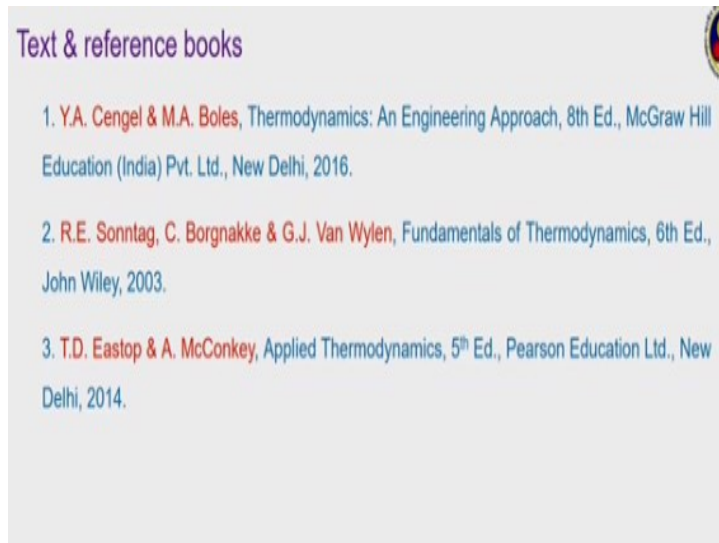
Also, a very basic discussion on the components of a standard air conditioner and finally, I would like to round off with brief idea on chemical thermodynamics by discussing about the combustion process, concepts of enthalpy of formation and enthalpy of combustion, adiabatic flame temperature and the first and second law analysis of reacting systems. So, you can see from the syllabus, it is quite an involved course, quite a heavy course in a way.

Because we are trying to cover almost all the aspects of applied thermodynamics in several places like here at IIT Guwahati we generally, we used to have two applied thermodynamics courses and now that has been combined into one for B. Tech students. We are having more or less a similar kind of syllabus here. One topic which is it not explicitly mentioned here that is reciprocating compressors.

Somewhere, I would like to discuss a bit about reciprocating compressors, probably in conjunction with the air standard cycles. Because analysis of reciprocating compressors is quite similar to the air standard cycles and also the concept of compressor is very important from air standard point of view. Now, some of the topics in a particular week will be covered in 3 or 4 lectures where some of them may need just 2 lectures.

So, overall, we may be having a total of 36, 37 lectures, like just in this first week itself the review of thermodynamic principles is going to take 4 lectures whereas some others like probably, this module number 5 is going to take only 2 lectures. So, let us see how we can proceed.

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These are the textbooks that I have already mentioned in the course webpage. The first two are the standard thermodynamics books, the book of Cengel and Boles. I am going to follow them most and also the classical book of Sonntag, here I have given a very old edition but at the much newer edition is also available to this particular book. Sonntag and the book of Cengel and Boles that will be suitable for most of the basic topics that we are going to talk in this course.

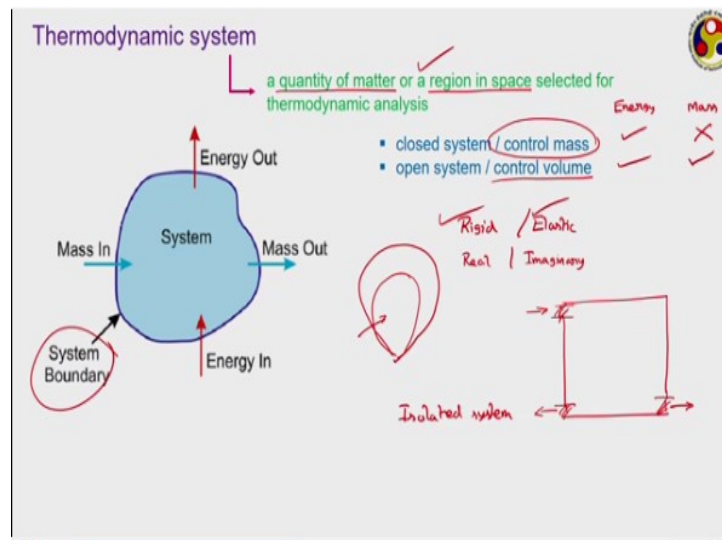
However, in certain cases you may have to look into different books like the book of Eastop and McConkey. It is a book specifically for applied thermodynamics. This one also I shall be using for certain discussions and even though I have not mentioned here but for certain other topics I may have to use some specialized books. I shall be mentioning that during those discussions, like when I will be talking about the reciprocating engines or air standard cycles.

Then, I may have to use or refer to some books of IC engines, whereas while talking about the refrigeration cycles are may have to refer to the books of refrigeration and air conditioning so, I shall be referring to those books suitably. Now, let us start the coverage of this particular week. Here we are going to review the basic thermodynamics course in just 3 or 4 lectures.

So, even though I have mentioned that I am going to go slowly in this course but this week, I probably have to go a quickly because whatever I am going to talk about, you are expected to know each of them. So, this is more to brush up your earlier knowledge and also to make you conversant to the convention that I am going to follow in this course and also the approaches of analysis that I am going to follow in this course.

Those of you who have already done the assignment 0, may have already faced questions similar to the one that we are going to talk about in this week.

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Any discussion of thermodynamics starts with the definition of a thermodynamic system. What is a thermodynamic system? A thermodynamic system is classically defined as a quantity of matter or a region in space where we are going to focus to perform any kind of thermodynamic analysis. The choice of system right from the definition you can see that it is upon us, it is upon the person who is doing the analysis.

We can choose any system suitable to the situation that you are dealing with. Even for a given situation, you may have different choices for the system depending upon what you are actually looking to identify. Depending on the choice of the system, the nature of analysis and the nature of different interactions may vary. Therefore, the choice of system is extremely important for any kind of thermodynamic analysis.

As shown here, it is a rough system where you can see the blue portion is the system that I am talking about is which we have selected for performing certain kind of analysis. So we have separate it out from the rest by using this purple line. This purple line is the one that is referred to as the system boundary. Anything outside the boundary is called surrounding and the boundary can be viewed as the barrier between a system and the surrounding.

Any kind of interaction between a system and surrounding takes place across the boundary. As shown here across the boundary we may have mass moving into the system or going out of the system, energy may be moving into the system or moving out of the system. But these are the type of interactions the system may have with the surrounding in form of mass or in form of energy.

And all these interactions are recognized at the boundary of the system itself. You can see that from the definition of the thermodynamic system, we can probably have two kinds of system one; quantity of matter or region in space.

The systems are classified in two classical categories:

Closed system

Open system

Closed system refers to a quantity of matter where you are talking about a fixed amount of mass and we often call them control mass.

Here we have fixed up a quantity of matter, i.e., a fixed quantity of mass. There will be only energy interaction between system and surrounding. Across the boundary of the system, there will be no mass interaction. If there is any kind of mass interaction, the mass of the system tends to change which we cannot allow as per the definition of a closed system.

For a closed system, we can have energy interaction but no mass interaction accordingly, it is called a control mass system. Open system refers to a region in space where in space, we identify a region and perform the analysis for that given space.

Hence, we call them a control volume system because we are often talking about a fixed volume in space. The boundary of the control volume system always gives away specific volume. For a control volume system, we definitely have energy interaction between system and surrounding. We can also have mass interaction because here we do not have any restriction about a fixed quantity of mass but the volume has to be constant.

The boundary of the system can be of different natures:

The boundary of the system can be rigid or elastic that is movable

The boundary of a system can be real or imaginary

This depends upon our choice like just think about a closed system because of a closed system is about a fixed quantity of mass but not anything about the volume. The volume of a closed system can change and volume change means the boundary will be moving. Consider this rectangle as the system, if this is a control mass system i.e., a closed system, then, with any kind of energy interaction, the boundary of the system may change.

Consider the example of a hot air balloon. The boundary of hot air balloon is drawn with red line. It is actually a rubber material which forms the surface of the balloon. Inside the balloon we have some hot air and outside is the surrounding. Using a source, say, a Bunsen burner we heat is added to this to the air which is present inside. Now that energy is added to the system, what will happen?

The temperature of the gas i.e., the hot air which is stored inside the balloon will increase. Due to the increase in temperature, the volume of the gas will also start to increase. What kind of system is this one? Here we are talking about a given quantity of mass of air inside the system. So, it is a control mass system and this red line is the boundary of the system. On supply of energy, the volume of the system can change accordingly, the volume of the

balloon may change to something like this. Therefore, it is not a rigid boundary rather it is a movable or elastic boundary. For control mass system, we generally can have movable or elastic boundaries.

However, if we take the situation of a rooftop water tank, may be made of brick or some hard material, say, plastic which we commonly see in our houses. We may be having a water inlet; water comes to the tank and have one or multiple water outlets. Let us consider a couple of water outlets. This is inlet number 1 and these are outlet numbers 2 and 3. What kind of system is this? Here the mass is allowed to flow into and out of the system, so it cannot be a closed system, it is an open system.

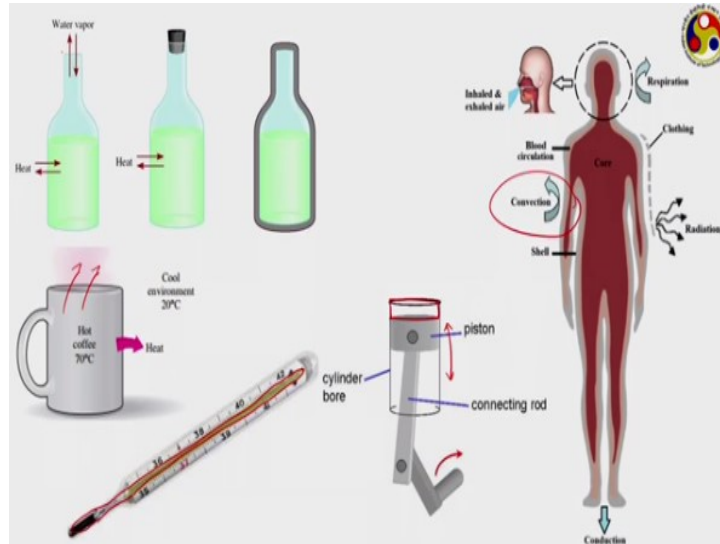
So, to decide a system whether it is open or closed, we have to check whether there is a mass interaction between system or surrounding. Now, in this case it is an open system and then what about the volume? The volume of the system is given by this red boundary. This is the actually hard plastic material that has an inlet side and two outlets. Here we are talking about enclosing a fixed region in space by this material. It is a rigid boundary, because the volume has to be constant and hence the boundary cannot move. Therefore, generally for control mass system it should be an elastic boundary or movable boundary; whereas for control volume system it should be rigid boundaries.

Now, consider the second type of definition; real or imaginary. In case of the balloon what kind of boundary do you have? Is it a real boundary or an imaginary boundary? Definitely, it is a real boundary because you can see the boundary which is enclosing the mass made of rubber material. So, you are having a real boundary. What you are having in the second situation? In the second situation, you may be thinking that you definitely have a real boundary because there is a hot plastic material, I fully agree or I do not agree fully.

I agree to it you partially because here though the boundary is present, the boundary is not enclosing entire system. In certain parts like, in this particular part and in this particular part, here you actually have to imagine the boundary of the system actually, this part was open and you are imagining certain lines to close the system. Therefore, here the boundary is partially imaginary and partially real. Accordingly, the boundary of a system can be real or imaginary and rigid or elastic.

In certain textbooks, there is a third type of system which is also called as an isolated system. An isolated system is just a special case of a closed system where there is no energy interaction as well. Therefore, for an isolated system both mass and volume remain constant. And it can be considered to be a special case of closed system, where there is no interaction at all between the system and surrounding and also no interaction at all across the boundary of the system.

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Quite a few examples of systems are given here.

In the first situation, you have a bottle partially filled with certain liquid and heat is being added or removed from there. As the top of the bottle is open, with additional removal of heat there may be movement of water vapour or certain other gases across the boundary of the system.

So, what kind of system is this? It is an open system. As we are having mass interaction and also with the kind of boundary, we are having an open system. Also, we are having a fixed volume that is rigid boundary but boundary is real apart from this small part; this part we are assuming an imaginary surface to close the boundary from thermodynamic analysis point of view, so partially it is imaginary.

Now, we are closing the bottle mouth using a cork. What is happening now? There is no mass interaction at all, mass is not allowed to come in or move out. But, because of the heat interaction, the energy content of the system will keep on increasing but the mass will not

change. Because of the heat interaction, energy content may increase or may decrease depending upon the direction of heat transfer. But there is no mass interaction and therefore it is a closed system now. Here the mass remains constant and also for this specific case, if the bottle is made of glass which has negligible thermal expansion, the volume also may not change significantly.

Now, consider the third situation; it is a thermal flask here, the bottle is not only closed but it is also insulated. Here no thermal or heat interaction is taking place. This is an example of an isolated system.

Let us take a few practical examples; a hot cup of coffee maintained at 70°C and kept in a cold environment of 20°C , then what will happen? Because the coffee cup is at a higher temperature, coffee is at a higher temperature. It will lose energy to the surroundings as the top is also open. So, you can find there is a heat interaction and also as the top is open, the water vapour may start to move out so, it is an open system and it is a control volume system where you are having this coffee wall and also an imaginary surface at the top forming the boundary.

Consider a standard medical thermometer. What kind of system is it? Here it is important to choose the system boundary. In the previous examples, a proper boundary was given. But here, you have to choose the boundary. What can be your choice for the boundary? Here, you are having the capillary tube in which mercury or whatever thermometric fluid is present, so that itself can be taken as the boundary. According to the choice of your boundary of the system it can be this yellow capillary which is forming this particular surface. So, this may be the boundary of the system which encompass only the thermometric fluid part.

When you keep the thermometer in contact with human body, there will be some kind of energy interaction. It is not an isolated system, as energy interaction is taking place. Is there any mass interaction between system and surrounding? As the boundary we have drawn is a rigid boundary, a real boundary in this case, you do not have to imagine the boundary. The capillary tube has a fixed wall. So, there is no mass interaction. Mercury or whatever thermometric fluid is not allowed to come outside this capillary tube and so it is an example of a closed system.

What about this one? A piston cylinder arrangement, where because of the connecting rod, the piston is continuously moving inside the cylinder. We have to choose our system in this case now. We analyse the thermodynamic behaviour of the gas which is enclosed in this cylinder. Our choice of system can be that, the side walls plus the top of the piston plus the cylinder head together can form the cylinder or the system. This is a real boundary that you are using but a movable boundary because the piston is continuously moving up and down, so it is a moveable boundary but movable real boundary. But what kind of system is this; closed or open? There is no inlet, outlet shown here, hence there is no mass interaction. So, this is an example of a closed system with real moveable boundary.

And my final example is of a human body. What kind of thermodynamic system a human body can be seen as? If we consider our skin as the boundary and everything inside that as a part of the system, everything outside the skin is the surrounding. Then what are the kinds of thermodynamic analysis and thermodynamic interactions we can have? Because of the respiration, we have air coming inside our system and also going out. So, it is actually an open system because there is a mass interaction. There are several kinds of thermal interaction and energy interaction taking place because of convective heat loss to the surrounding, we may be losing energy to the surrounding. There may be conduction through the part of our body which is in contact with the ground. There may be radiation losses under certain situations particularly to the clothing that we are wearing also. When we sweat, some of the sweat may evaporate from our body that also leads to another source of mass interaction. So, human body can be viewed as an open system.

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Properties of a system

↳ any quantifiable characteristics of a system

- intensive → T, P, ρ
- extensive → m, E, V, H, S

specific Volume = $\frac{V}{m} = v$

$\frac{X}{m} = x$

$h = \frac{H}{m}$
 $s = \frac{S}{m}$
 $e = \frac{E}{m}$
 $u = \frac{U}{m}$

Once we know about a system or once we defined a thermodynamic system, we have to identify the properties of the system. Properties are defined as any quantifiable characteristics of a system. The term quantifiable is important here because if we talk about something like colour that cannot be quantified i.e., more a relative kind of identification and therefore that cannot be identified as a property. Quantifiable characteristics can be a property of the system like pressure, temperature, volume, energy content, thermal conductivity, viscosity, acceleration, velocity, elevation etc. All these are different properties of the system because each of them can be used to define the system under certain situation and each of them can be quantified.

You must be knowing that properties are of two types:

Intensive properties

Extensive properties

Intensive properties are the properties which are not dependent on the size or mass or volume of the system. Whereas, extensive properties refers to the properties which are dependent on the size or mass or volume of the system.

Examples of intensive properties can be temperature, pressure etc., whereas example of extensive property is mass, which is the biggest and most suitable example. Also, we can have the energy content of the system, we can have volume of the system itself and several others will be coming in. As you have studied basic thermodynamics you must be knowing concepts of enthalpy and entropy. All these are extensive properties.

Next is one of the important conventions we are going to follow and its corresponding expressions. Generally, extensive properties are denoted with capital letters, like this 'E', 'V', 'H', 'S', this refers to extensive properties with mass being an exception, 'm' is used for mass. Extensive properties are always denoted with capital letters whereas, intensive properties are generally referred using small letters. Though temperature and pressure are exceptions, where they are referred using 'T' and 'P'. But other intensive properties are generally referred by small letters.

How to identify that a property is intensive or extensive? The easiest way is to see how much is the change in it or whether there is any change at all in the value if we divide the system into two equal halves just as in the example shown here. Here I have given you a system for which we know five different properties: mass, volume, temperature, pressure and rho (ρ); the density. Now, if we divide the system into two equal parts and check the properties of those two individual systems. What will happen? The temperature, pressure and density will remain the same but mass and volume will become half. So, these three properties are intensive properties whereas, these two are extensive properties because they are dependent on the size of the system. So, density can be another term which we are going to use ρ which is an important intensive property.

Now, any intensive property or extensive property per unit mass is called a specific property. For example, volume is an extensive property which we are going to use 'V' for this, if we divide V by mass then, we call this specific volume. So, specific volume is volume per unit mass. Similarly, we can define any specific version of any extensive property just by dividing it with mass. Now, the specific version of any extensive property is an intensive property.

Just think about the example that I have here. Here, what was the specific volume for this? It was specific volume for the original system was:

$$\text{Specific Volume, } v = \frac{V}{m}$$

Now, look at the two components, for this one what will be the specific volume?

$$\frac{\frac{1}{2}V}{\frac{1}{2}m} = \frac{V}{m}$$

which was the original one.

Similarly, for the second case also you are going to have V/m . So, specific volume actually is an intensive property and therefore, we are going to denote this one by ' v ', ' V ' refers to the volume; the extensive one, ' v ' will refer to the specific volume or intensive property. Similarly, any extensive property per unit mass is an intensive property. So, if capital X refers to an extensive property, ' X ' per unit mass will be given by ' x ', which is an intensive version. Accordingly, we can define say ' h ', the specific enthalpy as enthalpy per unit mass, ' s ' specific entropy as S per unit mass. We can define ' e ' as specific energy, E per unit mass, ' u ' specific internal energy as U per unit mass.

Can you think about any other examples of intensive properties? What do you think about velocity? Is velocity an intensive property or extensive property? Let us, say, C is the velocity of the original system. If I divide into two components what your velocity will each part have? It will remain C in both the cases therefore, this is an intensive property.

What about acceleration? Similarly, acceleration also is an intensive property. So, this way any property can be identified as either extensive or intensive. Also remember that the specific version or per unit mass version of any extensive property is an intensive property itself.

As per the convention we are going to use, small letters denote intensive properties and capital letters to denote extensive properties, exception being mass for which we use small m despite it being an extensive property. Also, for pressure and temperature, we are going to use ' T ' and ' P ' respectively despite them being intensive properties.

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State & Equilibrium

↳ the exact physical condition of a system

Thermodynamic equilibrium

- thermal equilibrium → T
- mechanical equilibrium → P
- phase equilibrium
- chemical equilibrium

$P_{\text{bottom}} = P_{\text{top}} + \rho g h$

Next is state, state is the exact physical condition of a system. Hence, to know the exact physical condition of a system, we have to specify all the properties that are relevant. Once we know all the properties of a system, we can say that we know the state of the system.

In thermodynamics, we always deal with equilibrium state; equilibrium state refers to a state of balance i.e., a state where there is no unbalanced potential inside the system. As the properties are not changing or if a system is in thermodynamic equilibrium, there is no unbalanced potential inside the system and the properties of the system are not changing with time and may not be also changing with space.

In thermodynamics, we always deal with the state of equilibrium. Even if the system is not in equilibrium, we try to reach a situation where it is very close to equilibrium, so that we can assume it to be in equilibrium and accordingly perform the analysis. So, to know the equilibrium state of the system, we need to know the values of each of the properties which are of importance and equilibrium can be defined from different point of view.

We can have thermal equilibrium which is associated with the equilibrium of temperature. A system is in thermal equilibrium means temperature is same everywhere and that there is no thermal potential in the system. Hence there is no net heat transfer is taking place from one part of the system to another part. For example, if this is a thermodynamic system and here at one part, the temperature is T_1 , another part temperature is T_2 . Now, if $T_1 > T_2$ then we know that there will be some kind of energy flowing from T_1 to T_2 . Then this system is not in thermal equilibrium. If the system is thermal equilibrium, it cannot have any such kind of

internal heat flow and therefore, these two temperatures has to be equal to each other. Otherwise, the system; the equilibrium or thermal equilibrium is not established.

Next is mechanical equilibrium; mechanical equilibrium is associated with pressure. But here we have a difference; a system in mechanical equilibrium does not mean that pressure is same everywhere. Say, we have a tank of water, where this is a free surface of the water and is filled with certain water having an elevation of h . Is the pressure at this particular point and the pressure at this bottom surface going to be same? They are not same. You have already learned fluid mechanics and from there you know that hydrostatic pressure varies with the elevation. So, if the pressure that is acting at the free surface is P_{atm} , then the pressure which is acting at this bottom surface will be:

$$P_{bottom} = P_{atm} + \rho gh$$

where ρ refers to the density of this liquid and g is the acceleration due to gravity. So, there is a continuous pressure variation like if we plot the variation in pressure with height, then at this point you may be getting a triangular profile like this, where the pressure is atmospheric at the upper surface and continuously increasing to reach to this particular level at the lower surface. This is perfectly logical and this system is called to be mechanical equilibrium. Here the pressure though is varying with space inside the system, it is to compensate for the body force field like the gravity in this example. And the mechanical equilibrium therefore is associated with the absence of any unbalanced forces in the system. Here the forces are balanced because the pressure force and the gravitational force are balancing each other.

Third is phase equilibrium. Phase equilibrium refers to the equilibrium of phases. Say, if you have a system which is having multiple phases. For example, you have a thermo flask which is filled up with a mixture of liquid water and ice. Now, if the thermo flask is maintained at 0°C under atmospheric condition then, ice and water will not be having any kind of phase change and so, the system will be maintained at a phase equilibrium. However, if they are at a different temperature then, depending on the temperature levels either water will be converted to ice or ice will melt to form water. Then, the system is not in phase equilibrium.

And finally, is chemical equilibrium i.e., the absence of any kind of chemical potential, no chemical reaction taking place in the system and therefore, the molecular structure is remaining the same.

So, this is how we can have four kinds of equilibrium situation in a system. And when a system satisfies all these equilibrium conditions then, we call it to be in thermodynamic equilibrium. Therefore, system can be in thermodynamic equilibrium when all these kinds of equilibrium conditions are satisfied. In this course of thermodynamics, we do not have to discuss too much about phase and chemical equilibrium. We shall be primarily considering the thermal and mechanical equilibrium. Chemical equilibrium will be coming into picture only in the last week of this course. It is in the module, where shall be talking about the chemical thermodynamics.

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The slide is titled "The state postulate" and features a logo in the top right corner. The main text states: "The state of a simple, compressible system is completely defined by two independent intensive properties." Below this, there are handwritten notes and diagrams. On the left, the properties $v = \bar{v}^1$, $T/P + n$, T , P , h , and s are listed. On the right, a diagram shows a rectangular block on a horizontal surface. A vertical arrow labeled z indicates the height of the block's center of mass. Next to it, the equations $PE = mgz$ and $\Rightarrow pe = \frac{PE}{m} = gz$ are written. Below the diagram, the equations $KE = \frac{1}{2} mc^2$ and $\Rightarrow ke = \frac{1}{2} c^2$ are shown.

Next is the state postulate. As I mentioned, to specify the state of a system, we have to specify all relevant properties and the system can have infinite number of properties. Because for every quantifiable property or any quantifiable scenario, we can define a property. Then, how many properties you need to define for a system for it to know the state that is being used by the state postulate which states that the state of a simple compressible system is completely defined by two independent intensive properties.

The state of a simple compressible system is completely defined by two independent intensive properties. Here, we have two phases to be careful of; one is simple compressible system. Simple compressible system is a system which is not being influenced by any kind of external effect like the system is not being subjected to gravitational acceleration, electricity, magnetism, velocity or any kind of or any such kind of body force field. When it is independent of any such kind of body force field then, we call it a simple compressible system.

Whereas, the second class of importance is two independent intensive properties, the properties have to be independent of each other. Like for system, if we define specific volume and density, are they independent of each other? They are not because we know that specific volume is just reciprocal of density and therefore, these two are not independent of each other and so specifying these two will not satisfy the state postulate.

In most of the situations, where only temperature and pressure are sufficient to deal with this condition of independent intensive properties. However, when you are going for a phase change process, you must be knowing that during a phase change both temperature and pressure remains constant and therefore, from the knowledge of temperature we can calculate corresponding pressure or vice-versa.

Therefore, in such a situation, we can take only temperature or pressure i.e., one of these two and we have to specify something else, say, second property or the third property to get two independent intensive properties. What can be this third property? We shall be learning it in our module 3 when talking about the properties of pure substances. But most of the practical situations particularly when dealing with solids or liquids or non-condensable gases, temperature and pressure are sufficient.

But it is not necessary to specify temperature and pressure like temperature and specific volume or pressure and specific volume or in a certain situation may be enthalpy and entropy, specific enthalpy and specific entropy to solve this particular condition of two independent intensive properties. If the system is not a simple compressible one, then we have to specify a third property along with the two which we have already selected.

Suppose, if the system is subjected to gravitational acceleration, what can be the third property? Let us say this is your datum and your system are located at this particular elevation, so g is acting downwards and the system is at an elevation of z , then the system is having some kind of potential energy and what is the measure of the potential energy?

The potential energy of the system will be

$$PE = mgz$$

or if we write in per unit mass sense, then it will be potential energy per unit mass will be

$$pe = \frac{PE}{m} = gz$$

Now, g being a constant, this z is the third parameter that we have to specify to have an idea about the corresponding potential energy.

Similarly, if the system is having some velocity, if the system is moving with a velocity c , then corresponding kinetic energy is

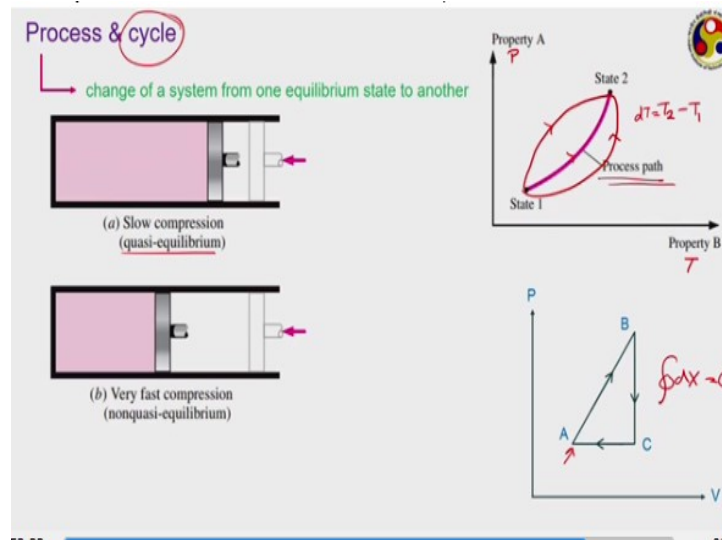
$$KE = \frac{1}{2} mc^2$$

or kinetic energy per unit mass will be

$$ke = \frac{KE}{m} = \frac{1}{2} c^2$$

So, we have to specify this velocity as the third parameter. Then the state postulate therefore can also be used for systems which are not simple compressible provided we specify a third parameter quantifying that additional influence.

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Next, we come to process; whenever the system is in a state of equilibrium particularly in an equilibrium with the surrounding then, there is no interaction. However, if the system and surrounding are not in equilibrium, then there will be some kind of interaction between the system and surrounding across the boundary of the system and that will lead the system from one equilibrium state to another. That is what we call a process. It refers to the change of a system from one equilibrium state to another. During the process, the system has some kind of interaction with the surrounding which can be mass interaction or energy interaction or

both. Accordingly, may not be all but some of the property values of the system gets modified. We generally represent the processes in terms of property diagram something like this, where we select two properties generally, intensive properties, independent intensive properties as the two axis and plot the process. And here is state 1 is the initial part of the process, starting point of the process, state 2 is the finishing point of the process, the pink line represents the process path.

So, whenever we are trying to represent a process on a property diagram, we generally have to specify three things.

No. 1 is the initial and final state like the state 1 and state 2 points are shown here, these are the initial and final states. No. 2 is the process path; the pink line i.e., the second thing that is how the initial and final states are connected in terms of the two properties that which we have selected as axis i.e., the process path. No.3 which is not shown in the diagram is the direction, you have to specify the direction of the process always. Because from here if you do not put this direction then it is not clear the system is moving from state 1 to state 2 or from state 2 to state 1.

Therefore, you have to specify the direction of the process and without this arrow, the diagram is incomplete i.e., wrong. So, we have to specify three things; first is state 1 and state 2 i.e., initial and final states, second is the process path and third is the direction of the process. Now, if a system or rather if a process is performed slowly then, it is possible to maintain the equilibrium state throughout the process between the initial and final states.

Take the example of a piston cylinder arrangement. If the cylinder or rather the piston is moved slowly. Say, if this is the initial position of the piston and these are certain gas molecules which are lying on the piston before you have started the piston move. As soon as you force the piston to move, then some additional forces acting on these molecules which are in vicinity to this, as the molecules which are far away from this piston, they are not able to sense this one. Therefore, there will be a sudden increase in pressure in this particular zone whereas, the pressure remains the same in other part of the cylinder. So, an imbalance is created and the equilibrium state is not possible to maintain.

However, if you move the piston very, very slowly so that whatever additional pressure the molecules are sensing, they are immediately able to transfer that to the surrounding

molecules. Then the pressure inside the system change very smoothly and hence we can identify almost all of the individual states in between. Say, this is the starting point and on application of certain force, if we are doing it slowly, we can identify almost all these intermediate states. We can also assume that each of these intermediate states are in equilibrium or at least very close to equilibrium, we call it a quasi-equilibrium.

Quasi means as if that is system is very close to equilibrium, if not perfectly in equilibrium. When the system or a process moves through a series of such kind of quasi-equilibrium or quasi-static states, then we can easily draw such kind of process diagram. However, if the system is being subjected to a very fast process, then there is an imbalance inside the system and there is unbalanced potential and therefore system is not able to maintain the equilibrium state and we cannot plot a process diagram like this.

Say our property diagram, we have selected pressure as one property and temperature as the other. Now, state 1 and state 2 we know the values of pressure and temperature but what will be the values of pressure and temperature at somewhere here or somewhere here? If the system is not in a state of equilibrium, we cannot identify these intermediate states and therefore we cannot draw this process path.

So, we generally represent the process by a dotted line which indicates that we are not sure about the intermediate states. We are only representing this one by connecting state 1 and state 2 with an arbitrary line, only when the system passes through a series of quasi-equilibrium states, then we know all the intermediate states and therefore, we can represent the process path by a continuous line.

When the system goes through a series of processes such that at the end of all this process it comes back to the initial state, then we call that the system executed one cycle. As shown here, the system starts with the; start at point A or state point A, moves to state point B and then, moves to state point C and then from C comes back to state point A. Therefore, there are three processes; A to B, B to C and C to A.

At the end of the processes, the system is back to its initial state. So, we can say that it has executed one cycle. At the end of one cycle the system returns back to its initial state and therefore, all the property values are restored. Therefore, over one particular cycle the change

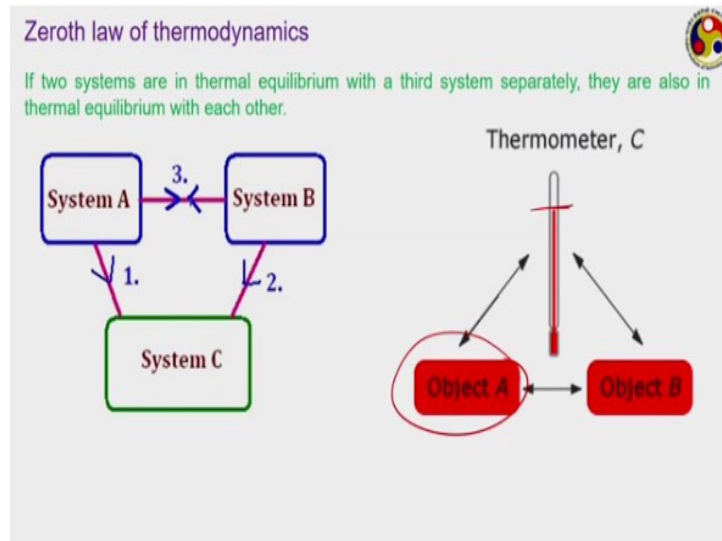
in any particular property is 0, that is why properties are called point function, they are dependent only on the state values, they are independent of the process.

Now, going back to the previous diagram here our initial state is state 1 and final state is state 2. If the system follows this pink line during the process or maybe this particular line during the process. The change in temperature will always be the same, the change in temperature will always be $T_2 - T_1$. Hence, the change in any property during a process does not depend upon what path it has followed, but depends on the two state points. That is why properties are called point functions and therefore, we can represent this one by an exact differential, can write it as dT .

$$dT = T_2 - T_1$$

As during a cycle, the system is coming back to the same state so, the change in any property will be equal to 0. So if 'x' refers to any particular property, then over a cycle the change in that property will be equal to 0 or on the contrary, if the cyclic integral of any quantity is 0, then that has to be a property of the system, a criteria that we shall be using in the next lecture.

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And that takes us to the zeroth law of thermodynamics, zeroth law, though historical point of view came after the first and second law was defined, conceptually it comes before the first law. The concept that it provides cannot be obtained from first or second law therefore, it is called the zeroth law of thermodynamics.

A very standard statement; if two systems are in thermal equilibrium with a third system separately, they are also in thermal equilibrium with each other. Just like the situation you have a system A and a system B and this is third system C now, A and B are said to be in thermal equilibrium. Similarly, B and C are also said to be in thermal equilibrium, then A and C also has to be in thermal equilibrium with each other.

If A and C are in thermal equilibrium, then there will be no flow through no transfer of heat between them when they are in contact. Similarly, there will be no transfer of heat between B and C, when they are in contact. So, if now, if we bring A and B in contact now, then there also will be no heat transfer between them establishing that they are in thermal equilibrium with each other. This establishes the concept of temperature and also provides the benchmark or idea of measuring temperature using thermocouple.

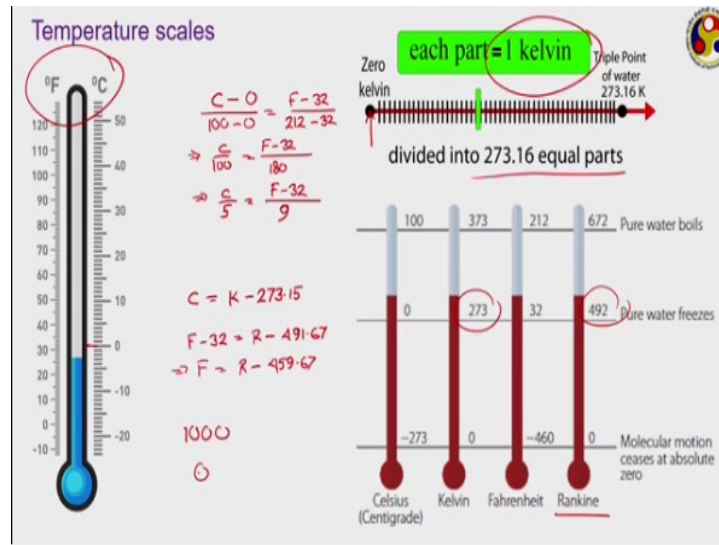
How can you define temperature without using zeroth law? Temperature specifically does not have any definition, we can define more in relative sense this one seems hot so, maybe at a higher temperature this one seems cold so, maybe at a lower temperature, it is a zeroth law which provides a definition of the temperature.

If system A and B are in thermal equilibrium then, some property has to be equal between them and that property is temperature. In a way, say, for system A and B to be in thermal equilibrium, their temperature has to be equal to each other. Or, for system A and B to be in thermal equilibrium, the property which has to be equal between them is temperature.

Now, if we replace one of the systems like the system C with a thermometer, you have a measurement principle or principle of temperature measurement. Like if object A and thermometer in contact with each other gives this particular level of thermometric fluid and object B and thermometer also gives the same level of thermometric fluid then A and B must be at the same temperature.

This way if we set up say, object A as certain base that is something with a known temperature then, we can easily form a thermometer scale and then taking this object B in contact with this we can measure the temperature of this object B.

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Accordingly, we define different kind of thermometer scales generally, we use certain standard temperature values. Suppose, we take ice under standard atmospheric condition then, we specify the temperature to be at 0°C and accordingly, we mark that point on the thermometer. Similarly, if we take the steam point which is 100°C under normal atmospheric pressure, then we take steam in; or thermometer in contact with steam and mark the corresponding values. And between these two limits suppose, this is your 0°C , this is your 100°C in between we form a uniform scale. And from using this thermometer now, we can measure the temperature of an unknown object.

The two most common thermometer scales are Celsius and Fahrenheit scales.

As you all know that under the ice point is given the value of 0 degree in Celsius scale and 32 degree in Fahrenheit scale. Now, these numbers we have decided that you have to understand. It is not that nature has given us these numbers, it is we who have decided that in Celsius scale, we are going to call the ice point as 0 and Fahrenheit scale as 32. And the steam point accordingly in Celsius scale has been given the mark of 100 degree in Celsius and 212 in Fahrenheit scale. So accordingly, any unknown temperature in Celsius scale can be given as; as we are having in uniform scale form by this.

If unknown temperature is C in Celsius scale minus the ice point which is 0 divided by steam point minus ice point, the two extreme points of the scale will be equal to the F which is that same unknown temperature in Fahrenheit scale minus the ice point which is 32 divided by steam point in Fahrenheit scale ($212 - 32$) that gives us

$$\frac{C}{100} = \frac{F - 32}{180}$$

i.e., very celebrated in formula:

$$\frac{C}{5} = \frac{F - 32}{9}$$

So, this way we can easily convert from Celsius scale to Fahrenheit scale or vice versa and also by knowing the two extreme points, we can develop any other temperature scales. Now, these two are relative temperature scales because this choice of steam point and ice point that has been decided by us. And if you are looking for absolute measurement you have to go to the absolute scale just like the Kelvin scale where absolute zero is marked as zero Kelvin. And the triple point of water generally is taken as standard which we call it given the value of 273.16 K. This division between this absolute zero and the triple point is been divided into 273.16 number of equal parts with each part signifying 1 K. So, Fahrenheit and Celsius scales are relative scales of measurement whereas, this is an absolute scale of measurement.

We all know the relation between Celsius and Fahrenheit scales and also the Celsius and Kelvin scales. Like, any value in Celsius scale will be equal to

$$C = K - 273.15$$

because the ice point has been given as 273.15 K in Kelvin scale. Similarly, the value corresponding to Rankine scale which is the absolute version of Fahrenheit scale that is given as:

$$F - 32 = R - 491.67$$

because 491.67 has been marked as the reference for ice point in Rankine scale. It is for simplicity it has been marked as 273 and 492 in the diagram but here I am giving the exact value. Now, using this, we can easily convert from one scale to another and here we can write as:

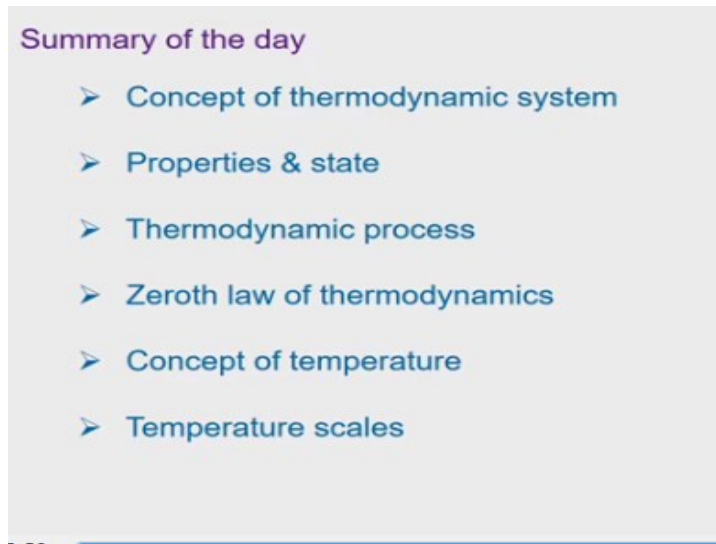
$$F = R - 459.67$$

As we know the relationship between all these temperature scales, we can easily convert one value to the other.

You can also define another temperature scale of your choice, it is up to you that you can take a temperature scale and where you call the ice point, a value of 1000 and call the steam point a value of zero and make an equal division between them. Here the value will keep on

decreasing with the increase in temperature but it is up to you. If you can make suitable conversion, then that is a perfectly consistent thermodynamic temperature scale.

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So that takes us to the end of today's discussion where we were basically reviewing the basic concepts of thermodynamics. We started with the concept of thermodynamic system, state and properties processes and cycles, we have seen how to plot the thermodynamic processes on property diagrams, then we discussed about the zeroth law of thermodynamics which gave us the concept of temperature.

The zeroth law allows us to define temperature or define the property temperature as a one which gives the condition for thermal equilibrium. And we briefly discussed about the temperature scales, so that is it for the day.

In the second lecture of this week, we are going to talk about the first and second law of thermodynamics and its application to closed and open systems. Till then, I am signing off, please go through this lecture and if you have any query write back to me immediately.

Thank you.