Thermodynamics for Biological Systems:
Classical and Statistical Aspects
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Lecture - 1
Introduction and Review

Welcome to this course on thermodynamics for biological systems - classical and statistical aspects. This course is some sort of a required course for anybody who wants to manipulate biological systems. This course will be offered by the two of us. I am G. K. Suraishkumar, I will be offering the classical thermodynamics part of it - the first 20 hours of the course. And then my colleague, Professor Sanjib Senapati will come up and address these statistical aspects. Both of us are faculty members, professors, in the department of biotechnology at IIT Madras.

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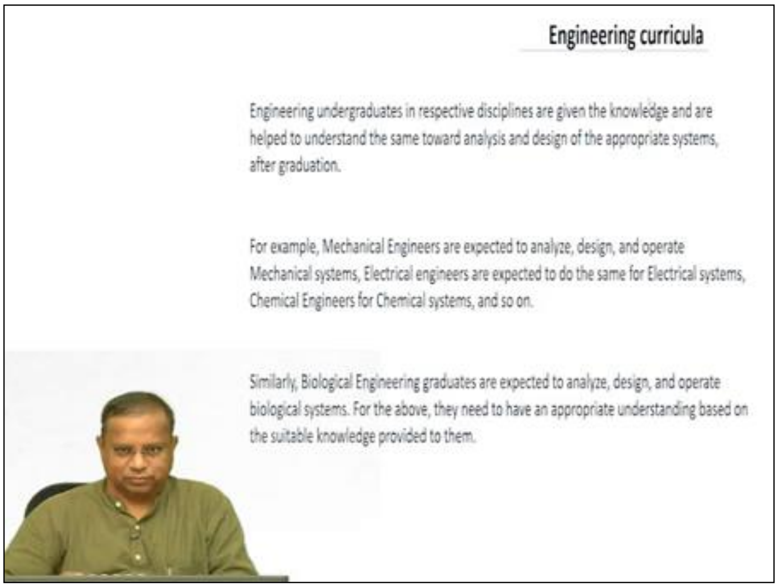

Let us begin at the need for this course from an overall perspective. When that becomes clear you would know the importance that needs to be given to this course, the amount of seriousness that you need to provide, or the amount of learning aptitude that you need to bring in to this course and so on and so forth. Need not be serious but the learning aptitude must be rather high. So, let us … let me tell you where this course fits into the overall … in the overall perspective of things.

So, let us start with the engineering curriculum. If you look at any engineering curricula it is something like this the engineering undergraduates in the respective disciplines, whatever it be - it could be electrical engineering, mechanical, chemical, biological engineering, metallurgical whatever you talk about - in the respective disciplines, are essentially given the knowledge we provide you with the knowledge or you pick it up from the various sources.

And then we help you understand the knowledge. I think that is where our main contribution comes in. And this understanding will help towards analysis of systems and operation … design … design first and then operation, of the appropriate systems. Electrical engineers would do it for electrical systems biological engineers would do it for biological systems chemical engineers adult or chemical systems and so and so forth.

This is the overall scheme in any engineering curriculum or of any engineering curriculum. For example … yeah … I think we have talked about this … mechanical engineers are expected to analyze design and operate mechanical systems electrical engineers are expected to do the same for electrical systems chemical engineers for chemical systems and so on and so forth. Similarly biological engineering graduates are expected to analyze design and operate biological systems - that is the reason why you are going through this 4 years of course.

For this they need to have an appropriate understanding based on the suitable knowledge that is provided to them … to the students.

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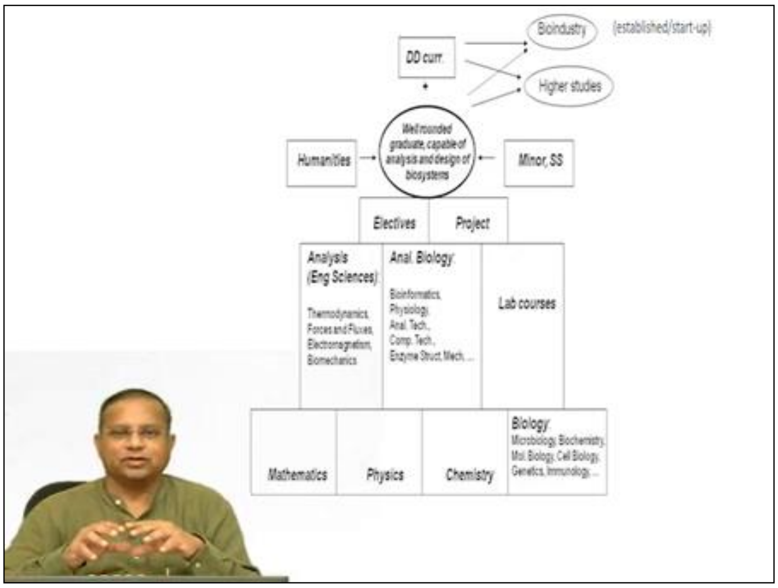

This is how in general, a curriculum is set up. Not many people are aware of this, think about this, and so on so forth. So, there is a lot of confusion regarding what is really a part of the curriculum, what is not, and so on and so forth. And this is essential to understand the role of thermodynamics, the central role of thermodynamics, for especially biological engineering or for any engineering for that matter. Initially we start out by providing you with a base in mathematics, physics, chemistry, and biology.

I think this would … yeah … mathematics, physics, chemistry, biology - this provides the base for you to pick up the various things. Once you have this base, which is provided through either the material at the higher secondary school level or the first-year engineering level … that is one of the reasons why the first year engineering strengthens your knowledge in these aspects. For biological engineering, students typically do not have much background in biology … and that is the reason why we give you pretty much a full complement of the fundamental biological material through various courses.

We spend quite a bit of time for the first two years doing that, but that becomes absolutely necessary if you want to manipulate biological systems. On top of this base you have courses that provide you with means of developing skills of analysis that could include analysis of the engineering sciences - this is where thermodynamics comes in. It is one of the central pillars of analysis but there are not many pillars there. Thermodynamics, then transport, and maybe mechanical aspects - these I would say are the 3 pillars of engineering analysis for biological systems.

And then of course you need to understand biology from an analytical perspective. There are a lot of courses for that supplemented with the laboratory courses where you pick on … pick up hands-on information … hands-on knowledge of the way the various systems work or the representatives of the various systems work. That is a whole idea of lab courses. There are various ways of doing lab courses. I do that a little differently, but this is essentially what it is.

On top of that you have electives; you could have a project. And then, any person especially in this age group … you know … typically between 18 to 22 or plus minus two years whatever it is; it is plus usually two years. They need … they are at a stage in life where they need to be developed into well-rounded graduates. And therefore, some humanities courses are provided towards that. Humanities course is play a huge role or essential role in doing that.

The engineering curriculum usually does not do that. You will have to bring in the humanities aspects into the engineering aspects that we do so that you become a well-rounded individual who is capable of contributing appropriately and significantly in the real world. And there could be a minor and so on so forth … that depends on the curriculum. For dual degree students we have a dual degree where they get a B.Tech and M.Tech at the end of 5 years. So, for a dual degree curriculum … ah … we provide some amount of research.

The output from this is either towards the bio industry - either established bio industry or a start-up bio industry. Start-ups are becoming popular nowadays. A lot of people are looking at that. Some people are successful. Or, towards higher studies … maybe to get into various aspects at a higher stage or to get into academia. This is the way the whole curriculum is set up. There is a certain purpose for it. And these various courses play essential roles towards developing a graduate an average student … the average … by average, I mean the mean of a population … that is what I mean by an average; most students are average students.

The … To develop an average student into a person who is capable of contributing significantly. And thermodynamics, as I mentioned, is an important pillar for the analysis of biological systems. And say, it is one of the … say, 3 pillars of … for analysis of biological systems. So, it is a very important course. It is very important information. It is a nicely … you know … the way thermodynamics has come up … it is based on its own set of axioms which are so powerful and the applicability is so wide to very many different branches or fields of engineering.

Also I like to mention this aspect about industry versus academia. Of course, the initial view for graduate students, students who graduate - undergraduate students - is towards the industry, could be. Maybe a fraction of you are interested in higher studies. Both are certainly valid. Only thing you need to realize is that the goals of the industry and the goals of academia are very, very different. This confusion somehow is so set in people's minds that they confuse a lot of things.

Academia is much bigger. Academia trains people towards industry - that is only one aspect of what they do. And there is … there are many more aspects to academia. More importantly, industry needs to work in the short term. The goals need to be short term … Of course, you could you could have visions and so on so for that the day-to-day operation needs to be in the short term towards short term goals and so on and so forth.

So, the way the industry needs to operate is very different. So, we can provide whatever is essential for that aspect. And the industry being short-term would change … would change quite frequently. And the graduate must be able to mould himself or herself to those changes. And that would happen only if the fundamentals are strong. Otherwise, the person will just not be able to cope up. And, this aspect is what academia provides. It prepares a person for the long term if the person is in the relevant industry and so on so forth.

So, to look at the utility on a very short term is inappropriate. That is where an industry needs to work with its focus at a particular time. Whereas, a focus of academia is much, much larger in terms of time. You need to keep this into account. And both are equally important. Both serve the mankind … humankind in significant ways, and they are essential aspects. There is no picking of one better than the other. It is only how you view the scope of the various things … and not to mix up the scope of these things.

If you limit academia to serving only the short term goals of the industry then you are doing academia a dis-service.

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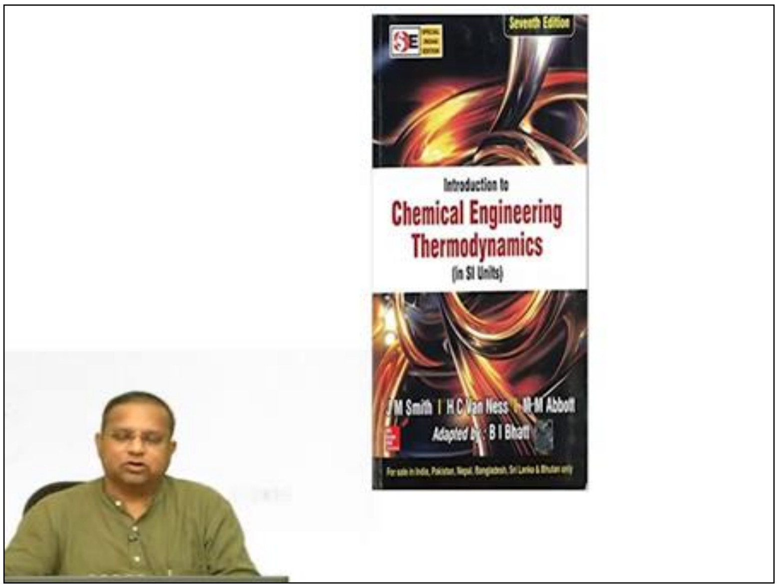

Coming back to this course … this is going to be your textbook for this course. It is Introduction to Chemical Engineering Thermodynamics. It is an old book. It is a convenient book … let me put it that way … it is a convenient book. It was my textbook, maybe many decades ago … a different version of it. It is by Smith, Van Ness. It was … it used to be by Smith and Van Ness earlier. It is now Smith Van Ness and Abbott the 7th edition. There is a special Indian edition now available which has been adapted by B.I. Bhatt.

This is going to be your textbook. It is available on any of these textbook sites … in other words textbook selling sites … uh … Amazon.in as an example. uh … I think the price is around 600 something.

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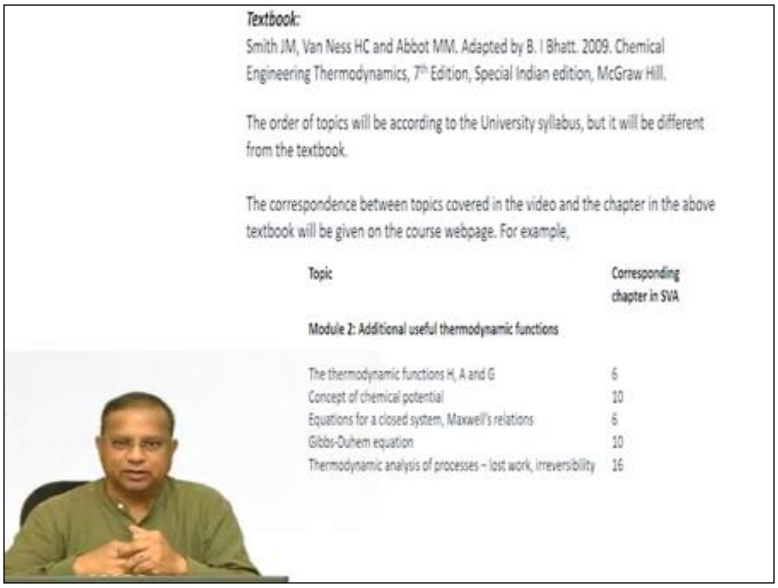

Those are the complete details of the book. Smith, Van Ness, Abbott adapted by B.I. Bhatt, 2009 it was published. Chemical Engineering Thermodynamics 7th edition. It is a special edition … Indian edition by McGraw-Hill. The order of topics will be according to your … a typical University syllabus. But it will be different from that given in the textbook. The order of topics has been designed to improve the understanding, the ease of application, and so on so forth of thermodynamics.

This book, I do not think does that very well… So we … It is a very convenient book to have. That is the reason I mentioned it was a convenient book to have. So, the order in which the material is presented will be different from that in the textbook. And of course this is for chemical engineering. We will be doing it for biological engineering. So, the material will be very different. And, of course, Professor Sanjib Senapati, when he begins his lectures, he will give you the textbooks that he will follow for his section of statistical thermodynamics. That aspect is not present in this book.

In fact, this is pretty much one of the first courses, I think, which will provide both these aspects together which is essential for biological systems. It may not be so essential for an undergraduate of chemical engineering, but certainly it is essential for an undergraduate of biological engineering to manipulate biological systems, to know about these two aspects. Since the order is going to be different … ah … the correspondence between the topics covered in the videos and the chapter in the above textbook that corres … the … which has the material which corresponds to the video - that will be given on the course web page.

For example, it will look something like this. A part of it is given here. You have the topic and the corresponding chapter in Smith Van Ness and Abbott. For example, module 2, Additional useful thermodynamics functions. The thermodynamic functions H A and G are from chapter 6, the concept of chemical potential is from chapter 10, equations for a closed system, Maxwell's relations are from chapter 6 again.

Then Gibbs Duhem equation is from chapter 10, thermodynamic analysis of processes such as lost work, irreversibility, and so on … from chapter 16 … and so on. It will go back and forth but do not worry this will be available to you. The material will be usually self-contained. However, it is highly recommended that you read the textbook. And to go back to the appropriate chapters in the textbook, you have this guide table that will be provided.

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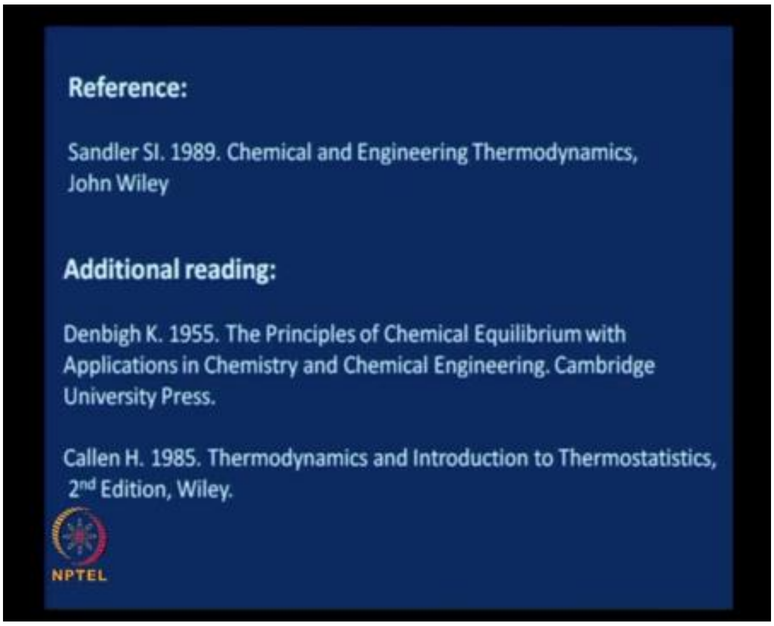

There are other books that you can refer to. One of the references that I would recommend is Sandler, 1989, "Chemical Engineering Thermodynamics", that was published by John Wiley.

Additional reading: these are very nice books, which would be helpful after you understand a little bit. These would be for approaches, completeness and so on, and so forth. A very nice approach is in the very nice development of the subject is given in Denbigh. It was published way back in 1955. It is called the Principles of Chemical Equilibrium with Applications in Chemistry and Chemical Engineering; published by the Cambridge university press. And, also a very good book is Callen. The title is Thermodynamics and Introduction to Thermostatistics, the second edition by Wiley.

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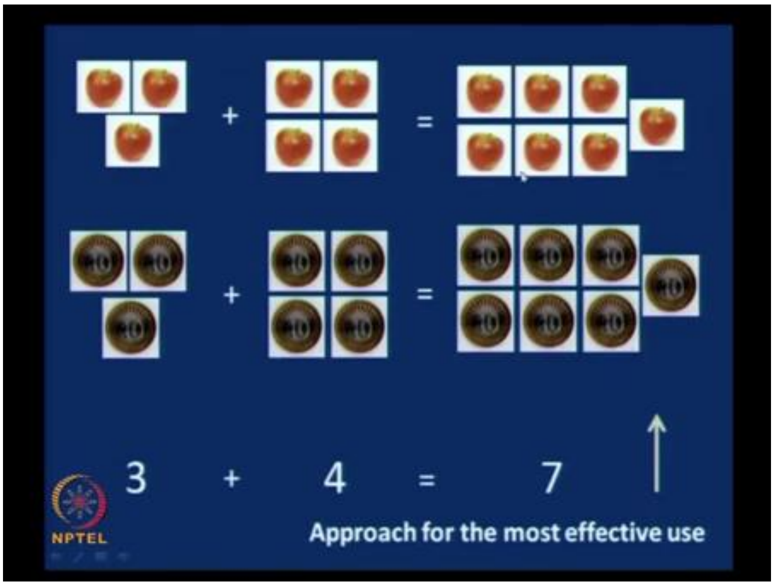

Let us also look at the approach that we will use in this course. I personally think it is a lot more effective, when we are looking at using thermodynamics to analyse and understand biological systems better.

The approach for the most effective use can be explained as follows. We have all learned Mathematics. And, if you think back to your primary days, to see how we really looked at mathematics, how your teachers would have introduced mathematics to you, it would be something like this.

A simple process of addition: if you look at 3 apples and you add 4 apples to it, you will have 7 apples. Similarly, if you took 3 coins and added 4 coins to it, you would have 7 coins. Instead of talking about 3 apples, separately, or 3 coins separately, and so on and so forth, if we recognize that this can be abstracted as the number 3 and this can be abstracted as the number 4, the sum would always be equal to 7.

We will be approaching, or using this particular approach, 3 plus 4 equals 7, in this particular course, which is called an axiomatic approach to Thermodynamics. And, we will present this first and use some examples to show specific applications to biological systems or processes of biological importance.

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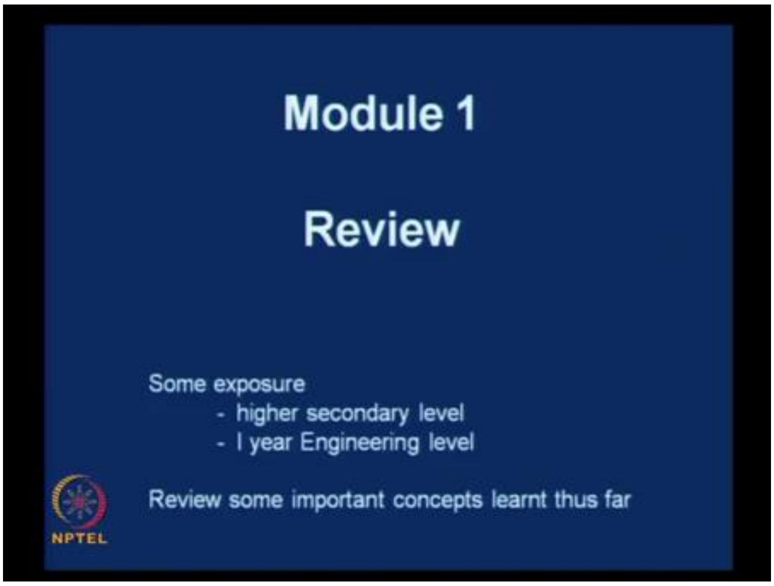

Let us first review. This is going to be module one. A review of whatever you know already. And, what you know already is through some exposure at the higher secondary level itself. You would have had some chapters in Physics or in Chemistry relating to Thermodynamics, at least the first law of Thermodynamics. And, definitely, a course at the first year engineering level, which deals with Thermodynamics. What we are going to do in this particular module, is to review some of the important concepts that we have learnt so far and what we need as the base to take things further in this particular course on Application of Classical Thermodynamics to biological systems.

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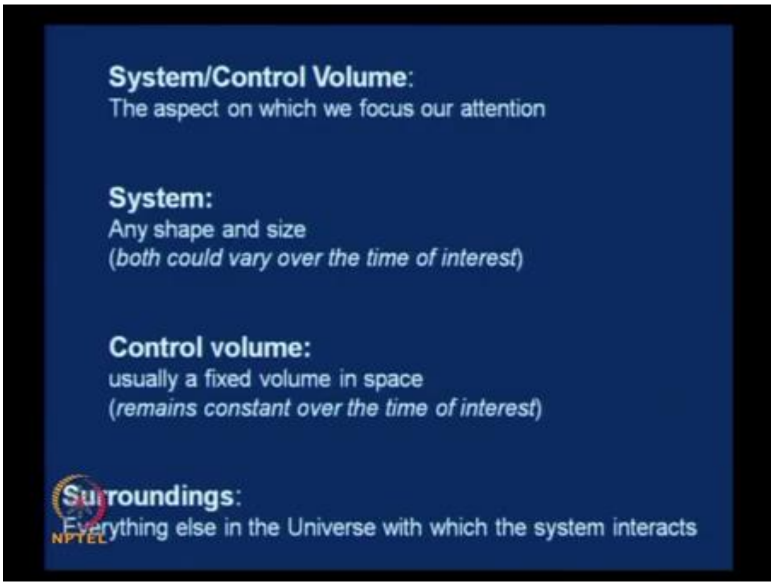

The first concept that we are going to look at is called the system or the control volume. It is very simple. The concepts are very simple. And, once you understand them and apply them, it makes it complete. System or the control volume is nothing but the aspect on which we focus our attention. I will explain this little further as we go along. Some slight difference between the two: the system could be of any shape and size, and could also vary over the time of interest of our particular dealing with that system.

Whereas, a control volume, usually, is a fixed volume in space. It remains constant over the time of interest.

The term "surroundings" refers to everything else in the universe with which this particular system interacts.

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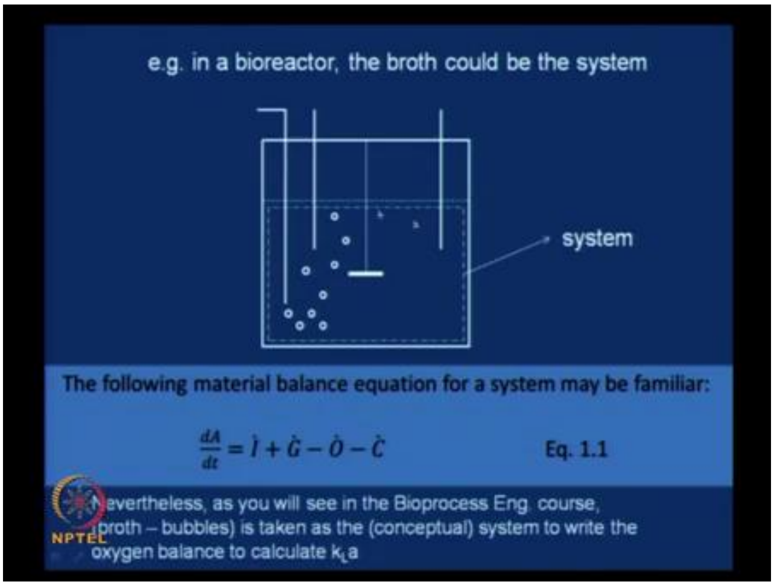

For example, we probably know – we are all bioprocess people, biotechnology people; so, we probably know what a bioreactor is, already. You would have been introduced what a bioreactor is, in probably one of your first courses. Very simply, bioreactor is nothing but a vessel in which bio-reactions takes place. You can qualify it by saying, it is highly instrumented and controlled vessel in which the bio-reactions take place.

We also know that the liquid in the bioreactor is called the broth. While analysing the bioreactor …; ok, let me tell you a little further about the bioreactor. This is the input of air into the system. We know that aerobic organisms require oxygen. The source of oxygen is air. And that is typically provided by bubbling air, sterile air into the bioreactor. This is a temperature measurement, may be. This is pH measurement for appropriate controls. This is a stirrer, which keeps the cells in suspension – rotating at a particular rpm – controlled. When we analyse this bioreactor, for certain situations, may be, the system could be the bioreactor broth. One of the ways of analysis, a very powerful way of analysis, is to look at material balances.

What is material balance? If you recall the course that you did it in may be process calculations, bioprocess calculations or a first equivalent course in the Biotechnology program, the material balance is a combination – the relationship between accumulation rate and the input rate, the generation rate, the output rate and the consumption rate.

In other words

$$\binom{input}{rate} + \binom{generation}{rate} - \binom{output}{rate} - \binom{consumption}{rate} = \binom{accumulation}{rate}$$

And, note that we learnt that, this is applicable only over the system for which it is written. As I said, this broth could be the system for the application of, let us say this material balance principle to some aspects. Nevertheless, as we will see later when you do your Bioprocess course Bioprocess Engineering course, we can consider a system consisting of the broth; and, you take the bubbles away from it, conceptually. In other words, the system is going to be the broth without the bubbles in it. This is not a real system, or this is not a reality. But, conceptually, we are considering the broth and removing the bubbles from it.

This becomes essential for easy analysis of the system towards calculation of something called the volumetric mass transfer coefficient, or the K_La. Essentially, we write a oxygen balance around that particular system consisting of broth minus the bubbles and that gives us the K_La.

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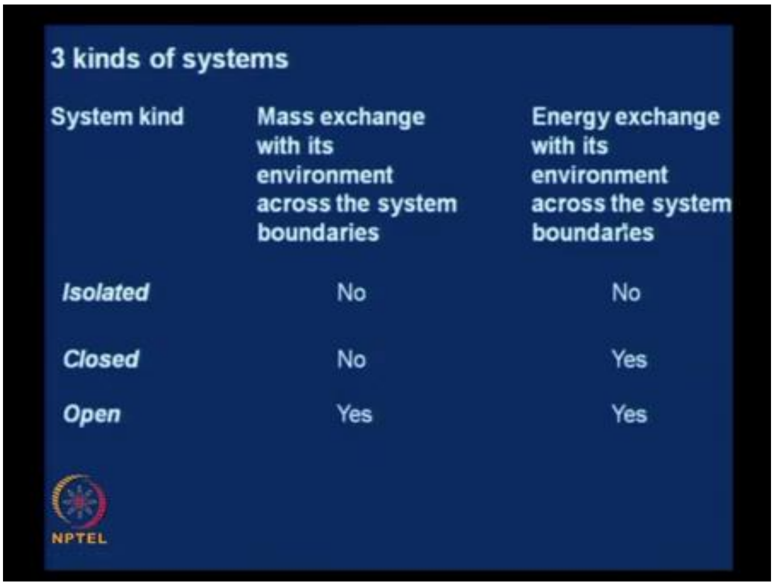

So, the choice of system becomes very crucial. And then, effective choice of system as you would know comes through practice. We also learnt that there are three kinds of systems, depending on, whether there is mass exchange between the system and its surroundings across the system boundaries. That, "across the system boundaries" is very important. Please make a note of that.

And, whether there is energy exchange between the system and its surroundings across the system boundaries.

The first kind is called an isolated system, where there is no mass exchange between the system and its environment (or its surroundings), across the system boundaries. And also, there is no energy exchange between the system and its environment (or surroundings) across the system boundaries.

The second kind of system is called a closed system, where there is no mass exchange between the system and its surroundings; whereas, there could be energy exchange between the system and its surroundings.

The third is an open system, where there could be mass exchange as well as energy exchange between the system and its surroundings.

It is easy to imagine closed systems. You take a closed box with some material in it. And, there is no way that material could escape; whereas, you can add heat to it and so on, so forth. That is a closed system. You could very easily imagine an open system, but it is very difficult to imagine an isolated system. Very rightly so; because isolated system is just a concept. It was very useful to develop ideas and relations and so on and so forth, as we would see in this course; whereas, it is not a reality.

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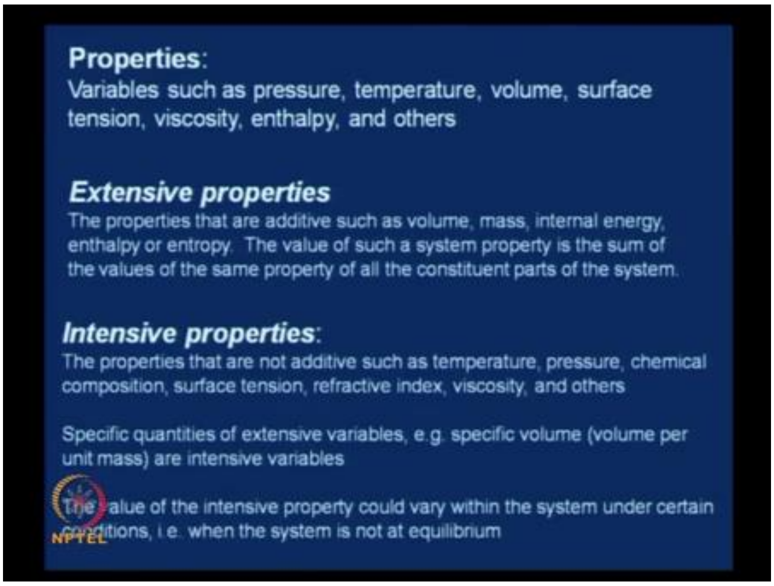

The next concept that we look at/review is the concept of property. What exactly is a property? Properties are nothing but variables such as pressure, temperature, volume, surface tension, viscosity, enthalpy and others of the system. It could refer to the system predominantly; of course you would refer to the surroundings also. There could be two types of properties; extensive properties and intensive properties. Extensive properties are the properties that are additive. You have more of the substance and you have more value of the property. For example, you take some amount of a substance, you add an equal amount of the substance, the volume of the substance could be 2V if the initial volume was V.

Therefore, the properties such as volume are additive. Mass is additive; internal energy is additive; enthalpy is additive; entropy is additive, and so on. So, the properties of the system that are additive are called extensive properties. Typically, the value of such a system property is the sum of the values of the same property of all the constituents of the system. If there are very many different constituents of the system and we add the volume of each constituent, the volume of the system, total system is the sum of the volumes of all constituent aspects or constituent parts.

In contrast, intensive properties are properties that are not additive. For example, temperature. Assuming that the system is homogenous, wherever you measure the temperature of that system, the temperature is going to be the same. So, such properties are called intensive properties, which do not depend on the amount of substance present. Or in other words, they are not additive. Some examples are temperature, pressure, chemical composition, surface tension, refractive index, viscosity, and so on.

Sometimes, we do a trick. We define some pseudo intensive properties for our own needs. We know that volume is an extensive property. Whereas specific volume, you know you divide volume by mass that becomes an intensive property. If you take a homogenous system, the volume by mass is a same throughout the system. Whereas, the volume itself would vary depending on the amount of the substance present in that system. And, we will also consider them as intensive properties in this particular course. So, the value of the intensive property could vary within the system under certain conditions too. It is not that it should be the same at under all conditions. For example, when the system is not at equilibrium, the value of the property, of the intensive property, would vary in the system.

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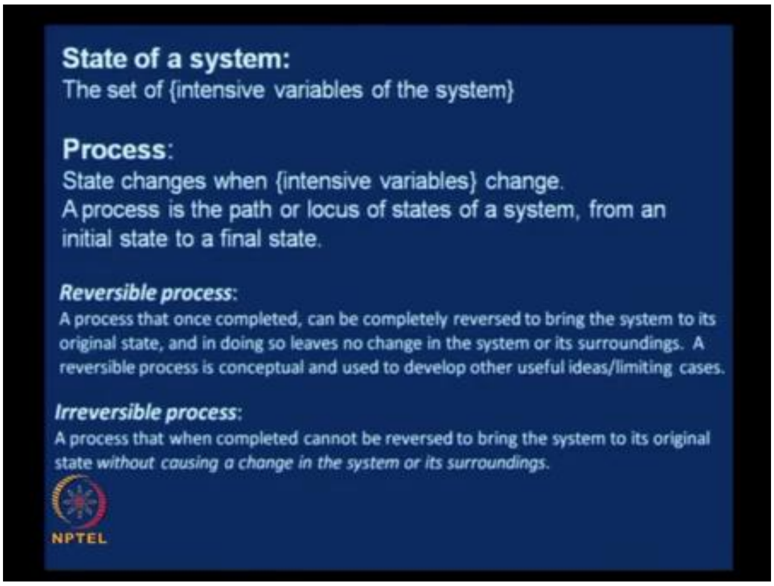

The next concept that we will review is the state of the system. The state of the system refers to nothing but a set of intensive variables of the system. For example, a system is at a particular pressure, temperature, volume, that set of properties, pressure of some atmospheres or some kPa, some temperature in degrees C, and so on. It is called the state of a system.

Next is process. Process is nothing but the path or the locus of the states of the system. For example, when the state changes, the state of the system changes, the set of intensive variables will change. As we were seen earlier, state is nothing but the set of intensive variables. The process is nothing but the path or the locus of states of the system. And, typically it goes from an initial state to a final state.

There could be many types of processes. We'll look at couple of them, which are important. A reversible process. This, as you know it is not realistic, but it is a very good concept. It is a very good concept, which we can use to develop arguments and test our results against. That is what it says here, a reversible process is conceptual. And, it is used to develop other useful ideas or limiting cases. Reversible process is a process that once completed, can be completely reversed to bring the system to its original state. And, in doing so, it leaves no change in the system or its surroundings.

The irreversible process is something that is not reversible. A process that when completed, cannot be reversed to bring the system to its original state, without causing a change in the system or its surroundings. Note this: "A process that when completed, cannot be reversed to bring the system to its original state, without causing a change in the system or its surroundings". Every part of this is important. There are many other processes such as isothermal process, isobaric process, isochoric process, adiabatic process and so on and so forth; which you would have already learnt about in your previous classes.

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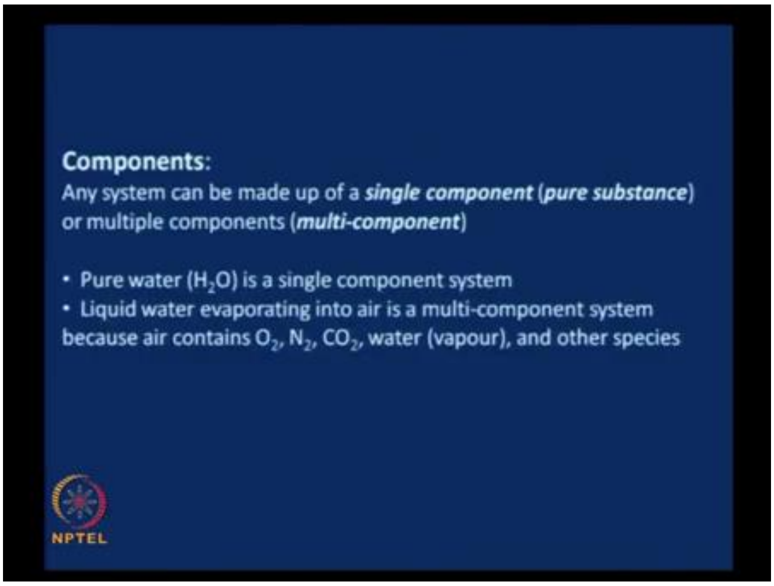

Next, let us talk of components, concept called components. Any system could me made up of, may be a single substance or multiple substances. If it is made up of a single substance or a single component, then, that single component is called a pure substance. Or, if there are multiple components, the system is called a multi component system.

For example, if you take pure water and you consider that as your system, then pure water is a pure substance and the system is a single component system. If we consider liquid water evaporating into air that becomes a multi component system because you have water evaporating into air; the air contains, as we all know oxygen, nitrogen, carbon dioxide, water vapour already present there, in addition you have water vapour going in and there are other species present in the air. And therefore, that becomes multi component system.

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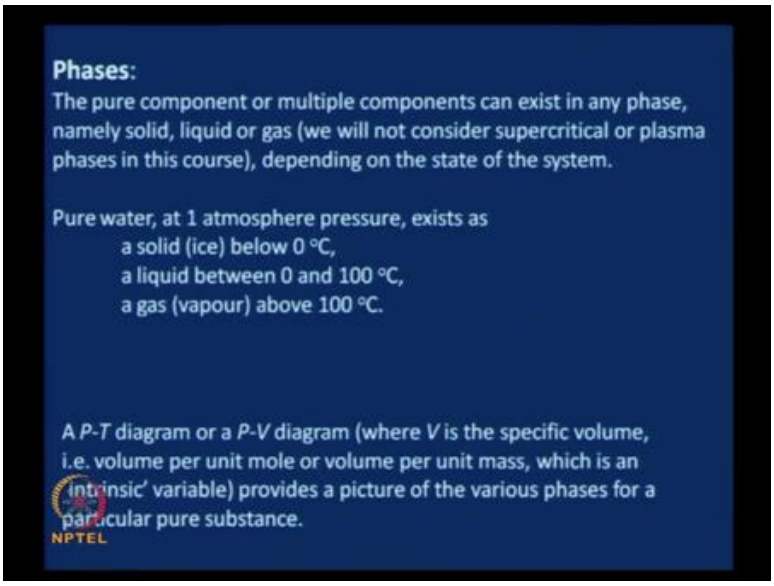

Let us look at phases. The pure component or the multi components can exist in any phase. What do you mean by phase? The phase could be a solid or a liquid or a gas. And, these are the only three phases that we will consider in this particular course. There are other phases; the super critical phase, the plasma phase, which we will not take up as a part of this course. For example, pure water at 1 atmosphere pressure exists as a solid or ice below 0 degree Celsius, a liquid between 0 and 100 degree Celsius and as a gas or a vapour above 100 degree Celsius. Therefore, the phase of a substance varies with the condition.

Typically, a P-T diagram, a pressure versus temperature diagram or a P-V diagram, P V P stands for pressure and V here, stands for specific volume because volume per unit mass. And, we all, we have already seen that volume per unit mass is an intrinsic variable. A P-T diagram or a P-V diagram provides the relationship between the various phases for a pure substance.

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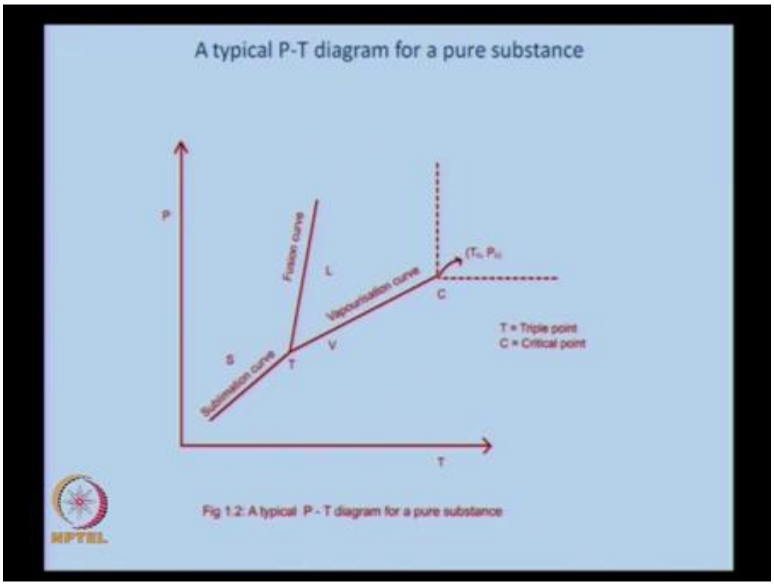

Let us look at typical P-T diagram first. This is a typical P-T diagram for a pure substance; P on the y axis and T on the x axis. In this region, what I mean by the region? The combination of temperature and pressure values.

In this region of temperatures and pressures, the substance is a solid, which is indicated by S. In this region of temperatures and pressures, the substance, pure substance is a liquid. And, in this region of temperatures and pressures, the pure substance is a vapour. Across this line, the solid becomes a vapour and we know that process as sublimation. Therefore, this is called the sublimation curve. Along this line, the solid becomes a liquid. We know that is called fusion. Therefore, that is called a fusion curve and along this line, which essentially means the along these values of temperatures and pressures, the liquid becomes a vapour. And therefore, this is called the vaporization curve.

Note this point T. This is called a triple point because as you note at this particular point, there is coexistence of three phases; solid, liquid and vapour. This point is C; the critical point above which, you have, what is called a super critical phase. Above this pressure and above this temperature, you have a supercritical phase here.

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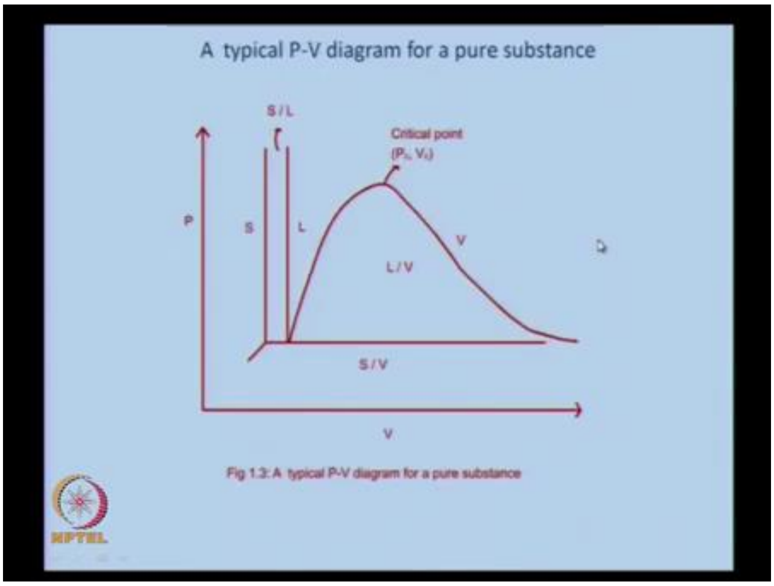

Next, let us look at a typical P-V diagram; a diagram between pressure and specific volume for a pure substance. As earlier, P is given on the Y axis; V specific volume on the X axis. In this region of specific volumes and pressures, solid exists. In this region of specific volume and pressure, liquid exists. And, in this region of specific volumes and pressures, vapour exists. And, unlike the P-T diagram, we have regions, instead of lines, where you have a combination of two phases existing. For example, in this region you have a solid-liquid combination existing. In this region, you have a solid-vapour combination existing. And, under this curve, in this region under this curve, you have a liquid-vapour combination existing. The critical point which we saw earlier is represented by (P_c ,V_c) here, on top of this particular curve.

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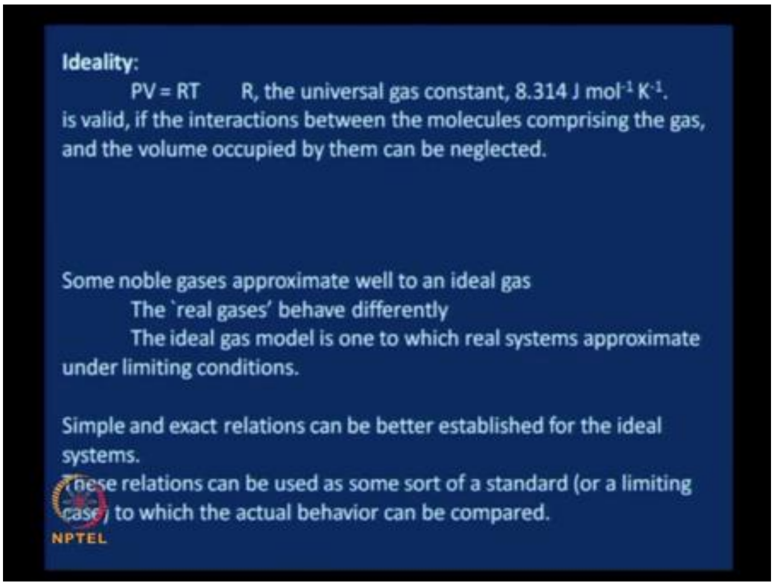

The next concept is ideality. We all know PV = RT. R is the universal gas constant. And, you know the value given here, 8.314 joules per mole per Kelvin, and so on. And, we all know, what an ideal gas is. An ideal gas is something does that does not have interactions between its molecules and also the volume occupied by the molecules can be considered negligible. Some noble gases actually, approximate very well to an ideal gas. In other words, some noble gases follow this P V = R T equation very well; the combination between pressure, volume, specific volume and temperature very well, whereas the real gases behave differently.

And, the ideal gas model, which is P V = R T, is the one to which the real systems approximate under certain limiting conditions. This you would have already seen. The ideal gas equation P V = R T; the real gases under certain conditions, do follow P V = RT. And, that is what we have just said. Simple and exact relations can be better established for ideal systems. And, these relations can be used as some sort of a standard or a limiting case to which actual behaviour can be compared.

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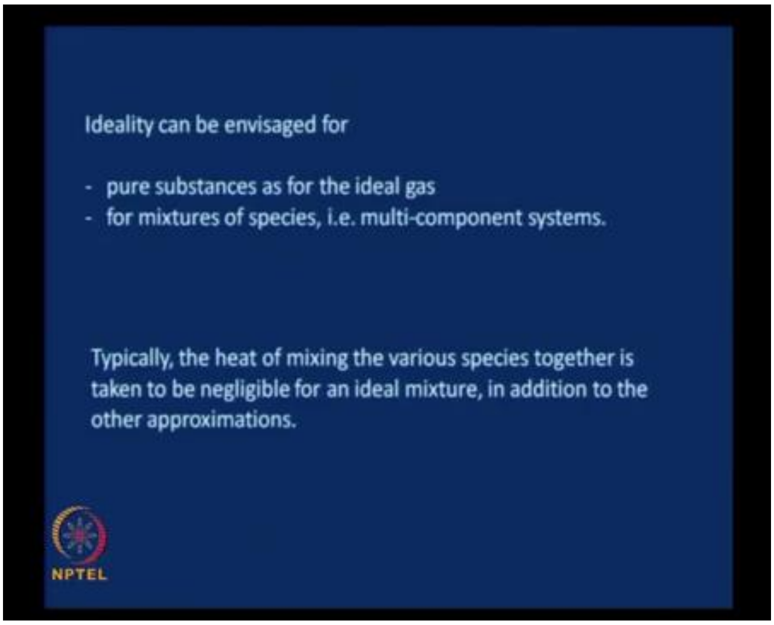

Ideality is not only for a pure gas. It can be, of course envisaged for pure substances such as ideal gases, as well as for mixtures of species, or even in the multi component systems. We saw what ideality is for a pure gas or, sorry, for an ideal gas P V = RT. And, for a mixture of gases, ideality comes in when the heat of mixing the various species together, as well as the changes in volume when the various species are mixed together are negligible.

We have been at this for quite a while now. Maybe about 20 to 25 minutes. It is a lot of information in a review mode. So, let us continue the review mode the next time we meet in the next class. See you.