Thermodynamics (Classical) for Biological Systems

Prof. G. K. Suraishkumar

Department of Biotechnology

Indian Institute of Technology Madras

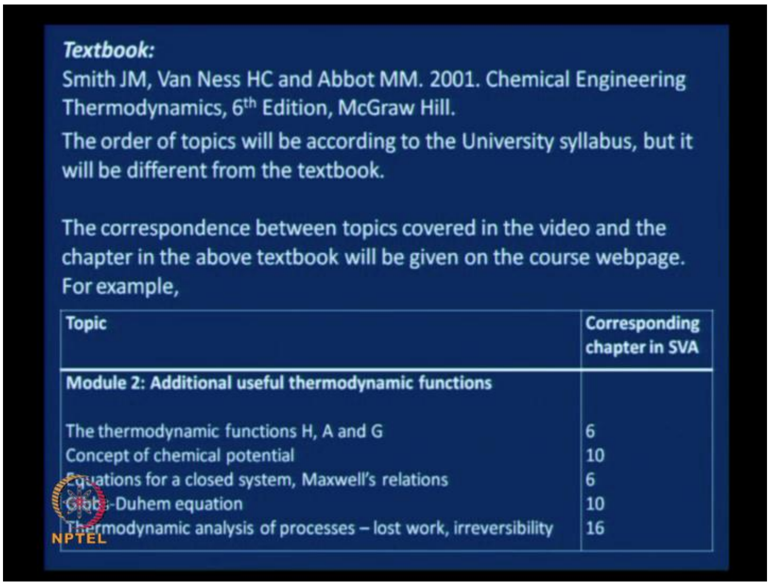
Module No. # 01

Lecture No. # 01

Introduction and Review

Welcome to the course on thermodynamics. This is for biological systems. More specifically, we can call this classical thermodynamics for biological systems. As I will explain later during this module, there is another type of thermodynamics that you can use for analysis of biological systems, which we will not cover in this particular course.

(Refer Slide Time: 00:37)



Textbook:

Smith JM, Van Ness HC and Abbot MM. 2001. Chemical Engineering Thermodynamics, 6th Edition, McGraw Hill.

The order of topics will be according to the University syllabus, but it will be different from the textbook.

The correspondence between topics covered in the video and the chapter in the above textbook will be given on the course webpage. For example,

Topic	Corresponding chapter in SVA
Module 2: Additional useful thermodynamic functions	
The thermodynamic functions H, A and G	6
Concept of chemical potential	10
Equations for a closed system, Maxwell's relations	6
Gibbs-Duhem equation	10
Thermodynamic analysis of processes – lost work, irreversibility	16

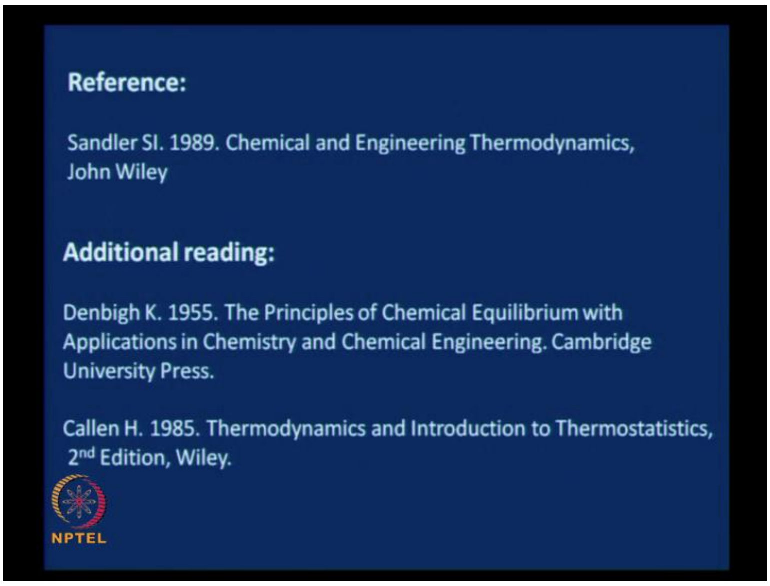
The textbook for this course is here. This is Smith, Van Ness and Abbot, Chemical Engineering Thermodynamics, sixth edition. The principles were extensively used for Chemical Engineering issues earlier. And, we will use some of those principles for biological systems, and a lot more. This will be your textbook.

Nevertheless, the order of topics will not be according to this particular textbook. It will be different. But, it will be according to your university syllabus.

So, you don’t have to worry about it being different from your university syllabus. Also, the correspondence between the topics covered in this video and the chapter – the corresponding chapter in the textbook – will be given on the course web page. For example, if you look at this table, I have given you a typical example here. You have a table, covering topic and the corresponding chapter in SVA, which stands for Smith, Van Ness and Abbot. Module two: additional useful thermodynamic functions. The thermodynamic functions H, A and G will be from chapter six. Concept of chemical potential will be from chapter ten. Equations for a closed system, Maxwell’s equations will be from chapter six. Gibbs, Duhem equation will be from chapter ten. Thermodynamic analysis of processes, such as lost work and irreversibility aspects, will be from chapter sixteen.

So, you can go back to these chapters to read up. I have tried to maintain the same notation as in the textbook for this particular video. But, the coverage will be a lot more effective, which will help in easier understanding of the material.

(Refer Slide Time: 02:38)



Reference:

Sandler SI. 1989. Chemical and Engineering Thermodynamics, John Wiley

Additional reading:

Denbigh K. 1955. The Principles of Chemical Equilibrium with Applications in Chemistry and Chemical Engineering. Cambridge University Press.

Callen H. 1985. Thermodynamics and Introduction to Thermostatistics, 2^{nd} Edition, Wiley.

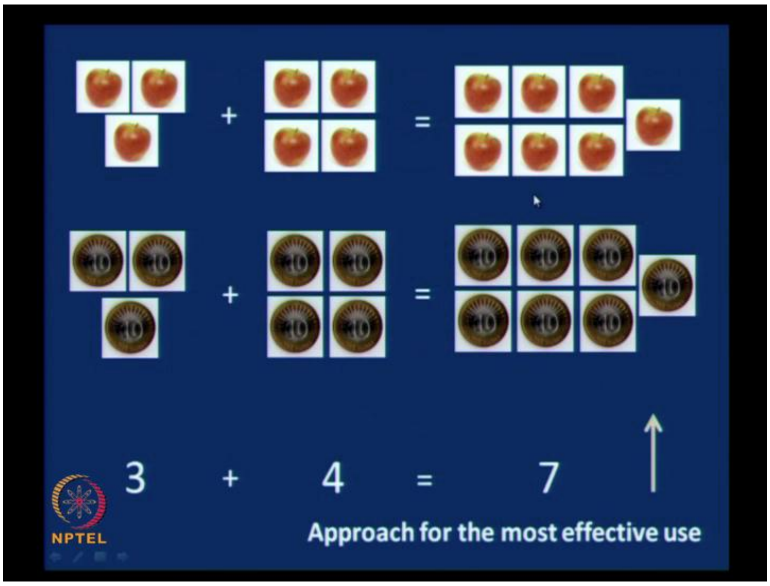
There are other books that you can refer to. One of the references that I would recommend is Sandler, 1989, “Chemical Engineering Thermodynamics”, that was published by John Wiley.

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.

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.

(Refer Slide Time: 04:11)

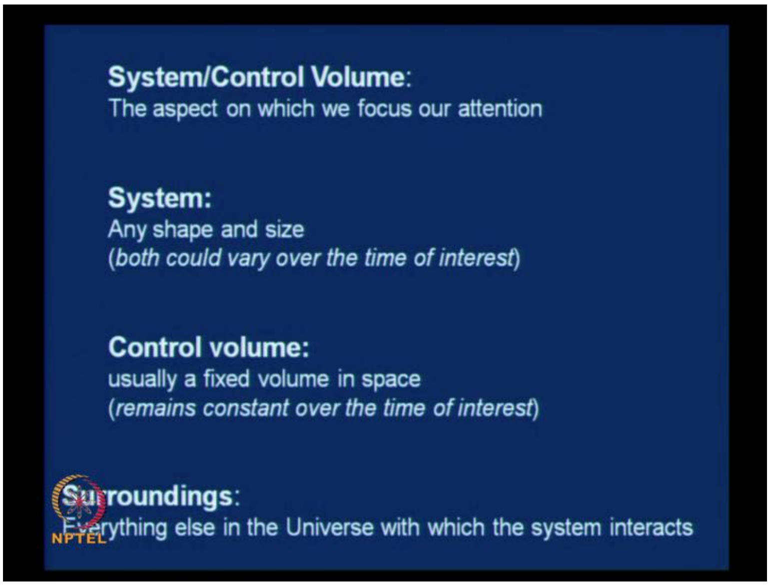


A simple process of addition: if you look at 3 apples and you add 4 apples to it, you will have 7 apples. Similarly, if you took 3 coins and added 4 coins to it, you would have 7 coins. Instead of talking about 3 apples, separately, or 3 coins separately, and so on and so forth, if we recognize that 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.

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.

(Refer Slide Time: 06:05)



System/Control Volume:
The aspect on which we focus our attention

System:
Any shape and size
(*both could vary over the time of interest*)

Control volume:
usually a fixed volume in space
(*remains constant over the time of interest*)

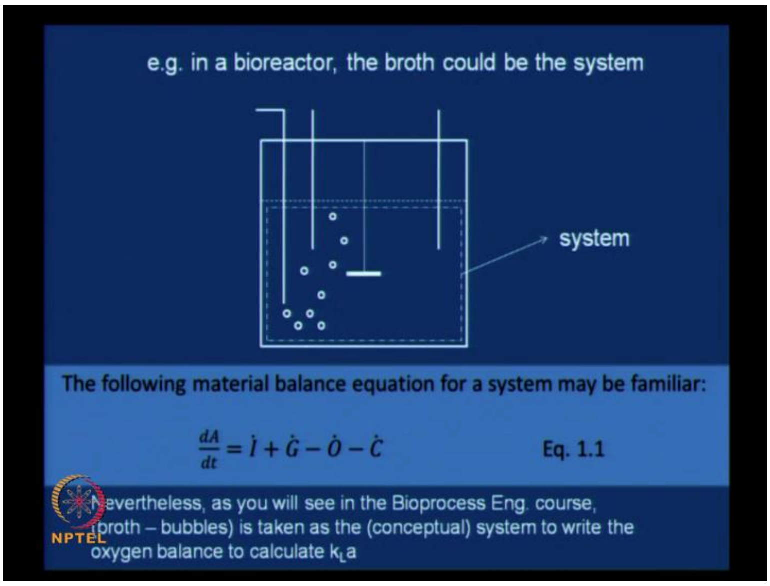
Surroundings:
Everything else in the Universe with which the system interacts

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.

(Refer Slide Time: 07:06)



e.g. in a bioreactor, the broth could be the system

The following material balance equation for a system may be familiar:

$$\frac{dA}{dt} = \dot{I} + \dot{G} - \dot{O} - \dot{C} \qquad \text{Eq. 1.1}$$

Nevertheless, as you will see in the Bioprocess Eng. course, (broth – bubbles) is taken as the (conceptual) system to write the oxygen balance to calculate $k_L a$

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.

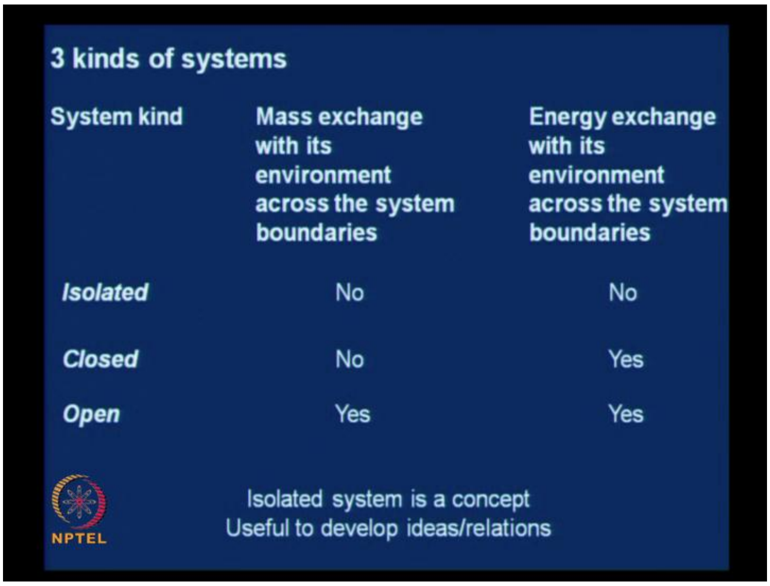
What is material balance? If you recall the course that you did it in may be process calculations, bioprocess calculations or a first equivalent course in the Biotechnology program, the material balance is a combination – the relationship between accumulation rate and the input rate, the generation rate,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

(input rate) + (generation rate) – (output rate) – (consumption rate) = (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.

(Refer Slide Time: 10:23)



3 kinds of systems

System kind	**Mass exchange with its environment across the system boundaries**	**Energy exchange with its environment across the system boundaries**
Isolated	No	No
Closed	No	Yes
Open	Yes	Yes

Isolated system is a concept
Useful to develop ideas/relations

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.

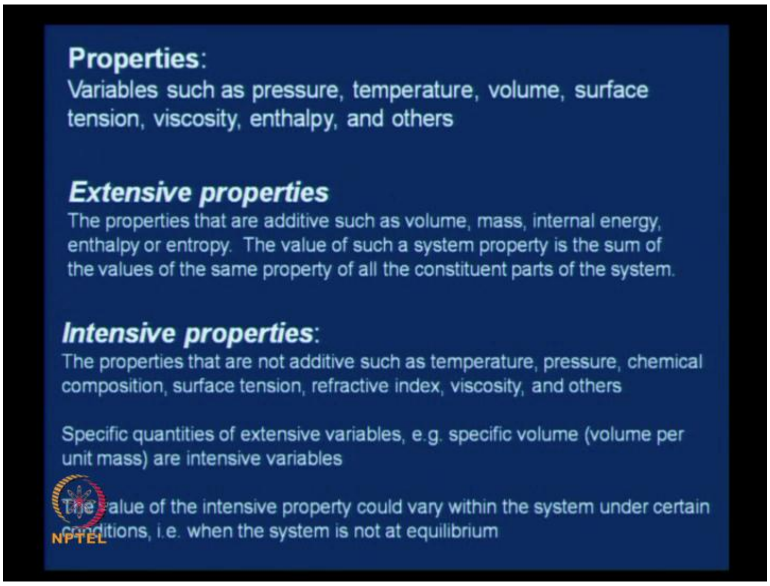
The first kind is called an isolated system, where there is no mass exchange between the system and its environment (or its surroundings), across the system boundaries. And also, there is no energy exchange between the system and its environment (or surroundings) across the system boundaries.

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.

(Refer Slide Time: 12:30)



Properties:
Variables such as pressure, temperature, volume, surface tension, viscosity, enthalpy, and others

Extensive properties
The properties that are additive such as volume, mass, internal energy, enthalpy or entropy. The value of such a system property is the sum of the values of the same property of all the constituent parts of the system.

Intensive properties:
The properties that are not additive such as temperature, pressure, chemical composition, surface tension, refractive index, viscosity, and others

Specific quantities of extensive variables, e.g. specific volume (volume per unit mass) are intensive variables

The value of the intensive property could vary within the system under certain conditions, i.e. when the system is not at equilibrium

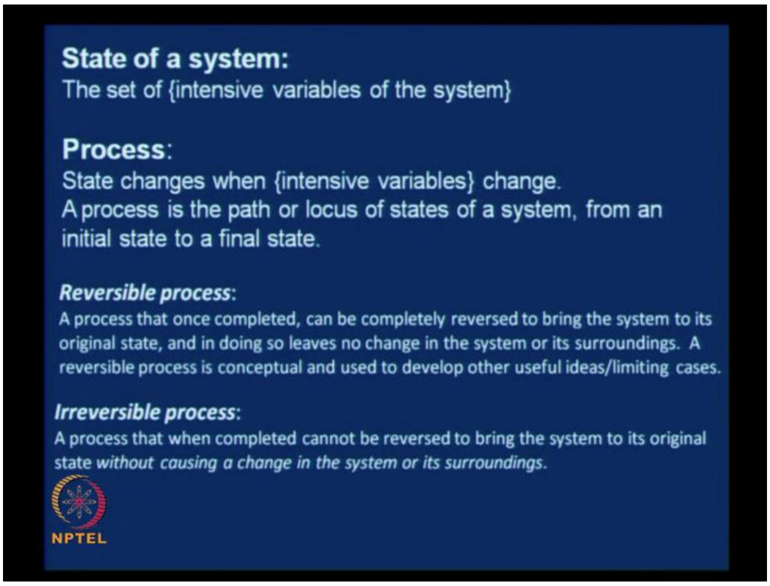
The next concept that we look at/review is the concept of property. What exactly is a property? Properties are nothing but variables such as pressure, temperature, volume, surface tension, viscosity, enthalpy and others of the system. It could refer to the system predominantly; of course you would refer 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.

(Refer Slide Time: 15:40)



State of a system:
The set of {intensive variables of the system}

Process:
State changes when {intensive variables} change.
A process is the path or locus of states of a system, from an initial state to a final state.

Reversible process:
A process that once completed, can be completely reversed to bring the system to its original state, and in doing so leaves no change in the system or its surroundings. A reversible process is conceptual and used to develop other useful ideas/limiting cases.

Irreversible process:
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.*

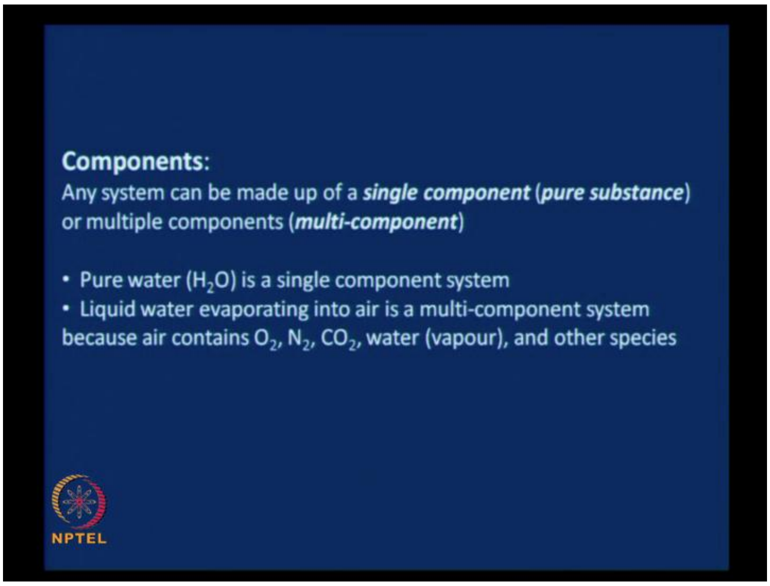
The next concept that we will review is the state of the system. The state of the system refers to nothing but a set of intensive variables of the system. For example, a system is at a particular pressure, temperature, volume, that set of properties, pressure of some atmospheres or some KPa, some temperature 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.

(Refer Slide Time: 18:32)



Components:

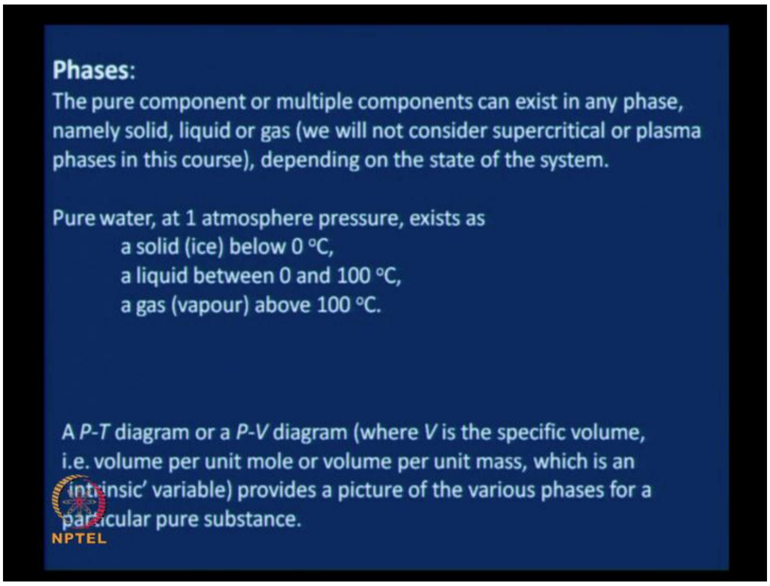
Any system can be made up of a ***single component*** (***pure substance***) or multiple components (***multi-component***)

- Pure water (H_2O) is a single component system
- Liquid water evaporating into air is a multi-component system because air contains O_2, N_2, CO_2, water (vapour), and other species

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.

(Refer Slide Time: 19:47)



Phases:

The pure component or multiple components can exist in any phase, namely solid, liquid or gas (we will not consider supercritical or plasma phases in this course), depending on the state of the system.

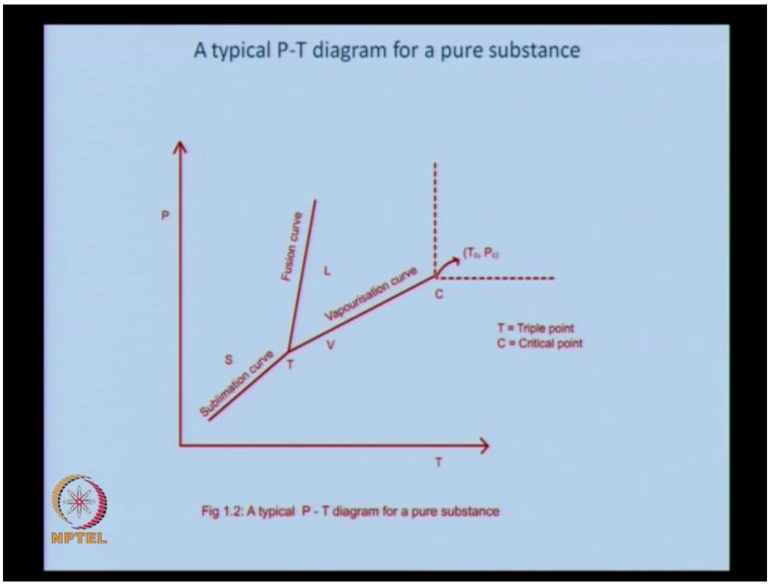
Pure water, at 1 atmosphere pressure, exists as
a solid (ice) below 0 °C,
a liquid between 0 and 100 °C,
a gas (vapour) above 100 °C.

A *P-T* diagram or a *P-V* diagram (where *V* is the specific volume, i.e. volume per unit mole or volume per unit mass, which is an 'intrinsic' variable) provides a picture of the various phases for a particular pure substance.

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.

(Refer Slide Time: 21:21)



A typical P-T diagram for a pure substance

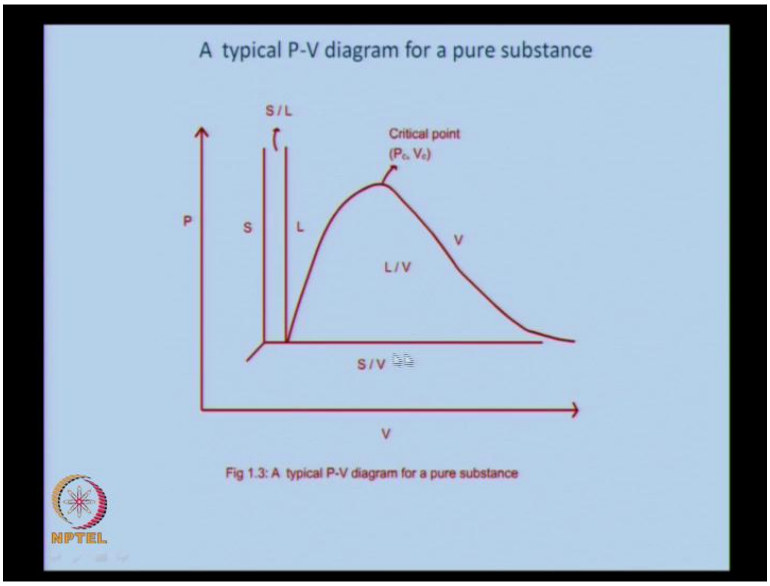
Fig 1.2: A typical P - T diagram for a pure substance

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 super critical phase here.

(Refer Slide Time: 23:13)

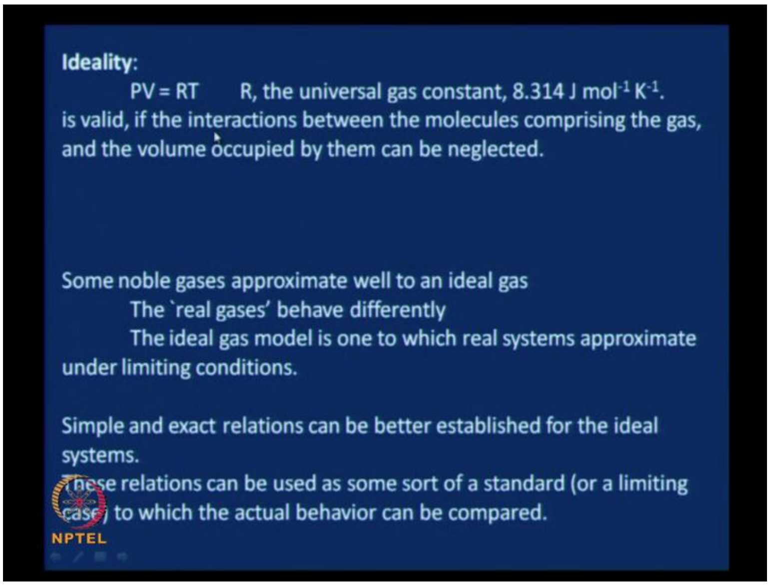


A typical P-V diagram for a pure substance

Fig 1.3: A typical P-V diagram for a pure substance

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.

(Refer Slide Time: 24:30)



Ideality:

PV = RT R, the universal gas constant, 8.314 J mol^{-1} K^{-1}.

is valid, if the interactions between the molecules comprising the gas, and the volume occupied by them can be neglected.

Some noble gases approximate well to an ideal gas

The `real gases' behave differently

The ideal gas model is one to which real systems approximate under limiting conditions.

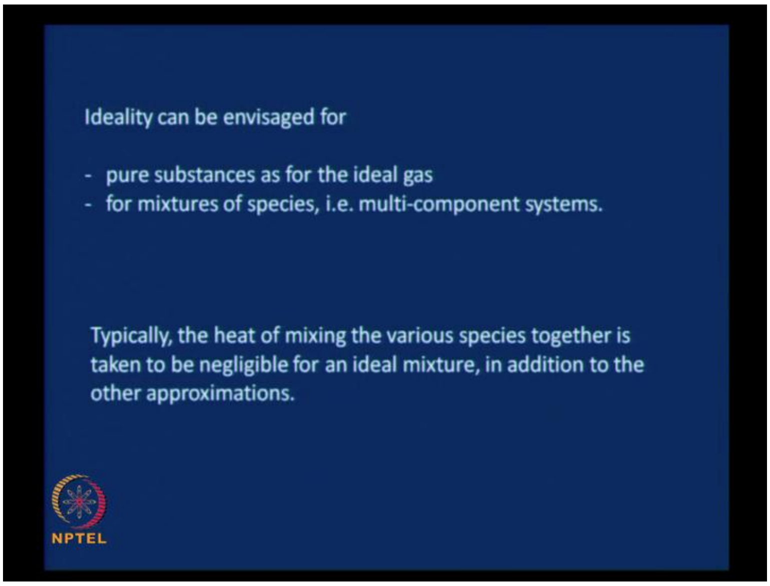
Simple and exact relations can be better established for the ideal systems.

These relations can be used as some sort of a standard (or a limiting case) to which the actual behavior can be compared.

The next concept is ideality. We all know PV equals 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.

(Refer Slide Time: 26:21)



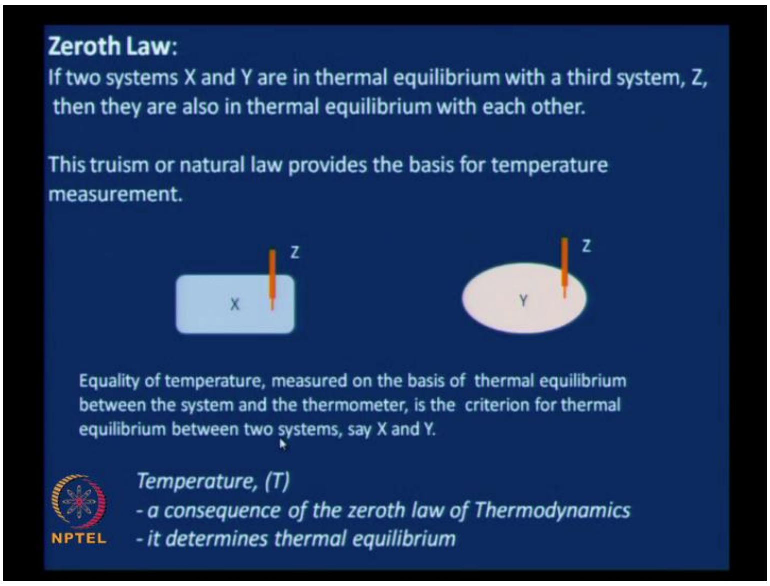
Ideality can be envisaged for

- pure substances as for the ideal gas
- for mixtures of species, i.e. multi-component systems.

Typically, the heat of mixing the various species together is taken to be negligible for an ideal mixture, in addition to the other approximations.

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.

(Refer Slide Time: 27:05)



Zeroth Law:
If two systems X and Y are in thermal equilibrium with a third system, Z, then they are also in thermal equilibrium with each other.

This truism or natural law provides the basis for temperature measurement.

Equality of temperature, measured on the basis of thermal equilibrium between the system and the thermometer, is the criterion for thermal equilibrium between two systems, say X and Y.

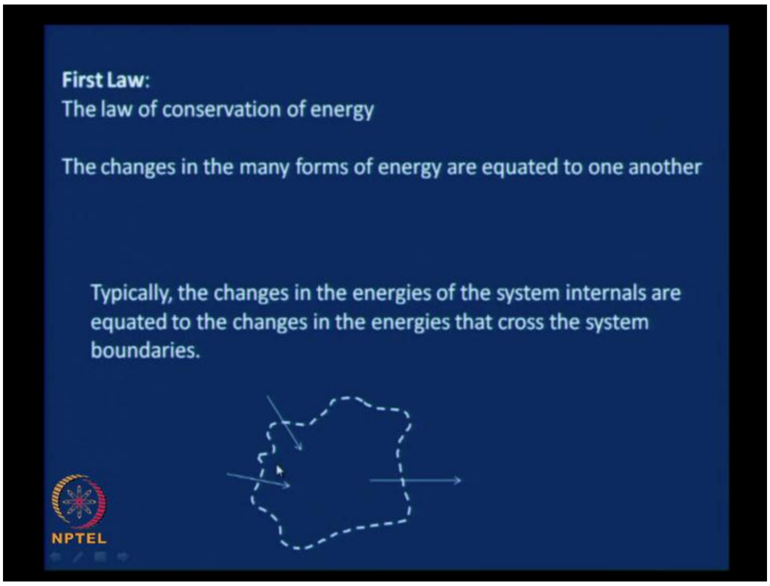
Temperature, (T)
- a consequence of the zeroth law of Thermodynamics
- it determines thermal equilibrium

Now, let us look at the three laws that you would have already studied – the three laws of Thermodynamics. The zeroth law first. The zeroth law states that if two systems, let us say X and Y, are in thermal equilibrium with a third system Z, then they are also in thermal equilibrium with each other. A very simple statement. And, it is actually a truism – we need not go about proving it by other means. To repeat, there are two systems, let them … let us call them X and Y. If they are in thermal equilibrium with the third system, let us say Z, then they are also in thermal equilibrium with each other.

This zeroth law actually, provides the basis for temperature measurement. As it is shown here, this is the substance X or system X, this is the system Y, and they are individually in thermal equilibrium with this Z here. The Z is the thermometer, which is used to measure the temperature of X or of Y. If X is in thermal equilibrium with Z and Y is also in thermal equilibrium with Z, then X and Y are in thermal equilibrium with each other.

Let us consider the condition that, we just said; X in thermal equilibrium with Z and Y in thermal equilibrium with Z – which means that the reading on thermometer would be the same. And therefore, the equality of temperature measured on the basis of thermal equilibrium between the system and the thermometer is the criterion for thermal equilibrium between the two systems say, X and Y. Therefore, temperature T can be considered as a consequence of the zeroth law of Thermodynamics. And, it is the one that determines thermal equilibrium.

(Refer Slide Time: 29:32)



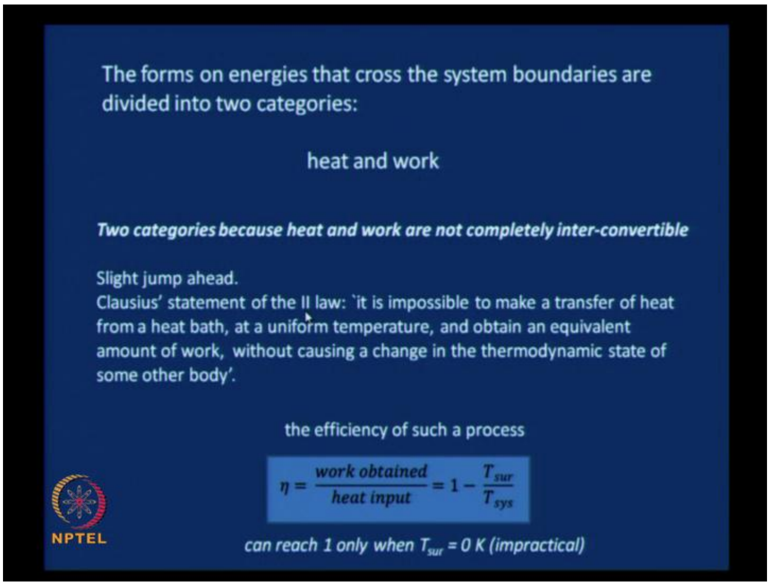
First Law:
The law of conservation of energy

The changes in the many forms of energy are equated to one another

Typically, the changes in the energies of the system internals are equated to the changes in the energies that cross the system boundaries.

Now, let us look at first law. The first law is nothing but the law of conservation of energy. The changes in many forms of energy are essentially equated to one another in the first law. It is nothing more to first law. Typically, the changes in the energies of the system parts are equated to each other. For example, the changes in the energies of the system internals are equated to the changes in the energies of the system that cross the system boundaries. This is the system that is indicated by the dotted line here. The energies that cross the system boundaries - these two are coming in and this is going out, and so on. The changes in energy inside the system are related to the changes that cross the system boundaries.

(Refer Slide Time: 30:32)



The forms on energies that cross the system boundaries are divided into two categories:

heat and work

Two categories because heat and work are not completely inter-convertible

Slight jump ahead.
Clausius' statement of the II law: `it is impossible to make a transfer of heat from a heat bath, at a uniform temperature, and obtain an equivalent amount of work, without causing a change in the thermodynamic state of some other body'.

the efficiency of such a process

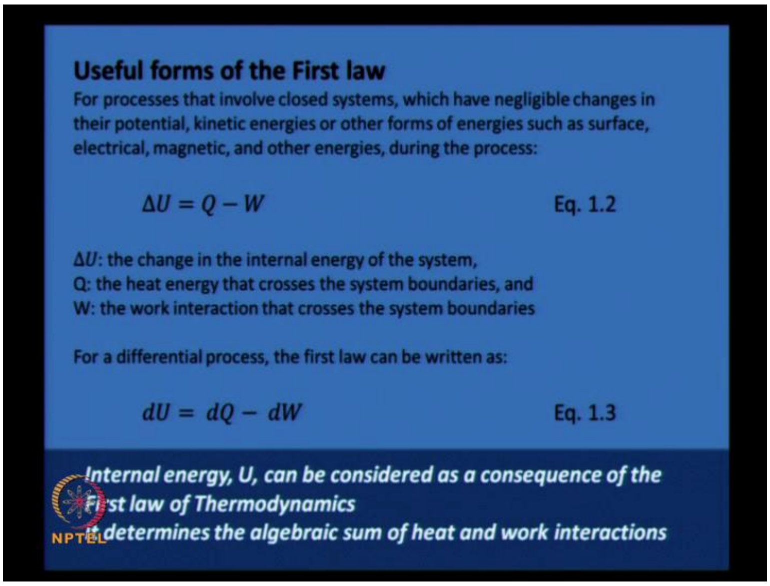
$$\boxed{\eta = \frac{\text{work obtained}}{\text{heat input}} = 1 - \frac{T_{sur}}{T_{sys}}}$$

can reach 1 only when $T_{sur} = 0$ K (impractical)

There are two forms of energies that cross the system boundaries. Or, the forms of energies that cross the system boundaries are actually divided into two categories: heat and work. Why do we need to divide these into two categories, heat and work? It is, essentially because heat and work are not completely inter-convertible. They are… you cannot convert heat into work completely. And therefore, you need to consider them as two separate entities. To understand this a little better, let us likely jump ahead. We are going to look at this later. But, since this is the review, you would have already looked at it, we can jump ahead to understand this a little better. The Clausius statement of the second law is as follows: “it is impossible to make a transfer of heat from a heat bath at uniform temperature, and obtain an equivalent amount of work, without causing a change in the thermodynamic state of some other body”. That is the complete statement of the second law. Let me read it again to get across a little better. It is impossible to make a transfer of heat from a heat bath at the uniform temperature and obtain an equivalent amount of work, without causing a change in the thermodynamic state of some other body. The efficiency of such a process is given by (work obtained)/ (heat input). And, you would already seen in the previous classes that can be related to 1 minus the ratio of the surroundings temperature to the system temperature.

The efficiency can reach 1, only when the surroundings temperature is 0 Kelvin. If you recall, these temperatures are in Kelvin. And, reaching 0 kelvin is impractical. And therefore, it is impossible to completely convert heat into work. And, that is the reason we need to consider them as two separate quantities.

(Refer Slide Time: 32:36)



Useful forms of the First law

For processes that involve closed systems, which have negligible changes in their potential, kinetic energies or other forms of energies such as surface, electrical, magnetic, and other energies, during the process:

$$\Delta U = Q - W \qquad \text{Eq. 1.2}$$

ΔU: the change in the internal energy of the system,
Q: the heat energy that crosses the system boundaries, and
W: the work interaction that crosses the system boundaries

For a differential process, the first law can be written as:

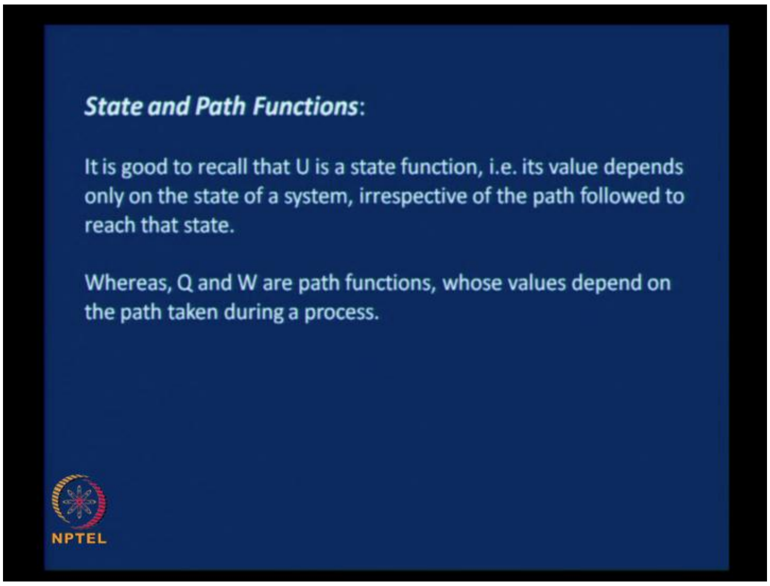
$$dU = dQ - dW \qquad \text{Eq. 1.3}$$

Internal energy, U, can be considered as a consequence of the First law of Thermodynamics
It determines the algebraic sum of heat and work interactions

The useful form of the first law, for us at least, is to begin with, when it is applied to closed system. For a closed system, when there are negligible changes in other kinds of energies, such as potential energies, kinetic energies, surface energies, magnetic energies and other kinds of energies, then you can relate the change in the internal energy (delta U) to the heat interaction across the system boundaries and the work interaction across the system boundaries.

(Delta U) equals Q minus W is a useful statement of the first law for us. This (delta U) is a change that occurs inside the system, Q and W are the energy interactions across the system boundaries. What happens inside is being related to what crosses in the system boundaries. For a differential process, we can write the first law as dU equals dQ minus dW; where these d represent the differentials. Therefore, internal energy, U, can be considered as a consequence of the first law of Thermodynamics. It essentially, it determines the algebraic sum of the heat and work interactions in a process or heat and work interactions for a system.

(Refer Slide Time: 34:19)



***State and Path Functions*:**

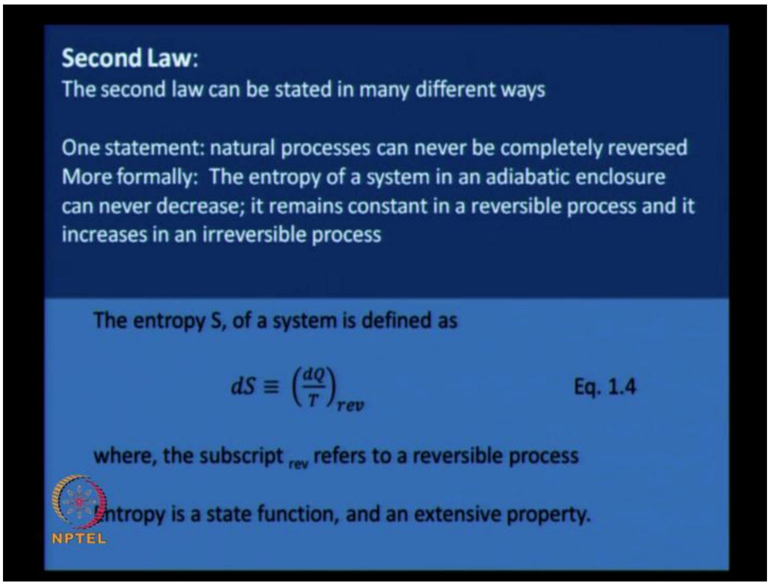
It is good to recall that U is a state function, i.e. its value depends only on the state of a system, irrespective of the path followed to reach that state.

Whereas, Q and W are path functions, whose values depend on the path taken during a process.

We also need to understand, what state and path functions are, very clearly. You would have learnt that the internal energy is a state function. In other words, its value depends only on the state of the system, irrespective of the path followed to reach that state. For example, if the system is undergoing a process from state 1 to state 2, whether the path of the processes one way or the other way, and so on and so forth. By path, we mean the set of intensive variables changing and so on and so forth. Whether, the path is one or the other, as long as it is a state function, the value of that function depends only on the state of the system. The value of internal energy at state 1 would be the same and the value of internal energy at state 2 would be the same; irrespective of the path taken to reach 2 from 1.

Whereas, the heat interaction across a system boundary and the work interaction across a system boundary are path functions, whose values depend on the path taken during the process. This is a very important concept. In fact, we will be visiting this again and again. And, at an appropriate time, I will tell you an important aspect of this, which helps us significantly in developing relationships in Thermodynamics.

(Refer Slide Time: 35:57)



Second Law:

The second law can be stated in many different ways

One statement: natural processes can never be completely reversed
More formally: The entropy of a system in an adiabatic enclosure can never decrease; it remains constant in a reversible process and it increases in an irreversible process

The entropy S, of a system is defined as

$$dS \equiv \left(\frac{dQ}{T}\right)_{rev} \qquad \text{Eq. 1.4}$$

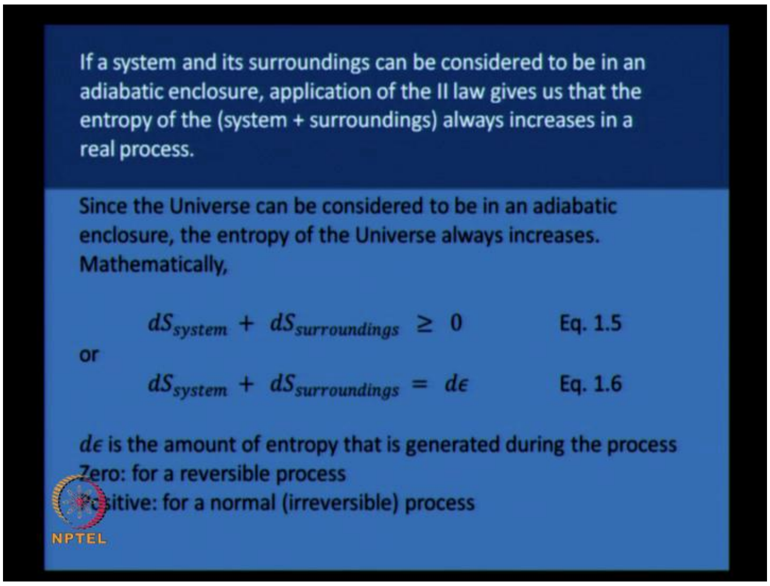
where, the subscript $_{rev}$ refers to a reversible process

Entropy is a state function, and an extensive property.

Now, let us look at second law. The second law can be stated in many different ways. And, one of the statements is as follows. Natural processes can never be completely reversed; is, one way of stating it. More formally, the entropy of a system in an adiabatic enclosure can never decrease; it remains constant in a reversible process and it increases in an irreversible process. That is another formal way of stating it. The entropy of the system, as you would know already is defined as dS equals dQ by T in a reversible process. As you know Q is a path function. If dQ reversible by T is a way of stating … is a way defining entropy dS.

Entropy is a state function, and is an extensive property. State function depends only on the state of the system and not on the path taken to reach the system. Extensive property means that, more the amount of the material there, higher the value of the property.

(Refer Slide Time: 37:24)



If a system and its surroundings can be considered to be in an adiabatic enclosure, application of the II law gives us that the entropy of the (system + surroundings) always increases in a real process.

Since the Universe can be considered to be in an adiabatic enclosure, the entropy of the Universe always increases. Mathematically,

$$dS_{system} + dS_{surroundings} \geq 0 \qquad \text{Eq. 1.5}$$

or

$$dS_{system} + dS_{surroundings} = d\epsilon \qquad \text{Eq. 1.6}$$

$d\epsilon$ is the amount of entropy that is generated during the process

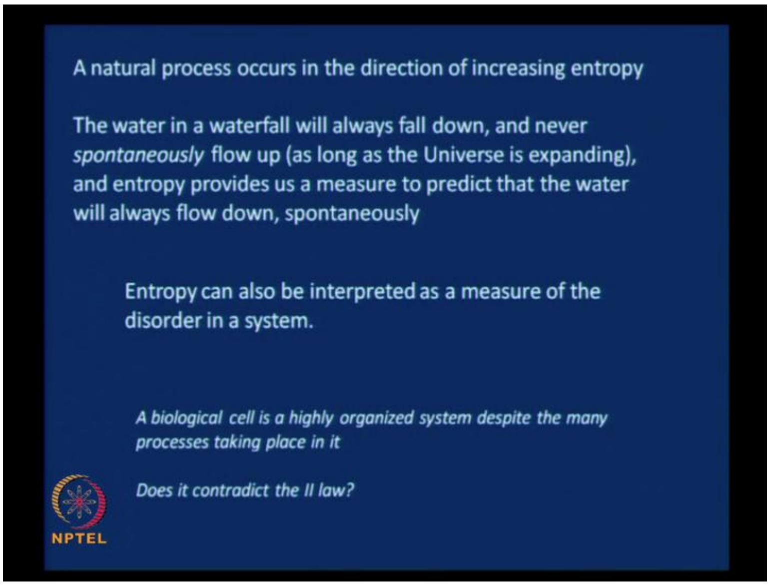
Zero: for a reversible process

Positive: for a normal (irreversible) process

If a system and its surroundings can be considered to be in an adiabatic enclosure, very important, please note this; if the system and its surroundings can be considered to be in an adiabatic enclosure, application of the second law gives us that the entropy of the system of both the system and the surroundings, always increases in a real process.

Now, the universe itself can be taken to be in an adiabatic enclosure; because universe contains everything. It is nothing beyond the universe. So, the whole thing can be considered to be in an adiabatic enclosure, which means there is no heat interaction. For the universe as a whole, the entropy of the universe always increases. You can state this mathematically as the changes in entropy of the system plus the changes in entropy of its surroundings should always be greater than or equal to 0. And, if you want to replace this by an equality, we say that the change in entropy of the system, dS of the system and dS of the surroundings equals d epsilon. d epsilon is the amount of entropy that is generated during the process. It is, of course 0 for a reversible process. As we know, as we saw earlier, the definition of reversible process is positive for a normal or an irreversible process.

(Refer Slide time: 39:04)



A natural process occurs in the direction of increasing entropy

The water in a waterfall will always fall down, and never *spontaneously* flow up (as long as the Universe is expanding), and entropy provides us a measure to predict that the water will always flow down, spontaneously

Entropy can also be interpreted as a measure of the disorder in a system.

A biological cell is a highly organized system despite the many processes taking place in it

Does it contradict the II law?

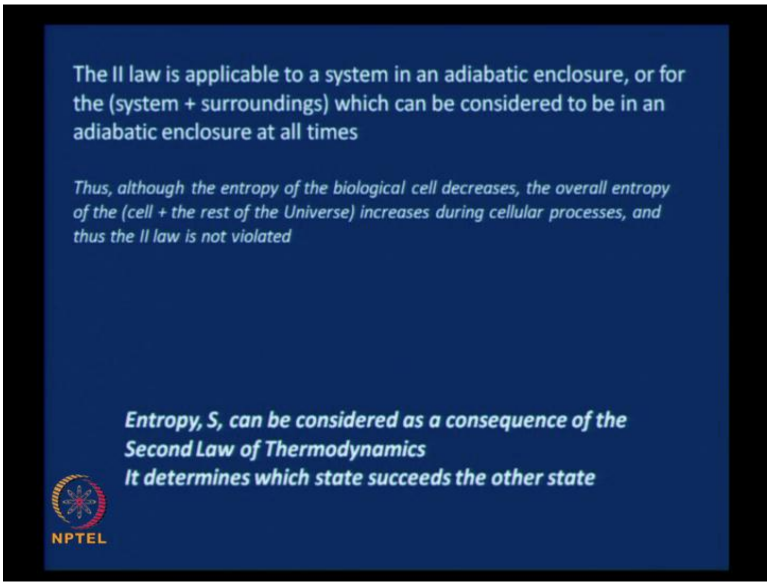
A natural process occurs in the direction of increasing entropy. We have already seen that, if you take the entire universe as a system, the entropy of the system has to increase. Further, as long as we have an expanding universe, the natural process will always happen in the direction of increasing entropy. The water in a water fall will always fall down and never spontaneously flow up, and the entropy provides us a measure to predict whether the water will flow down – to tell that, the water will flow down spontaneously. Always flow down spontaneously.

Entropy can also be interpreted as a measure of the disorder in the system. It is a concept; order, disorder. Order: everything nice and packed, and so on and so forth. Disorder: not so packed, random not so ordered.

Now, let me pose this question to you. And, let you think for a few minutes before I give you the answer. This course is about application of Classical Thermodynamics to biological systems. And, so let us start here, right away. The biological cell, as we all know, is highly organised. There are many processes taking place in it. But, the biological cell itself is highly organised. What I would like you to think about is that, does the biological cell contradict the second law? Take a few minutes and think about it, and I will give you the answer.

The answer is it does not.

(Refer Slide Time: 41:16)



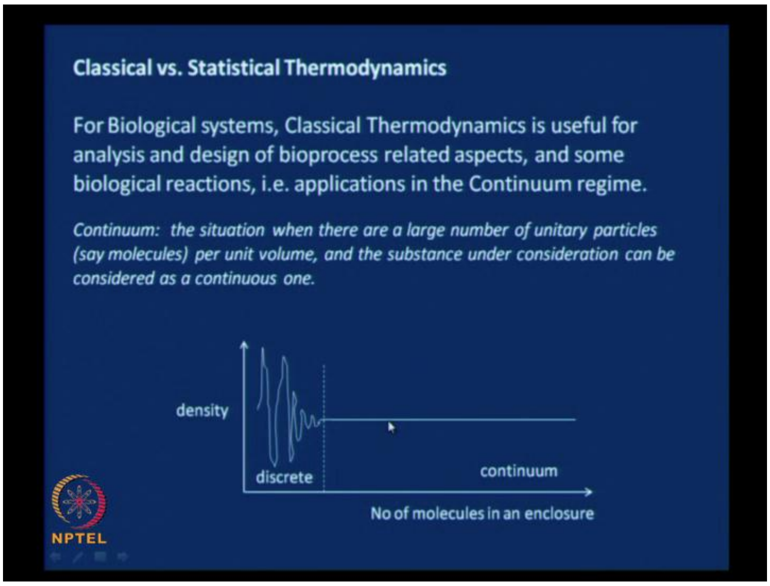
The II law is applicable to a system in an adiabatic enclosure, or for the (system + surroundings) which can be considered to be in an adiabatic enclosure at all times

Thus, although the entropy of the biological cell decreases, the overall entropy of the (cell + the rest of the Universe) increases during cellular processes, and thus the II law is not violated

Entropy, S, can be considered as a consequence of the Second Law of Thermodynamics
It determines which state succeeds the other state

So far, we have not come across something that violates second law. That is because of the following reason. The second law is applicable to a system in an adiabatic enclosure, or for if you take the system and surroundings as a whole, which can be considered in an adiabatic enclosure at all times. Therefore, although the biological … the entropy of the biological cell decreases as employed in the higher order in a biological system, the overall entropy of the cell and the rest of the universe, increases during a cellular process. And therefore, the second law is not violated. Entropy S; entropy as indicated by the letter S, denoted by the letter S, can be considered as a consequence of the second law of Thermodynamics. It determines which state succeeds the other state.

(Refer Slide Time: 42:17)



Classical vs. Statistical Thermodynamics

For Biological systems, Classical Thermodynamics is useful for analysis and design of bioprocess related aspects, and some biological reactions, i.e. applications in the Continuum regime.

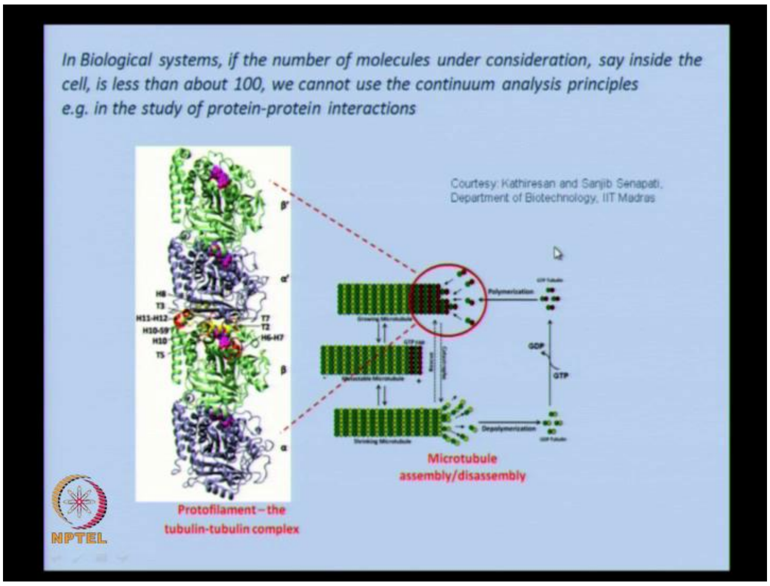
Continuum: the situation when there are a large number of unitary particles (say molecules) per unit volume, and the substance under consideration can be considered as a continuous one.

Now, let me make a comment that I mentioned, in the very beginning of this lecture. That is the relationship between the… difference between Classical and Statistical Thermodynamics. For biological systems, Classical Thermodynamics is useful for the analysis and design of bioprocess related aspects and some biological applications or biological reactions. Essentially, when you can consider something to be in the continuum or the continuous and so on and so forth, then you can apply Classical Thermodynamics principles, to come up with useful relationships.

Let us look at continuum a little clearer. Continuum is the situation when there are large number of unitary particles, they could be molecules per unit volume and the substance under consideration can be considered as a continuous one. If I represent that … or to understand that a little better, if we look at a plot of, let us say density, system property, verses the number of molecules in that enclosure and let us say that we are slowly decreasing the number of molecules in that enclosure. Till a certain point, there will not be much change in the density. And, in this region, we can say that continuum exists.

After a certain point, because the number of molecules per unit volume have gone down significantly that, if you take a reasonable volume, the number of molecules keep on changing, then the density will start fluctuating. And, as you go lower and lower, their fluctuations will become higher and higher. And this becomes a discrete case. A continuum case and a discrete case. The principles that are developed in this course will be applicable only for the continuum regime.

(Refer Slide Time: 44:46)



In Biological systems, if the number of molecules under consideration, say inside the cell, is less than about 100, we cannot use the continuum analysis principles e.g. in the study of protein-protein interactions

Courtesy: Kathiresan and Sanjib Senapati, Department of Biotechnology, IIT Madras

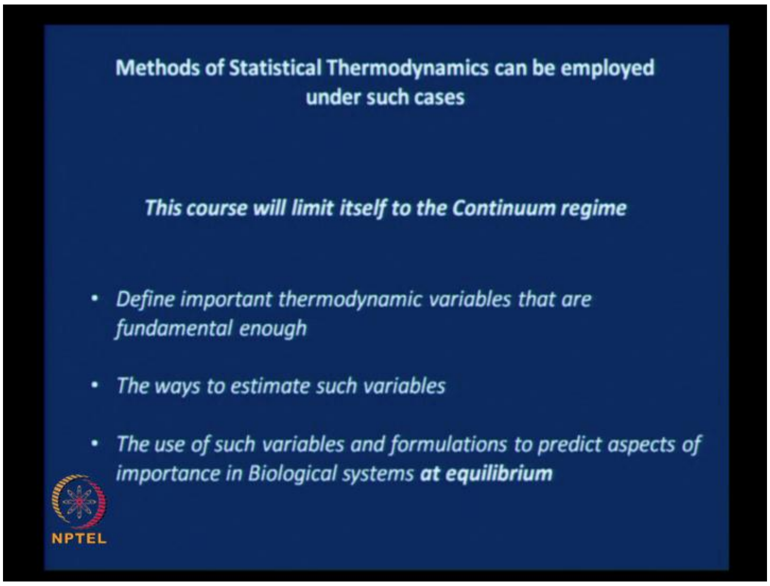
Microtubule assembly/disassembly

Protofilament – the tubulin-tubulin complex

By a rule of thumb in biological systems, if the number of molecules under consideration say, inside the cell, if it is more than a 100, we can still use the continuum principles. Whereas, if it goes below 100, we cannot use these principles.

For example, in the study of protein-protein interactions, we cannot use the Classical Thermodynamics principles. This is an example of protein-protein interaction. This slide is from a colleague of mine, Dr. Sanjib Senapati, from his lab. They are … they were looking at the microtubule assembly–disassembly using Thermodynamics principles. And, they don’t use Classical Thermodynamics principles at all, because the concept of continuum is not valid here.

(Refer Slide Time: 45:35)



Methods of Statistical Thermodynamics can be employed under such cases

This course will limit itself to the Continuum regime

- *Define important thermodynamic variables that are fundamental enough*
- *The ways to estimate such variables*
- *The use of such variables and formulations to predict aspects of importance in Biological systems **at equilibrium***

But, the methods of Statistical Thermodynamics can be applied under such cases. This course will limit itself only to the continuum regime. And, what we will do in this course is, first define important thermodynamic variables that are fundamental enough.

We will also look at the ways to estimate such variables. And then, look at the use of such variables and formulations to predict aspects of importance in biological systems at equilibrium. Therefore, it will be predominantly, analysis at equilibrium. In the next class, we will start a second module and look at details.