**Chemical and Biological Thermodynamics: Principles to Applications**
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Lecture - 01
Fundamentals of Chemical thermodynamics

In this course, we plan to start from basic principles of chemical thermodynamics and then slowly and slowly go towards the applications and take the course to advanced level. In the first lecture, let us first discuss the fundamentals of chemical thermodynamics.

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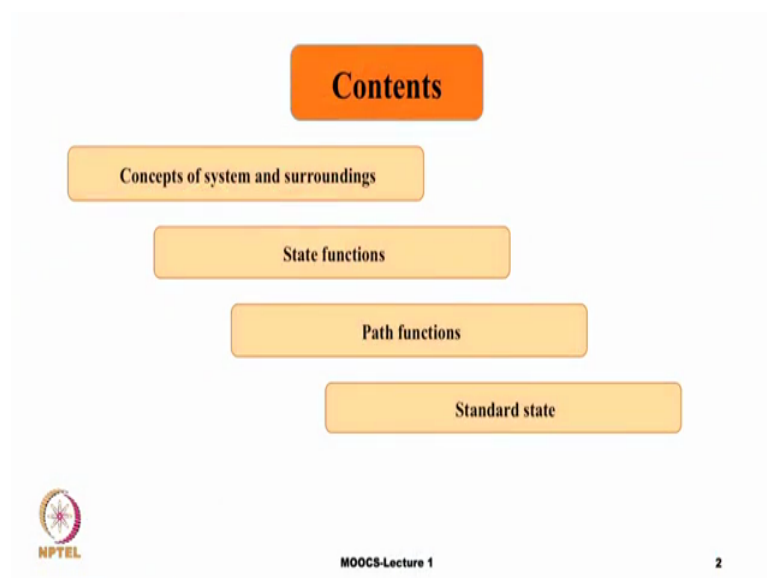
The contents of this course in the first lecture will be starting with the concept of system and surroundings, state functions, path functions and standard state. There are several misconceptions when it comes to basics of chemical thermodynamics. Over a period of time, several books have come to the market; and if we look at very old books in chemical thermodynamics, they were using different signs and conventions, but later on the current books they follow the signs and conventions adopted by IUPAC - International Union of Pure and Applied Chemistry. So, therefore, if we follow the signs and conventions recommended by IUPAC, there is no way we can go wrong in understanding the basics of chemical thermodynamics, writing various equations and

there is going to be uniformity. So, in the first lecture let us discuss the very basic principles and try to get rid of any misconceptions, misunderstandings that we may have.

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Let us first discuss the meaning of thermodynamics. What is thermodynamics? Thermodynamics is a branch of science, which deals with the transformations of energy that enables us to discuss all these matters quantitatively. I specifically emphasize on the word quantitatively, because there are two ways of understanding a process, one is in a qualitative manner in a sense that the process happens or it does not happen; and the second is that we want to make it quantitative; we want to give it some numbers. For example, in thermodynamics we talk about the enthalpies, we talk about the free energies entropy changes, so that makes the process understanding in a quantitative manner.

There are three basic concepts of thermodynamics, three fundamentals of thermodynamics – work, heat and energy. And out of these three, the most fundamental is work. The reason why I am saying most fundamental is work is that work is something which you can actually see with your eyes being happening. In other words, work is said to be done in a process if that process can lead to change in height of a weight somewhere in the surroundings. I will give an example soon. Heat is another form of energy; and energy is the capacity to do work; out of these three, the most fundamental is work for the reason that I just explained.

Let us take a look at this picture. In this picture, it is evident that in order to lift a weight, one has to do work. But when one is doing work we can actually see that the weight is being either lifted or the weight is being lowered that is what I said that work is said to be done in a process if that process leads to change in height of a weight in the surroundings.

Now, in the second picture, it does not have to be man in a pulling the rope and that leads to lifting of the weight, it can be electrical current also. There are electrical work for example, the electrical current can you know pass can be passed through a motor which can be connected to a pulley and then eventually we can see the height of a weight somewhere being raised or lowered in the surroundings.

Heat, heat is another form of energy. It is actually the flow of energy due to the temperature difference. If we see in the figure, when something is being heated on a hot plate, there is a temperature difference between the hot plate and the contents of the container. And this is as a result of the temperature difference the energy flows and that form of the energy is called heat energy.

Energy, what is energy? Energy is capacity to do work. Like here we see that the cell is charged to different levels that means, the capacity of this system to do work is different. The one, which is on the rightmost side has the maximum capacity to do work. Similarly, if we take an example of a spring, when the spring is bound completely it has the maximum capacity to do work; when the spring is unbound it does not have a capacity to do work. So, energy is the capacity to do work.

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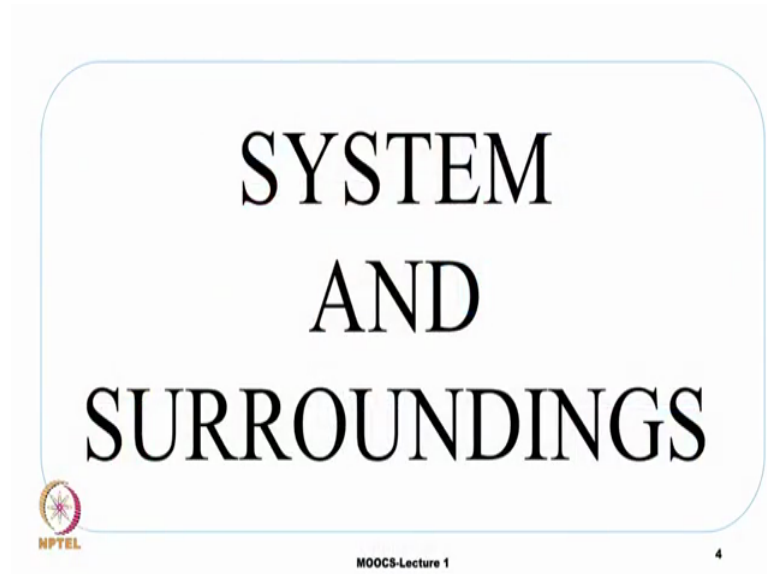
It is very important to understand the meaning of system and surroundings in thermodynamics. And as I mentioned earlier thermodynamics is the branch of science and technology, which is not only just important for understanding basic sciences, it is very much required for applied sciences and technology. We will take several examples later on, but let us first of all try to understand what do we mean by system and what are surroundings.

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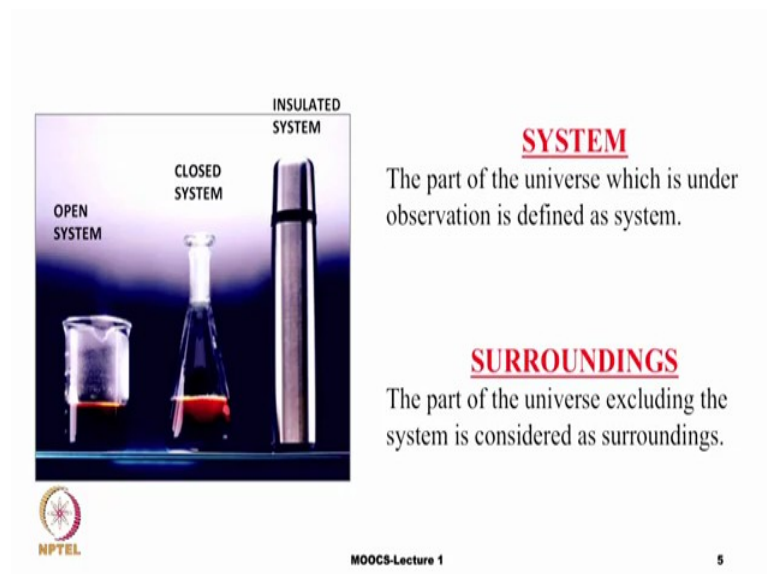
System is that is a part of the universe which is under observations. For example, when we are doing chemical reactions in the lab, the container in which the reaction is carried out it can be beaker or it can be a flask or in industry it can be big reaction chambers. In other words, a part of the universe in which we have a special interest that is called system. For example, I am a teacher, and when I am teaching in a classroom all the students myself are part of the system form a system, and everything else is surrounding. So, we divide the universe into two parts - one is system and other is surrounding. System and surroundings are separated by boundary. And it is the nature of the boundary, which will decide or define the type of the system.

Let us discuss, what are the various types of the system. There are three types of the system one is open system, other is closed system, third is insulated system. The definitions are very easy. We study the definitions of the open system, closed system, insulated system from class 12 onwards or class 11 onwards when these things are introduced, but as we will realize later that the scientists and technologies have made use of these very basic definitions and have developed very sophisticated techniques.

Let us first try to understand what is an open system. An open system is a system which allows the transfer of both matter or mass and energy. For example, a beaker containing water, if you heat the beaker the water will get evaporated, water vapours will escape can freely go out, water vapour is a matter is a mass that is escaping as well as the energy is escaping because water is hot it is the vapours are escaping. So, this is an open system. A closed system is the one in which the energy can escape, but the matter cannot. If the same beaker is closed, and you do not allow the water vapours to escape, the matter cannot go out water cannot leave, but the heat can transfer that forms a closed system. And if neither matter nor energy is allowed to escape the system that is called an insulated system or many times we say isolated system.

So, what decides that the system will be of what type it is the walls, walls of the container. If the wall of the container allows both the mass and energy to leave it will be open system, but if the walls of the container only allows the energy to escape and not the matter, then it will be closed. And if nothing is allowed to leave, so basically it is the walls of the container if it is an insulation insulated type then it will form an insulated system.

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Some examples of open system in addition to what I just described. A reaction which is carried out in an open test tube, and vapours are allowed to escape. Even a classroom when I am teaching in a classroom and I keep the doors open of the classroom, my voice my sound can reach outside. But if I do not allow the students to leave the classroom that means, we are not allowing if I and students form you know the matter is not allowed to go out, but only my sound can go out, it is a closed system. An open system will be if the students are also allowed to go out. The container, which is being heated on a hot plate the waters are allowed to escape, then it is another example of an open system

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In the closed system, only the energy can go matter cannot go. I just took an example of the classroom that if the doors are open the students are not allowed to go out or I do not go out, only my voice my sound can go out then it is a closed system, because energy is allowed to go out that matter cannot. In fact, in a pressure cooker, if you allow the water vapours to go out along with the energy, it will be no more closed, it will be an open system. An isolated system is the one in which you do not allow the matter and energy.
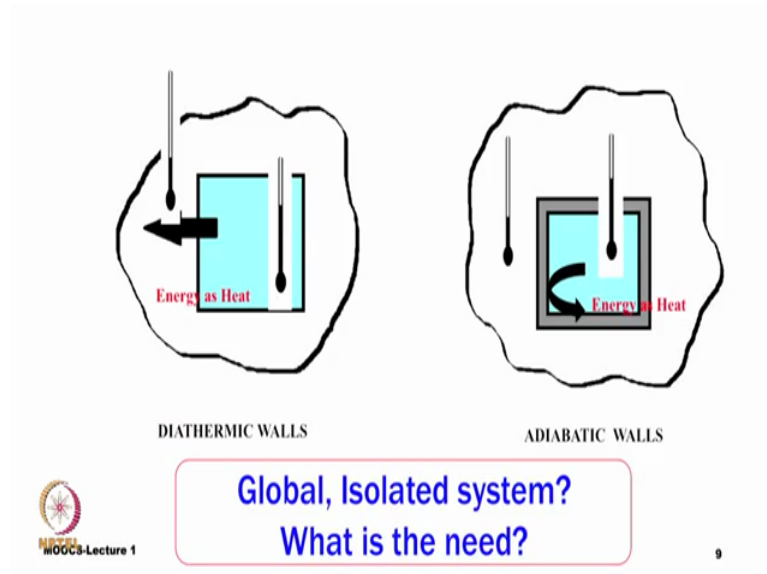
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To take the example, you know the usual example of thermos flask you know when we use the thermos flask for keeping the a tea or milk warm it keeps for a long time it does not allow either the energy nor the matter to go out. Of course, it has to be complete insulated for a complete of prevention of the matter or energy to be left.

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As I mentioned earlier that it is the nature of walls that will decide whether the system is open or closed or insulated. Any wall which will allow escape of energy in the form of heat from the system is called diathermic wall, it is like a glass beaker. And if you heat water in a glass beaker, you can see the heat leaving from the beaker, you can touch the beaker from outside and see that it is hot, because a glass will allow the exchange of energy from it in the form of heat. It will allow the transfer of energy through it in the form of heat, so such walls are called diathermic wall. And if it is an insulation that it does not allow the exchange of energy in the form of heat it is an adiabatic wall, and it forms an adiabatic system.

If both type of walls have their own advantages. There are certain systems in which the diathermic walls can be useful; and there are certain systems in which you require only adiabatic walls. For example, if I have a system in which I want to keep the temperature inside and outside that is the temperature of the system and surroundings same through an equilibrium between system and surrounding, then the requirement of walls will be of diathermic wall. And secondly, if I do not want any heat to escape, and I want to measure only the heat exchange or heat being produced in the system without getting an effect from the surroundings, then we need an adiabatic wall, and I will take some examples later on.

If we look at some of the old books, some those books have introduced another terminology and that is called global isolated system. What is the need of introducing another terminology global isolated system? The reason for introducing such a concept in some of the books has been following.

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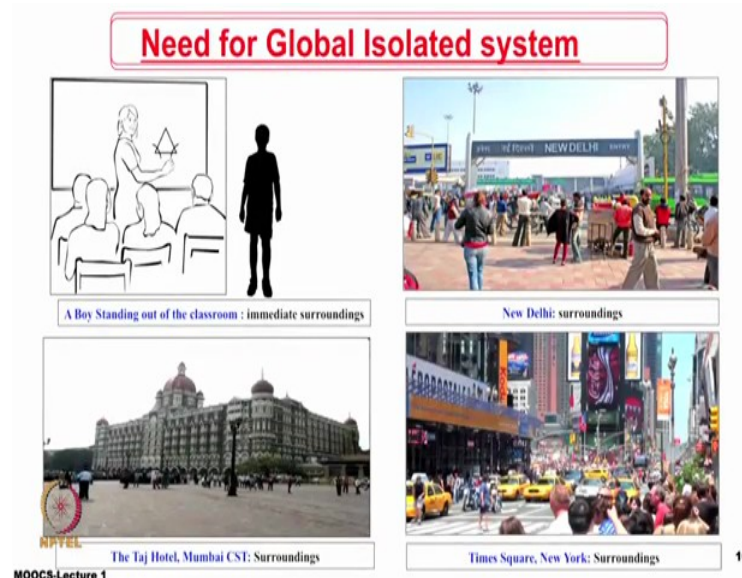
Let me take a very simple example of a classroom. Suppose, I am teaching in a class and I just took an example that if the door is open and the students are allowed to go out and come in then it is an open system. If I close the door, do not allow any students to go out and only my voice can be heard outside, then it is a closed system. Now, in a closed system, where no student is allowed to go out and my voice can freely go out, a person who is standing outside the classroom is standing in surroundings. My classroom is the system everything else is surroundings. A person standing let us say outside in the corridor can hear my voice and can endorse that I am definitely teaching in the classroom and I am not singing a song.

So, immediately a person who is standing outside the classroom is in the surrounding; and a person who is standing outside hotel Taj in Mumbai that is also surrounding or a person who is standing at New Delhi railway station that is also surrounding or a person who is standing at Times Square New York that is also surrounding. So, there are different surroundings, we have divided system into different parts, open system, closed

system isolated system. But can we divide surroundings into different parts may not be a good idea. However, many times observations are made in the surroundings.

For example, again I take the same example that I am teaching and is person who is standing just outside the classroom is able to hear. So, he is making or she is making an observation that teaching is going on in the classroom, and can also tell that what topics are being covered. However, the person who is standing at hotel Taj or at New Delhi railway station or in New York cannot say that whether I am teaching in the classroom or I am singing a song. So, there is a difference in where we make observations. Sometimes observations are made directly in the system, and sometimes observations are made in the surrounding, it depends where you put the sensor.

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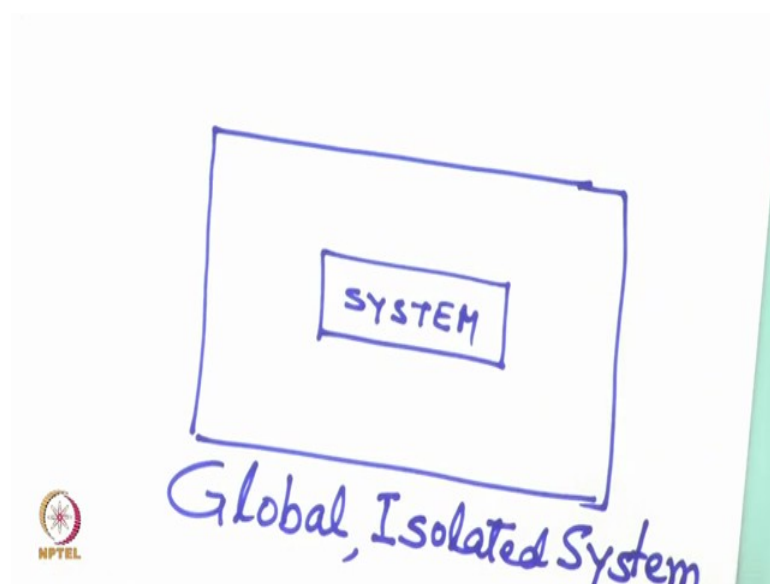
So, therefore, some authors felt that it is a good idea to introduce a system which is called global isolated system and that global isolated system is a system plus it is immediate surroundings. It is like I have, let us say this is my system in which the reaction is going on and then I put an immediate surrounding and cut off the remaining surroundings from it. This is what some books write this as global isolated system. I am introducing it, so that there is no confusion in case we come across this terminology in different books. It is also like in the practical laboratory, you have a water bath and then you dip your system or the beaker in which you are carrying out the reaction in the water

bath. So, that is a system and immediately that water bath - the water of the water bath is forming immediate surroundings, so that is the need for the global isolated system.

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As I mentioned earlier that the concepts of system surrounding are very easy and various scientists or technologies have made use of these simple concepts to come up with very sophisticated instrumentation methods. Taking an example, let us discuss about a calorimeter. What is a calorimeter? It is a device which measures the heats of reaction calorimeters have existed for a long time; but over the time, there has been a need for much improved sensitivity of calorimeters.

Let me take an example of an acid base titration. When an acid is titrated with an alkali, the heat of reaction is quite significant. Similarly, in the human body, several reactions are taking place; these are biochemical reactions. And generally the biochemical reactions which are taking place in our system, do not produce large amount of heat. Therefore, if we have the calorimeters, which can measure heats of the order of micro calories or micro Joules, it will allow understanding or studying the system, which produce very small amount of heat. The biological, for example, biological reactions the reactions which are taking place in our body we can study such reactions with such sophisticated techniques.

So, how this concept was used, you know there can be two types of calorimeters one is isothermal. Isothermal means the temperature is same and second is which operates

under adiabatic conditions. Adiabatic means there cannot be any exchange of heat energy between system and surroundings. So, the picture that you are seeing here is an example of an isothermal titration calorimeter, where the system is a cell - a small cell, which is enclosed in an adiabatic enclosure, and there is another cell which is called the reference cell. So, these two cells are kept at the same temperature that is why it is called isothermal and the whole system is kept at the constant temperature the details of this calorimeter we will discuss later on. But I want to highlight over here is, it is the simple concept of an insulated system which is being made used here to develop such sophisticated techniques that today we have the calorimeters which can measure the heat of the order of micro Joules of course, with much more improved electronics available.

So, this use of systems and of course, surroundings allows us to develop technology to such a high levels. Since, I am taking an example of isothermal titration calorimetry, this calorimeter can be used to study the systems in which very small amount of heats are produced. For example, in biological or living systems understanding of proteins small molecule interactions, protein carbohydrate interactions, protein lipid interactions, nucleic acids small molecule interactions, nucleic acid lipid interactions, protein nucleic acid interactions, nucleic acid nucleic acid interactions, antibody ligand interactions, receptor interactions and any interactions in effect when you mix something with another thing small amount of heat is definitely going to be liberated, unless the system is completely entropically controlled.

So, therefore, to reiterate that these are not simply the definitions of system and surroundings, the concepts of the isolated system and open system has led to the development of such sophisticated calorimeters that today we are able to measure heats of the order of micro Joules.

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Few more our definitions which I will go through, one is a state function. State function is a property or is a function which depends only on the current state of the system; and it is independent of how that particular state has been obtained. The examples of state functions are internal energy Gibbs free energy, Helmholtz free energy, entropy, temperature, volume. For example, one litre sample of nitrogen at a fixed temperature and pressure for example, 300 Kelvin and 300 kilopascal has the same internal energy irrespective of how the sample has been prepared.

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Any property, for example, U is a state function, G is a state function, H is a state function, so therefore, dU, dG, dH, dA, dS etcetera, these are exact differentials. And delta can only be written for a change delta can only be written if dU is exact differential then delta U will be U final minus U initial and then this applies to all the properties which are state properties. For example, again dG integration from an initial state to final state is equal to delta G, which can be written as G final minus G initial.

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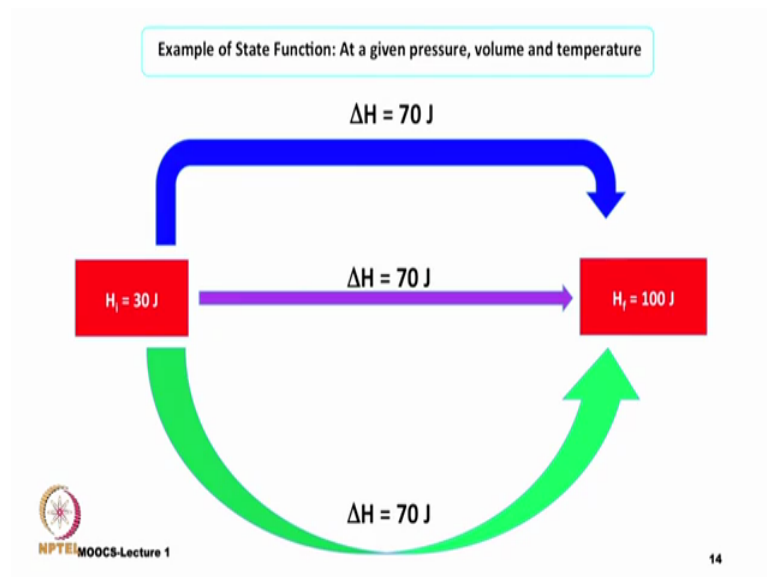
This is an example of a state function that if you fix the pressure volume and temperature. And you have an initial enthalpy of thirty Joule and final enthalpy of 100 Joule whether you follow the green path or you follow the violet path or the blue path, the change in enthalpy is going to be same irrespective of the path followed.

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There are some other properties, which are path functions. And the examples of path functions are work and heat because the value of the work depends on the path chosen the value of the heat depends on the path chosen. The work done in changing the state of the system from same initial state to same final state may be different under different isothermal or adiabatic conditions.

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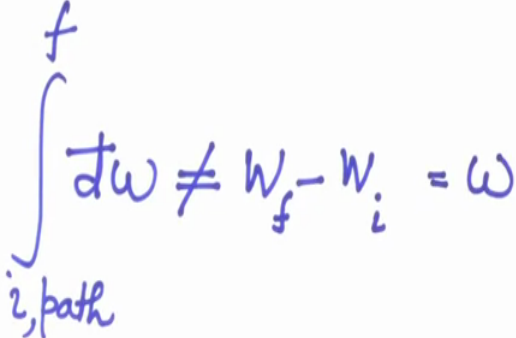For path functions their derivatives are in exact differentials, you cannot use delta for a path function. Delta q is not equal to q final minus q initial; integration of dq from initial

to final is going to be q. Similarly, for the work delta w cannot be written, you can only write as work because it is a path function. So, integration from dw from initial to final state.

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$$\int_{i,path}^{f} dw \neq W_f - W_i = \omega$$

For a path initial function, you generally write from initial state to final state, for example, dw is an inexact differential is not equal to work final minus work initial rather you simply write this is equal to works because it depends on the path taken, which is highlighted in this figure.

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Example of Path Function: At a given pressure, volume and temperature

$W_1 \neq W_2 \neq W_3$
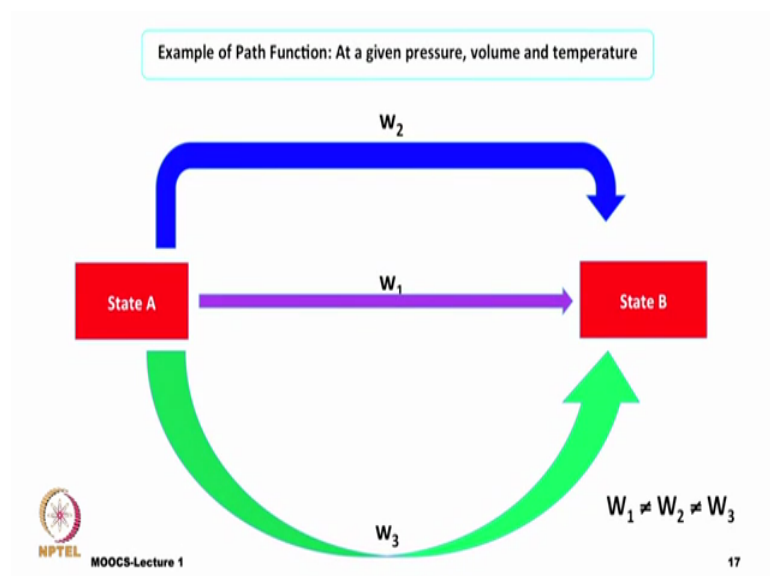
That is if you want to go up a hill, if you use the steps which are made to go up the hill or if you take a roundabout take 10 circles to go up the hill, the work done is definitely different. So, whether you follow the green path or the violet path or the blue path the work is different.

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Finally, in today's lecture, I will give examples and define extensive and intensive properties. Extensive property is the one, which depend on the size or the extent of the sample. For example, mass and volume; this depends on how much sample has been given. The mass will depend upon that volume will depend on that. Intensive property is the one which does not depend on the size or extent of the sample for example, temperature you know you take 5 ml of water or you take 100 ml of water the temperature can be same. You take density, you from a large pool of water if you measure density by taking 1 ml or 10 ml, it does not matter, it is it will come out to be the same the pressures, for example, will also be same. However all the molar properties when you convert a property intensive property divided by the number of moles it becomes per mole then it becomes extensive, because then it will not depend on the size of the sample, it will depend per mole.

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Irrespective of being a "State Function" or
"Path Function" Internal energy (U), heat (q),
and work (w) are all measured in the same
units [recommended in joule (J)].

☞ $1\,J = 1\,kg\,m^2\,s^{-2}$

MOOCS-Lecture 1   19

And as I said that we must follow the signs and conventions which are recommended by
the International Union of Pure and Applied Chemistry. And irrespective of whether it is
a state function or a path function, the internal energy heat and work, all these basic
fundamentals of thermodynamics will be mentioned will be written in same units, which
is 1 Joule. And 1 Joule is equal to 1 kilogram meter square second minus raised to power
minus 2 per second square.

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Signs and conventions
(as recommended by IUPAC)

Addition to the system: Assign +ve sign

Leaving the system: Assign –ve sign

Example:

10 kJ work done on the system: w = +10 kJ

30 kJ heat escapes from the system: q = - 30 kJ

MOOCS-Lecture 1   20

Signs and conventions must be adhere to as recommended by the IUPAC. Whenever something is added to the system assign a positive sign, whenever something leaves the system assign a negative sign. For example, if work is done on the system then we say w is equal to plus 10 kilo Joules, when 30 kilo Joule heat escapes from the system q is equal to minus 30 kilo Joules. And if we adhere to these signs and conventions we will never make any mistake in writing different equations which we find written in a different manner in different textbooks, but I recommend that use the signs and conventions recommended by IUPAC then we will never make any mistake.

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In the last slide of this lecture, I would like to define what is standard state and remove any misconceptions which are there in standard states or about standard state. What is the standard state? The correct definition of standard state is that it is the state of a substance at a specified temperature in it is pure form at 1 bar. The pressure should be 1 bar and the substance should be pure in it is pure form temperature can be any. In generally, I have seen that the misconception is that we generally say that the standard state is defined at 25 degree centigrade, no, it is incorrect. The temperature can be any the pressure should be 1 bar and the substance should be in it is pure form.

I generally a discuss this by taking an example of this well known equation delta g naught is equal to minus r t log k, you see the left hand side quantity is a standard state quantity and the right hand side quantity has a temperature which is not fixed, but it is a

general temperature. So, therefore, temperature cannot be fixed at to 25 degree centigrade to define the standard state, temperature can be any. So, let us keep this in mind and if there are any queries or any doubts that we will definitely discuss during the tutorial session.

So, I hope that these basic concepts of thermodynamics in terms of system, surrounding and the three fundamentals of thermodynamics will be very useful when we discuss the next lectures.