**INDIAN INSTITUTE OF TECHNOLOGY MADRAS**
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# Thermodynamics and the Chemical Industry


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## Lecture 2
## James Prescott Joule an the First law

We are going to discuss the Thermodynamics for chemical engineers. Actually the discussion will be quite general but let me put the subject in perspective, what you have are processes which are divided into rate controlled processes and (near) equilibrium processes. Under rate controlled processes you will have several courses, you will have heat transfer, you have mass transfer, momentum transfer, this is a fluid mechanics, and here we have thermodynamics. This stage cascades its characteristic of classical chemical engineering operations history.

Chemical engineering itself I must give you some history, basically it started about 100 years ago, started as an offshoot of industrial chemistry. There have been some paradigm shifts in chemical engineering, started actually I think with Arthur Little. First initial 25 years of chemical engineering in MIT and Cambridge and so on, they are simply descriptive industrial chemistry, they simply describe the industrial processes and if you had a good description of paper making then you went there to the placement, and they also had a placement in those days. You go there and you would answer all questions about paper and you would be taken immediately as a chemical engineer in the paper industry.

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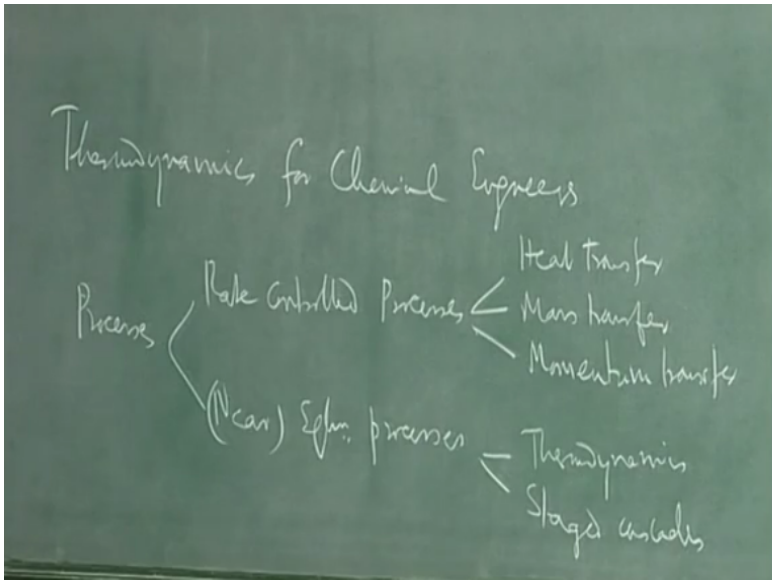

Then Arthur little in 1925 I think, it is around that time, he suggested why are you guys doing this in University, you have to be more general than this. There are common processes in all the chemical industries, you teach that in because all of a sudden they did not have to know the details of the paper industry. It is a damn nuisance knowing all the details because they will keep changing every other day and all the changes appear very vital for the industry but for you it is like noise. Now unless you have invested money in it, unless you are getting some returns from it, the changes are inconsequential.

The conceptual changes are very few. So that is when they started this unit operations and you still have good books like Mc Cabin Smith and classical books by Germ Banker and all these, but any case reactor theory became part of it in educational institutions in India only in the late 60's or early 70's. But that was the age of unit to processes and unit operations.

1962 Wordsworth and Lightfoot wrote this book on transport phenomena. What really happened was in the mid 50's suddenly chemical engineers were not getting jobs. The nuclear industry became very important. And all of a sudden nuclear industry found the chemical engineers were fairly ignorant of molecules of atoms and that there was energy in it and so on.
So there was no point in hiring them if you have to explain to them that the whole industry is based on production of energy from the atom. And all of a sudden there was a shift from engineering, from technology to what is called engineering science and that is when Wordsworth and Lightfoot wrote their book and when they came to Minnesota they were both Ph. D's in mathematics.

So this came about. So this was called the period of you might say chemical engineering science. Earlier it was called the period of the "The Age of the Handbook" you might say. I do not know if any of you have a chemical engineering handbook and you had to buy this book, the very fact you carried it under your arm exactly like doctors carry a stethoscope. The proof of being an engineer was to carry a slide rule in one hand and the handbook in the other.

But even now the handbooks are the source of all design, eventual design, because in practice design a synthesis and you want to put things together you finally have to bridge a gap in ignorance. Let me explain philosophically. What we do in courses in university and this is not a derogatory description, this is an actual description.

You take a large problem, this is true in science, this is true in engineering. You find that there are conceptual difficulties that are very hard to solve. So what you do is divide the large problems into two parts, one of which contains the conceptual difficulty, you put it aside and then you solve all the problems concerned with the other half where there is no conceptual difficulty.

Those also require a lot of intelligence and cleverness. Once you have solved all that you are then a lucky generation gets away with five years of research on that. All those problems are solved. Then you go back to the other half. You do the same clever thing. You divide that into two halves, keep away the conceptual difficulty unless there is an Einstein who comes along and solves this. Meanwhile you solve all the problems in the other half. This is how analysis proceeds and till the last conceptual bit is solved you cannot synthesize it for design.

For design you have to use emprism. An emprism is still used partly because we do not understand turbulence. So coming back you have this age of unit operations, the age of the handbook, the age of unit operations and then you have the age of chemical engineering science. You really don't have a paradigm shift afterwards although after about 20 years of great enthusiasm about mathematical modeling and chemical engineering science.

People discovered you are not wise enough to advise the industry very often. So you go back and ask what can we do and one of the paradigm suggested by James Way was head of MIT, chemical engineering department. He said back to industry. It is not a good paradigm; it has not been universally accepted because unfortunately industry is very focused on the bottom line so you cannot use the industry as a guide for education.

Education has to be general and then you will find applications, if you are sufficiently intelligent you will find applications in the industry. So as far as this, the curriculum here is concerned we have all these courses, you have all these processes been combined into transport phenomena. This transport phenomenon is really based on phenomenological theory.

Phenomenological theory is simply conservation laws. All laws in nature are conservation laws. The conservation laws that you will be concerned about as chemical engineers are primarily conservation of mass, conservation of energy and conservation of momentum. In your right, the conservation laws they are simply general laws that say input minus output is equal to accumulation. So in a sense it is only common sense.

But the biggest problem in phenomenological theory is that your experiments are done by a stationary observer. You can only do experiments by sitting in the lab, sticking a pressure gauge maybe on one location in the pipe. The fluid that is flowing through is changing constantly. The way the laws are written, conservation of mass is for example written, simply by looking at the same mass of elements all the time.

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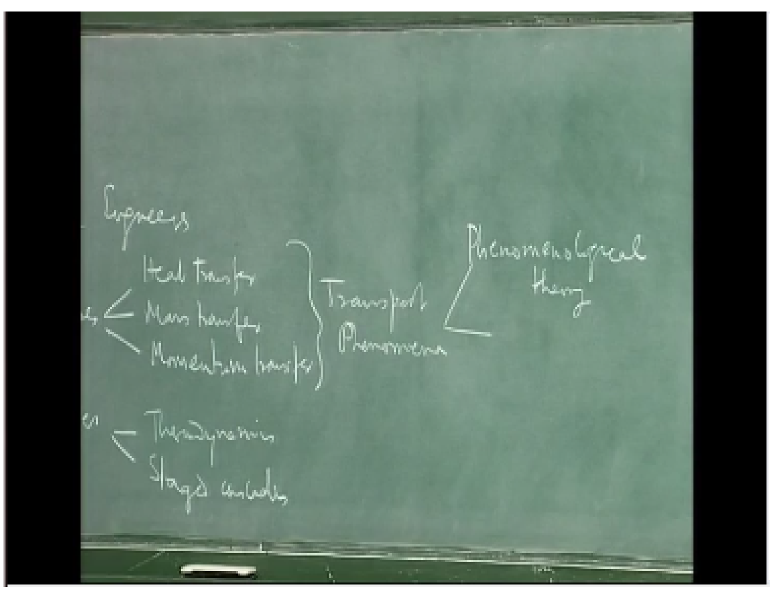

That means if you had to do the experiment on the same mass of elements you will have to sit on it and move with it. So the Legrangian observer is the observer who moves with the mass, with the center of mass, that observer is the one for whom the laws are written. In order to convert this from the Legrangian observer to the Oilerean observer, observer who is standing in the laboratory, you use what is called the Renault's transport theorem.

It is a simple theorem that relates what happens, what an observer, moving observer sees to what a stationary observer sees. This transformation gives you the phenomenological laws in a way in which you can solve them but it is not yet the full story because when you write the phenomenological laws you have to talk about what comes in.

Through the surface or what comes in from a distance like four body forces, gravity and so on if you are talking about fluid flow, or surface forces like pressure or shear stress and so on. You have to write symbols for these. Those are not included in the original description.

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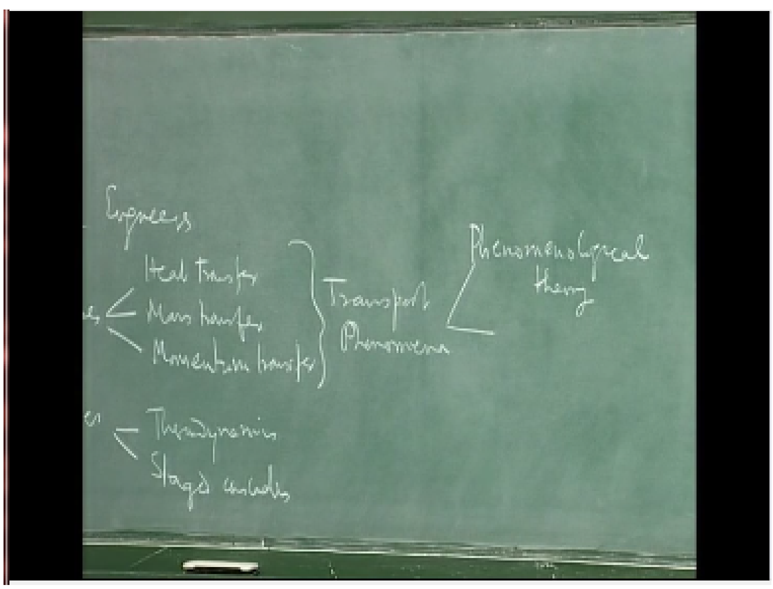


The original description, transport phenomena assumes that if you know temperature as a function of position and time, if you know density of each species as a function of position and time and if you know temperature, this is for energy, this is for mass and for momentum V as a function of positioning.

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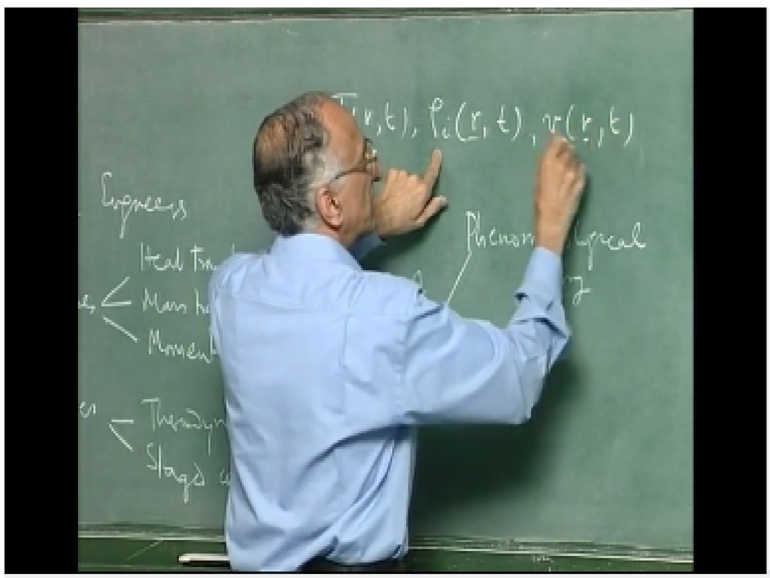

If you know these three independent, this N +4, this is N components 1 and three components of velocity. If you know N +4 variables as a function of position and time completely then you have a complete engineering description, you can derive any quantity you want, you can do all the calculations. In order to calculate these, you have to use the conservation of energy, you have to use the conservation of mass, and you have to use the conservation of momentum.

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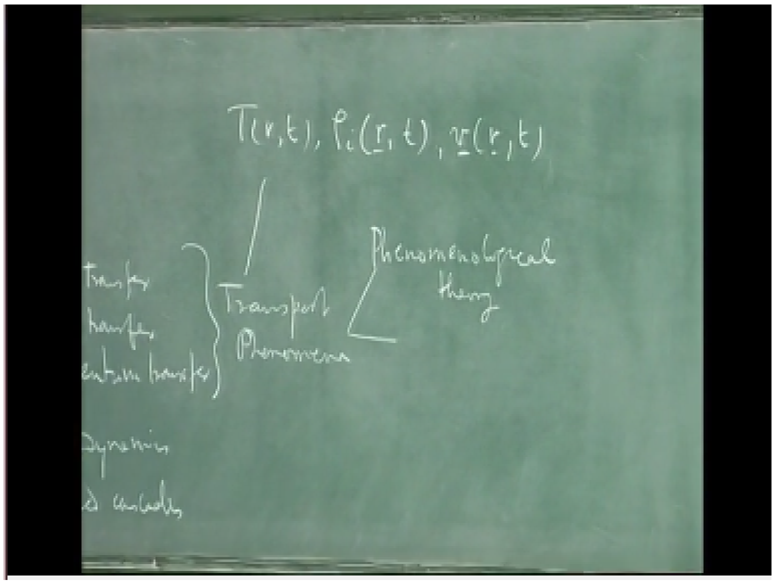


But when you use these you introduce new variables, when you write the phenomenological theory for these you introduce new variables. As I said the first step in phenomenological theory is what does the observer see? You have to look at what the Legrangian observer sees and relate it to what the Oilerean observer sees. That you do.

The next step is to write fluxes. Motion of energy across a boundary Q, the heat flux, or motion of mass which is a diffusion flux because if you are a center of mass observer the relative movement is the diffusion flux. Similarly for momentum you look at the shear stresses. But for all these you use new symbols. So in writing the phenomenological theory in sense it is a totallagy.

That is you write it in terms of new variables that you have to then connect back to here. Connecting these variables, the fluxes again as functions of T r v and r and t, writing this, this is called constituto relation. This tells you how the matter that you are dealing with is constituted.
So you need the phenomenological theory. This is the universal laws that you believe in. At least that have been so far not contradicted because there is nothing proved in science. You only have un-contradicted experience so far. You combine these with boundary conditions because you

have to define a system, write the phenomenological law for it, write the constituto relation for it. Finally substitute boundary conditions and of course there is faith in calculus.

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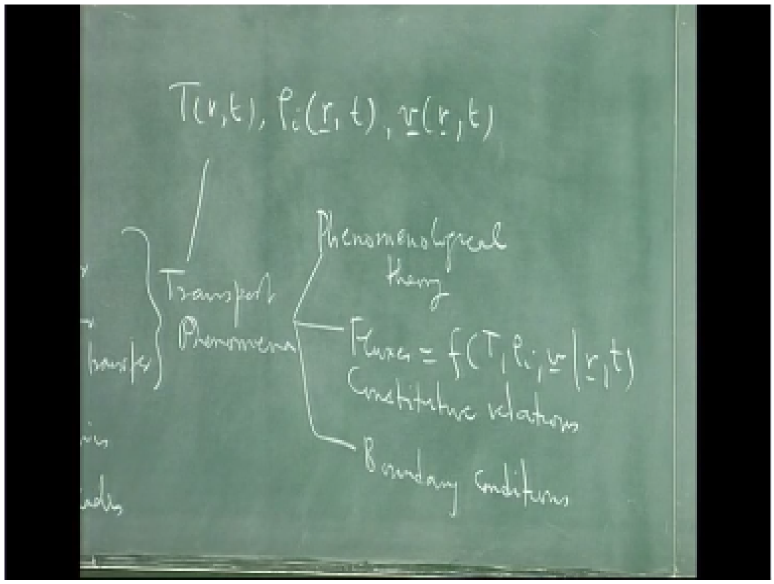


When the variables are continuous you can differentiate them and so on. So all of this comes under what is called continued mechanics. You have shown that the systems you are dealing with are large enough to contain a very large number of molecules. The change in the number of molecules is always discreet. You may go from perpendicular 23 to perpendicular 23+1, but this 1 in perpendicular 23 is so small you can construct a differential change.

So if you are dealing with very small systems you have problems. So this is your transport phenomena. This is what you will deal with effectively. Very often you will not write differential equations because these equations are very hard to solve. The whole theory of mathematics that has developed in order to solve these equations especially when these relationships with non-linear and even in the phenomenological theory what the moving observer sees becomes a non-linear term.

So all of these are non-linear equations, they are not easy to solve; the ones you can solve are linear equations. Of course you can hit the idiot box on the head and get answers. I mean if you hit it hard enough, know its different software you will get numbers but you do not know whether the numbers are right, you have problems of convergence. Very often you have a PhD thesis in it. You spend three years proving that the result is in fact correct. The number is finally right.

So this is what you do in all the other courses and if you cannot solve the differential equations they get very complex you have empirical equations, relating variables of interest to the variables that you can measure. So empirical equations are very, very important part of design. In fact this is empirical in itself, the flux itself. If you write Newton's law saying the [indiscernible] [00:12:40] times the gradient of velocity you are writing an equation that you observed from experiment. All constituto relations come from experiment although in continue mechanics, they tell you what the structure is.

Thermodynamics here itself has a constituto relation. You call it an equation of state. What you do here is define a certain number of variables; there is one relation between variables that comes from experiment. That is the equation of state. So in thermodynamics you have the two laws which are equivalent of the phenomenological theory. Actually three if you like but the third law is only simply defines for you; the so called third law of thermodynamics simply tells you a state in which the entropy is zero so that you can have calculate absolute entropies.

But you have essentially you deal with two laws and constituto relations. So you do not call them constituto relations here. The nomenclature is that you call it equation of state.

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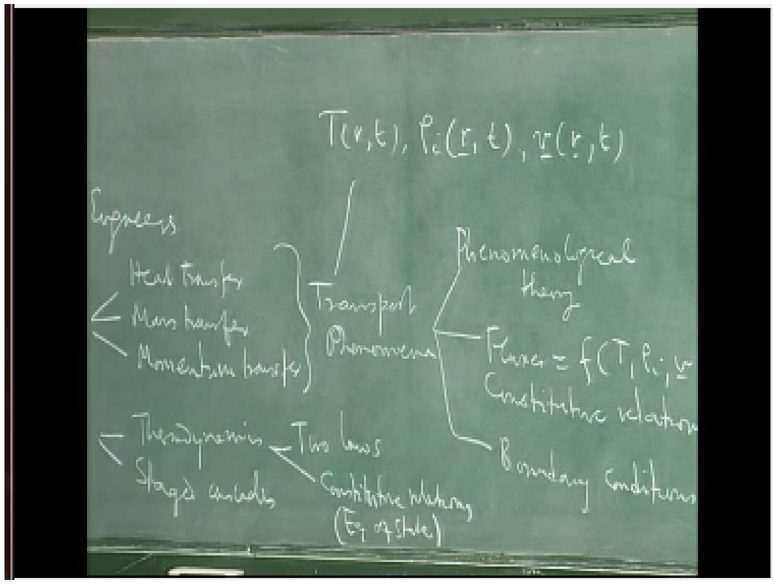


What stage cascades does is use mass balance again and thermodynamics. Coming back here, you will find the thermodynamic input in stage cascades is in the form of an equilibrium cloud. An equilibrium relationship will be given to you. We will say analyze this disclamation column given that the equilibrium between vapor and liquid is described by this equation. That equation is given to you. That is what you derive in the thermodynamics course. So what we do is look at thermodynamics here. I am going to look at the two laws and the constitute relations.

As far as the two laws of thermodynamics are concerned I must tell you the first law came after the second law. The first law of course is about constancy of energy and the second law is about ever increasing nature of entropy.

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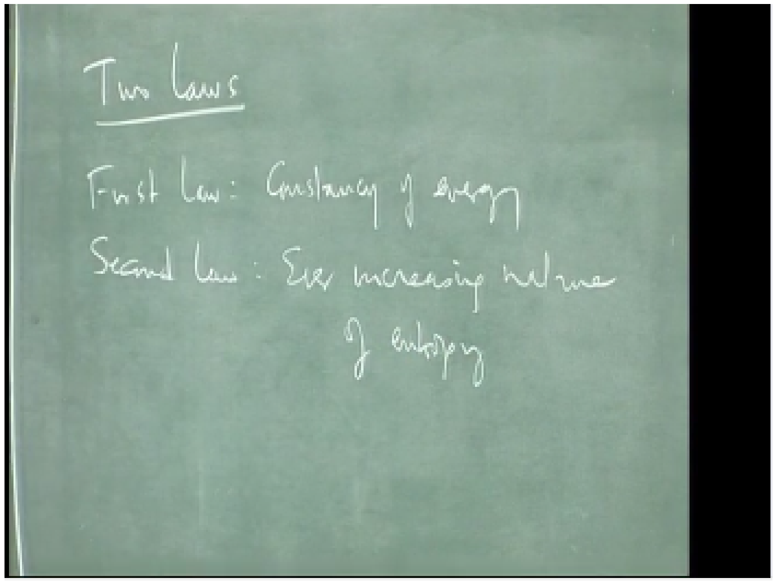


But basically there are some fundamental concepts that we assume that everybody understands. So I will just state them and sort of keep going and occasionally somebody might disturb those foundations.

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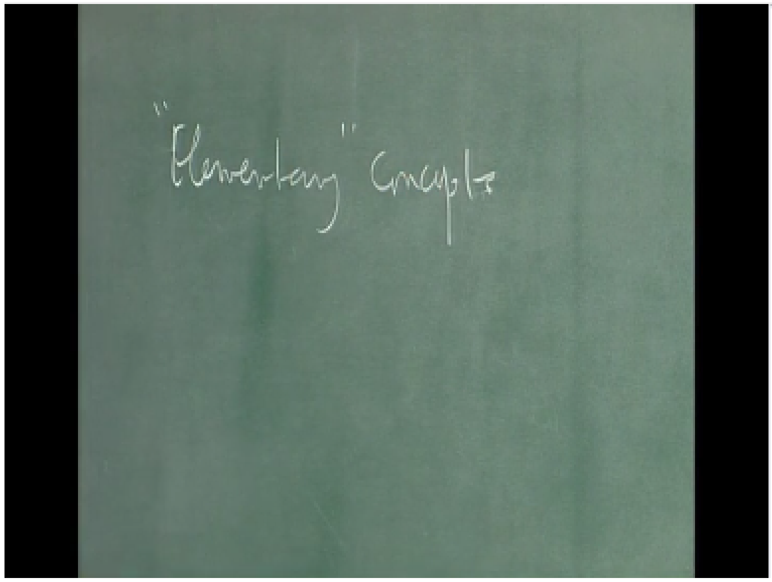


First thing is the elementary concepts. They are not all that elementary but use the word elementary so that nobody asks you questions. By definition the elementary concepts are concepts that you are supposed to understand. So there is heat, there is degree of hotness, this is one, and this is the second one. The third one is work.

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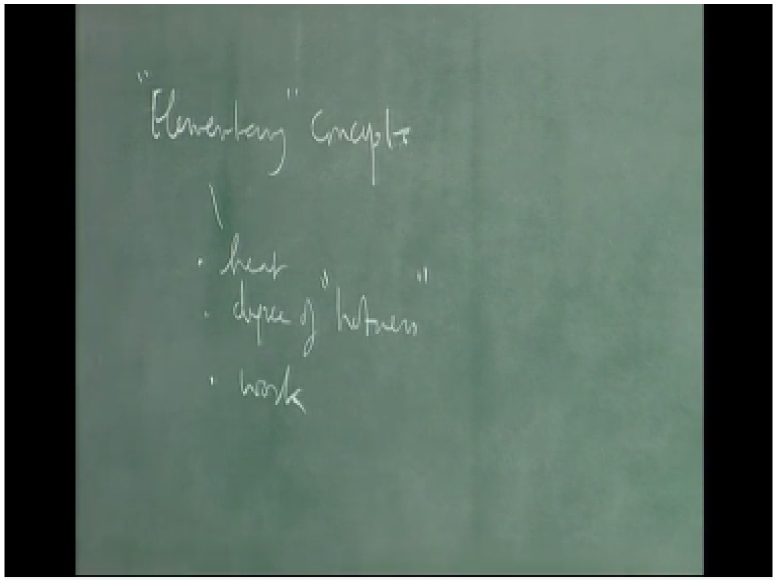


See mechanics came long before this thermodynamics came. So you had already assumed that you know what a force is, you assume that force times the distance moved by the point of application in the direction of the force gives you work and so on. So people knew what mechanical work was. People knew what heat was intuitively. So these are assumed pre concepts and we will add other concepts when we go along.

This list is not really complete because from time to time you will come up with ideas. Mostly these but you will come up with small ideas and then it gets very difficult to explain, I will put it under elementary concepts. If it is not so difficult to explain in relation to others it will come under theory.

Okay, as I said basically thermodynamics should be divided into three parts. The first part will be thermodynamic theory which is very rigorous which is a nice set of logical arguments, deductive arguments. The second part constitutes equations of state and other empirical information about this constituto relations. The third part is applications. So far whenever the application does not agree with experiment we have always found that if we improved the second part, thermodynamic theory does not have to be attached at all.
If you improve the second part where you understand properties of matter and its inter relationships from experiment, if you improve that, the application always turns out to be, theory turns out to be right. It predicts things correctly. So far that is the experience. But that is not the end of the world because the number of things you have to measure when it comes to properties is enormous.

So there are at least 1000 labs all over the world measuring properties continuously for new systems because you do not know whether a new system behaves exactly like an old system or it is different. You sort of predict on the basis of analogies that you always have to make a measurement. So industries sponsors a lot of this work for property measurements.

In fact I think 75-80% of literature will consist of property measurements and the big complaint is that nowadays after the computers have come in, kids do a lot of mathematical modeling and simulation without worrying about measuring properties. Measuring properties is not easy accurately. So you take the easier way out of modeling with existing properties with the number of people making such measurements is reducing so rapidly that at some point you are going to have difficulty.

So let me get back here. As far as the first law is concerned, although the history is different, we will deal with the first law first and you should read if you have time, I think you have time, it is a matter of organizing it, you should read Joule's experiments. I will not go into detail.

He simply went into a large number of experiments in which he converted work to heat, as I told you Joule is famous for having sent many of the members of the Royal Society scurrying for the back door and they apparently had to close the back door quickly, otherwise they would lose all the members from the Royal Society.

Nobody wanted to listen to Joule but when you are first establishing a principle, what Joule said was everybody knows that there is heat and work as mechanisms for exchanging energy with the surroundings.

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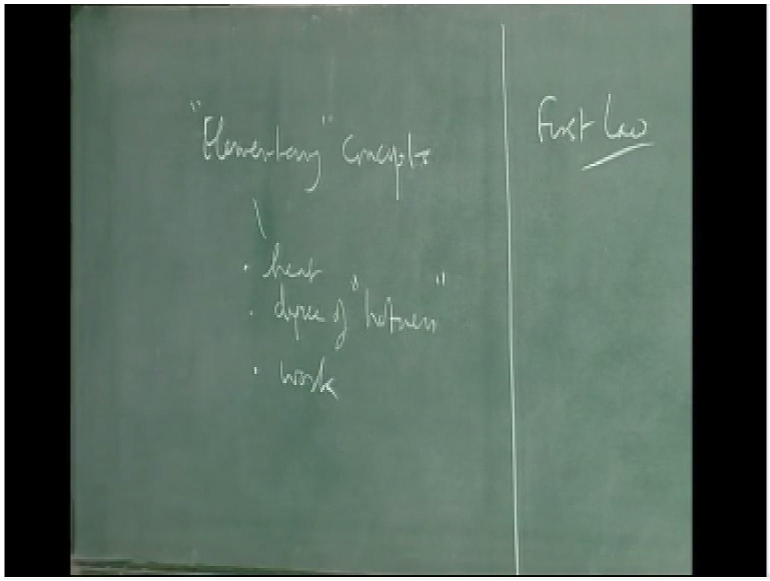


But Joule was the first one to simply assert that there are exactly two ways of doing it. Every energy exchange is either a heat exchange or a work exchange and there are no other ways of doing it. So essentially assertion is that there are exactly only two ways, two fundamental ways to exchange energy between, or I will say for exchange of energy between system and surroundings.

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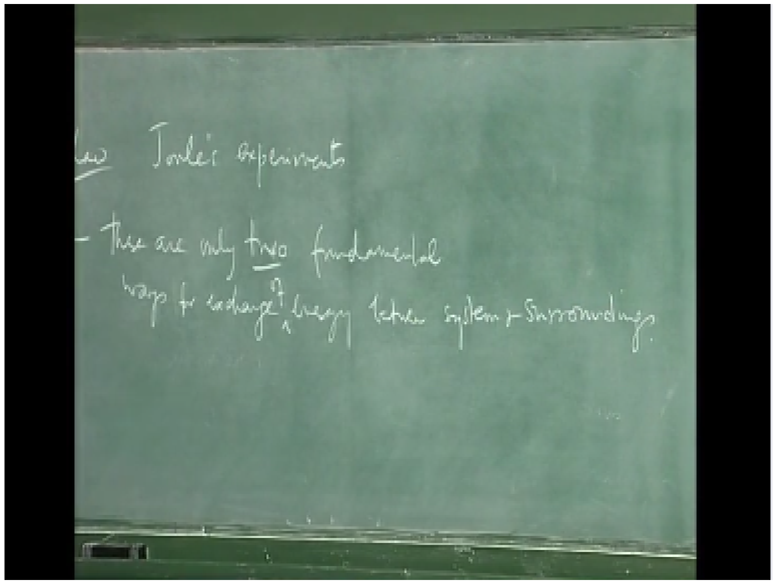


So I will put under elementary concept system, although you can define a system is anything that for which you can define a boundary, well defined boundary. Anything inside it is a system, everything outside it is the surroundings in thermodynamics. So only two ways and he said essentially and there exists a property of state and put it here.

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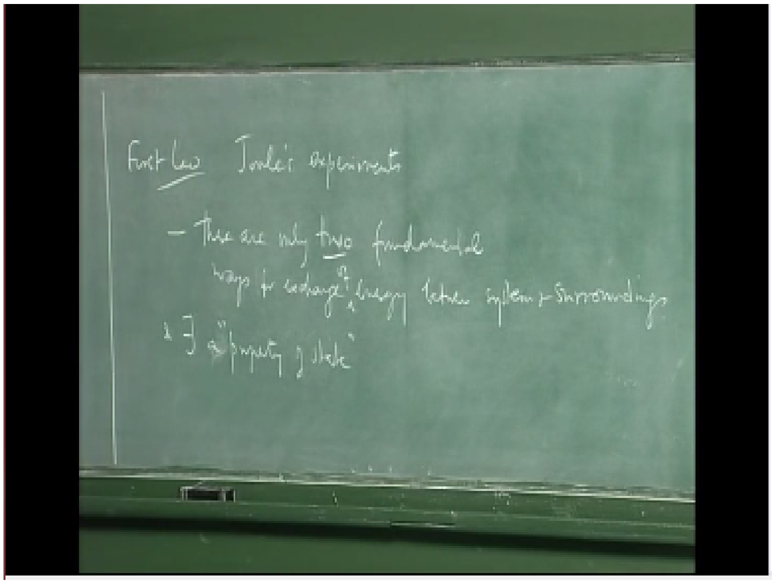


But not all of these are indefinable, these are essentially concepts that you are supposed to understand, these are definable elementary concepts. This is property of state and I will tell you what property of state is. There exists a property of state, we called it internal energy such that the change in internal energy was a perfect differential whereas work and heat were functions of path.

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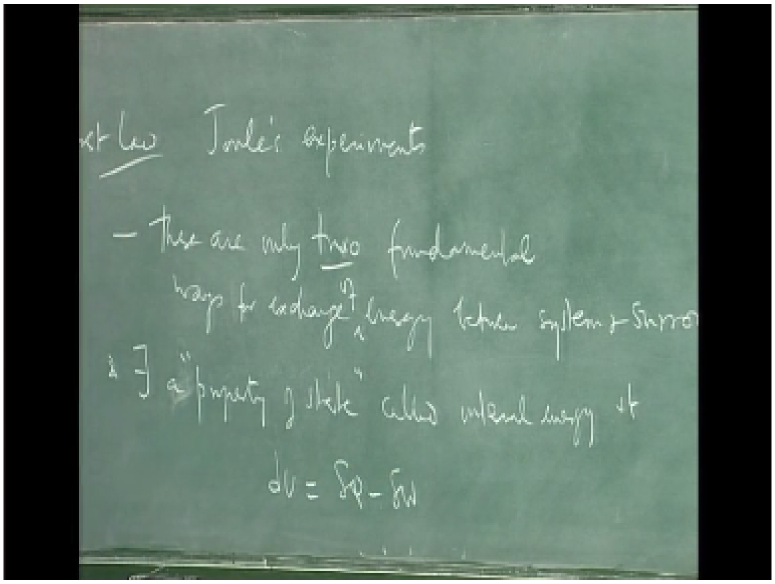


This is of course for this particular case of a closed system so let me introduce here under system there are three kinds of systems.

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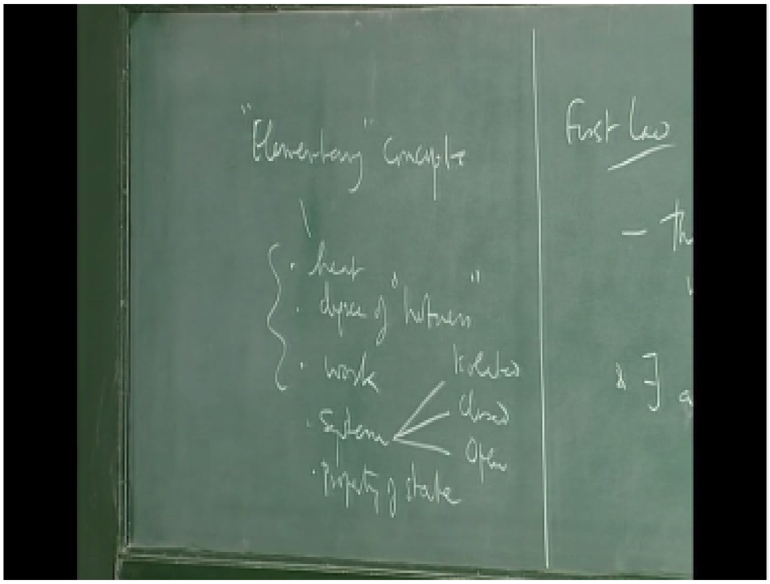


So I will step back a bit, system is any region of interest for which there is a well-defined boundary, a system is isolated when it has no interaction with the surroundings, the only truly isolated system is the universe, there is no other but many systems are effectively isolated in the sense that their interaction with the surroundings is negligible.

A close system is one that the exchanges energy with the surroundings but not mass, so chemists mostly deal with close systems, chemical engineers mostly deal with open systems because they have flow systems, processes of mass coming in and mass going out plus energy exchange with the surroundings. There is no real conceptual difference; the isolated system is very, very useful conceptually because you can write laws for isolated systems.

Whatever you say about an isolated system you can maintain its right because nobody can verify it okay, but the trick here is to say things that are meaningful, from what you say about an isolated system you should derive results for a close system which can be measured and verified. Otherwise what you say are the rantings of a mad man or a loner, it does not matter, you can say what you want, you have a constitutional right but nobody will listen to you.

If you want collective activity you have to say things about an isolated system that lead to results for a close system that can be verified experimentally. For example Gibbs when he did the statistical mechanics of molecular systems or large systems he said large, a macroscopic system can exist in many microscopic states.

The simplest example would be temperature for example. I am jumping the gun a bit; temperature is the measure of average kinetic energy of molecules in the system. So you can have one molecule going a little faster one molecule going a little slower and maintain the same kinetic energy, so you can have many possible states, that is each molecule can be in different states but the total energy can still be the same.

So there are many, many microscopic states that correspond to the given macroscopic state, that is when you make measurements on a beaker of water like this you think the whole thing is quiet, if you had the width to see the molecule you will just go mad, the molecules will be running around at 10 to the power of 5cm per second on an average so they will be hitting this every 10 to the power, this is only the few cms so every 10 to the power of -5 sec you have a collisions if you can hear it then you will go mad again.

Imagine pumping at the rate of 10 to the power of 5 times a second, that is the minimum and there are about 10 to 23 molecules here so you are talking about 10 to the power of 28 collisions per second, so the whole thing is a madhouse, luckily you do not see it because you are seeing averages and the average behavior is constant therefore you claim that it is a equilibrium, it is a trust and so on.

So that is only an illusion, the real factor that there is a tremendous amount of activity and you have, so Gibbs said in an isolated system all microscopic states that correspond to the same macroscopic description are equally probable. So this is pure philosophy because you know nothing about it, the only way to do it is to do it equitably.

Now since I know nothing about the states I assume that they are equally probable but that statement would have had no meaning expect from that he derived laws that corresponded exactly to the closed system laws in classical thermodynamics. So similarly what you have to do is you have to realize that isolated systems are very useful conceptually but you have to derive results for closed and open systems.

Chemists use close systems and you can derive all of thermodynamics for chemical engineers from closed systems. This book by Devine which is my favorite book is the only book which I have read cover to cover in thermodynamics. Devine’s book has practically only closed systems, tell little bit of treatment about open systems, I think he has added it as an apology afterwards, his first edition did not even have it. Devine wrote this book on principles of chemical equilibrium which I like very much. My recommendation is the following, the many, many books in thermodynamics are very good but if you go to the library what happens is you will read one book and you sort of get bored.

Then you read the other next book, you read another book, you read 25 books all of them you will read chapter 1 so you will not get anywhere. My recommendation is just pick the first book you got, make sure it is a decent author or do not pick a lousy book, take a decent authors book and read the whole of it and then formulate it in your own mind, that is the easiest way to do it. Ultimately it is nobody's special possession, once you understand it, it is yours as much anybody else's. If you do that you will be much better off, in fact there is an old principle, it means take that chance to tell you anything. Some principles of teaching, the first principle is nothing can be taught, there goes my job, okay, but the fact is a teacher can only facilitate learning and you have to be in face.

After all I send out a message, if you are in a mood to listen you will receive the message otherwise you will not, you will be thinking of something else which is alright because somewhere along the line you hear these words and they will come back to you later, and even if they do not come back it is not a big loss, its only human experience that you are gathering, you will gather it somewhere else.

So the first principle is this, the second principle, this is a very important principle that Aravind says, he says suppleness and comprehensiveness of mind is actually developed by multiple approaches to the same problem not by solving many problems, equivalent of these words. The idea is that the many problems, you know if you use many approaches to solve a problem you understand the physics of it very well.

You can apply it any time to any other problem of interest and when problems come in real life that are interesting to you, you will use these techniques, the idea is only to teach you a technique, again saying that education is not about filling a bucket, it is about teaching a student to open the tap. In Madras sometimes it is a problem, taps do not give any water, you can nevertheless, the idea is simply to teach you techniques.

The methods of science are always much more important science itself, than the results because the results can change, think it is. There is also another quotation, a very good one, I have forgotten. There is a Nobel laureate in chemistry who said he was appalled at the number of things he had insisted that students learn that turned out to be wrong afterwards.

This is part of teaching in any case, but coming back I would suggest that you try and do one problem in many ways and never, everybody recommends that you do a large number of problems, I myself have not done a large number of problems but I found it very useful to study a problem and see if it is different from the previous ones. If it is not do not do it, if it is do it. There is one more last story, cannot resist some of these stories.

It is a story by a mathematician, I may have told you this before, they are my favorite stories. I think both the mathematicians were given a glass full of water, asked to make tea, so they made, went through the process put leaves and boiled and made tea, then they were both given an empty glass and asked to make tea again, so the mathematicians filled it with water put it on the table and said QED by previous theorem tea is made, you do not actually get tea with a mathematician but he simply tells you that there is a proof that tea can be made.

My recommendation is use the method of the mathematicians as far as possible; do not keep doing the problems again and again because conceptually it does not give you understanding. Anyway let me get back here, so the idea here what Joule did was to take, his classical this thing was a calorie meter, he had a stirrer, he had an attachment by which he measured the input of work, he stirred it and found the temperature went up.

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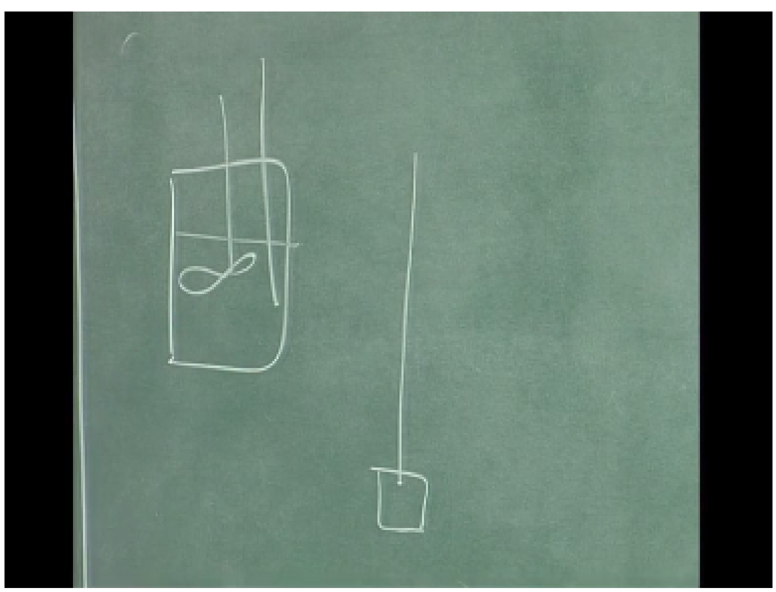

He had of course a thermometer which again brings you back to what a thermometer is, again it is a empirical device for measuring degree of hotness and things have been done experimentally, then you have the degree Fahrenheit and the degree Celsius, these have been introduced all these you know so we stick a thermometer in, he measured the temperature rise by putting in a certain amount of work. What he did was he had a system of pulleys and so on so that he defined work as simply the moving up and down of a weight so you could calculate the exact work done and by moving this up and down he had a series of pulleys which caused this stirrer to rotate and the temperature went up.

All this has to be done very accurately, he insulated the calorie meter, measured the temperature rise, then he cooled it back and the same temperature rise he caused by a certain addition of heat, then he did this in a thousand different ways, every time he found that when he brought the integral over a cycle of delta Q – delta W was = 0 over a path whereas the actual work done could vary with the path, so the work will be very different.

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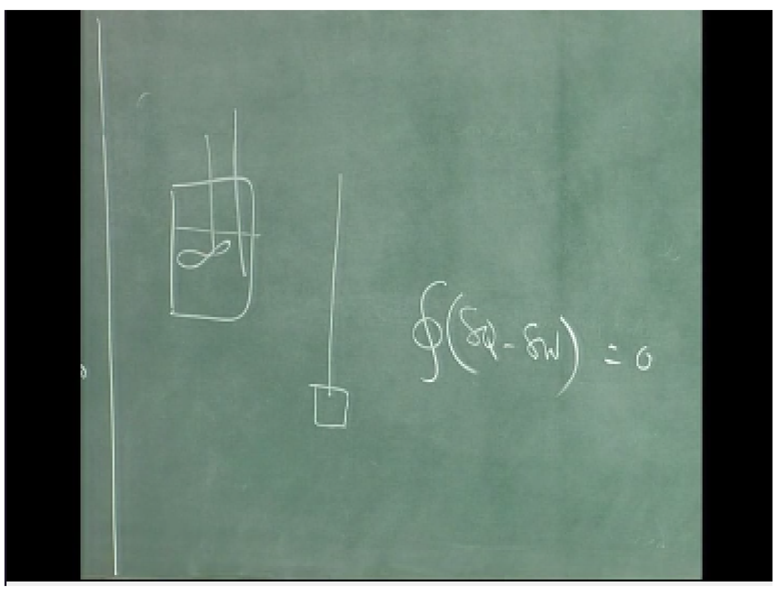

But in mechanical system, thermo mechanical systems he showed that the cyclic integral of delta Q- delta W = 0 although the cyclic integral over delta Q itself or delta W itself was never 0, so Q and w are functions of path but the difference is independent of path, therefore he said this quantity can be called a perfect differential and he wrote this is du.

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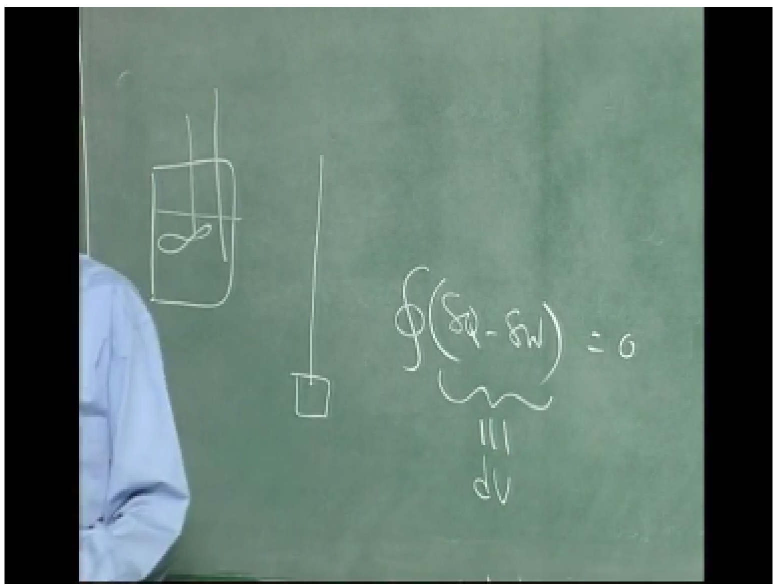


This is the summary of two hundred years of work you might say and I write DU = delta Q - delta W, it is like the old saying that the science is very accurate, Newton says just f =ma and the whole thing is very clear to everybody, it has got all the elements in it whereas look at Shakespeare in order to communicate human confusion he writes a whole play called King Lear and you cannot summarize the whole thing in the one sentence and communicate any idea, you need a lot of redundancy so that you get some idea of the conflicts in life and what comes through and so on.

So that is what they said but actually this is false because when you write F you assume what a force is then you have to ask what a force so it simply, science is a language that we all accept and therefore we communicate with one another, we are able to communicate but there is lot of history behind writing a physical term, whereas in language you still need this redundancy, you do not have simple ways of expressing, because there are many subtle ways of it.

So anyway, so this, what this does is then empowers you to use u in Calculus. This brings you to first I must have told you what is status; I am sort of putting the cart before the horse.

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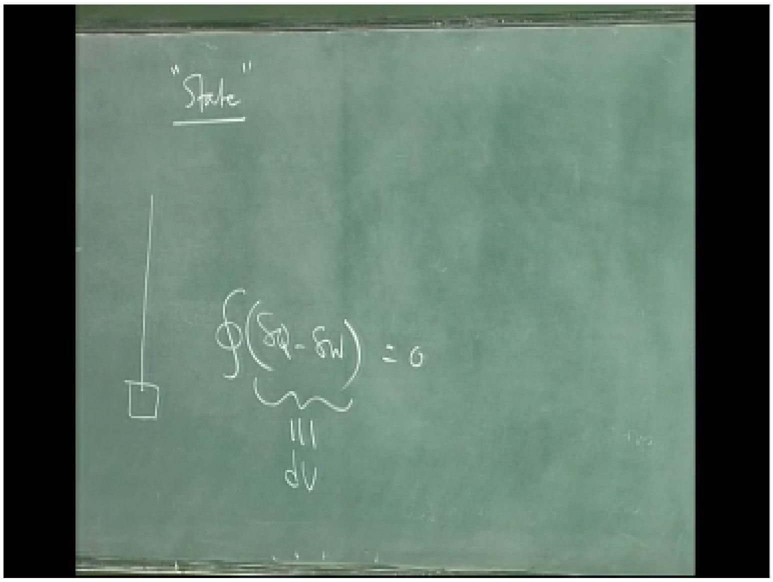


The state of a system is simply the number of variables required to be specified before you can reproduce the system in another place okay, the number of variables, suppose I have a beaker of water, I have to tell you what the pressure is, what the temperature is, and say it is water, so three statements tell you the constitution its pure water, I say it as at room 25 degrees C and one atmosphere pressure then I have completely specified the state of water. How do I know I completely specified it, only by experiment?

I know the number of variables required, finally Gibbs derived a face rule but in the face rule you know its number of components minus number of phases plus two, that is the famous Gibbs face rule but the number of components is suspect, if the number comes out to be wrong and the state changes that means you did not measure all the components, there may have been one component that you did not measure or there may have been a phase that you have missed. If it is a solid state it can come in several phases without your knowing it unless you examine it very carefully.

So in a sense while that rule is correct it assumes that you know number of phase and the number of components, so the number of variables required to specify the state of a system is a completely empirical thing, so state of a system simply means specification, state is defined by the assignment of values to a minimum number of parameters which can be reproduced exactly.

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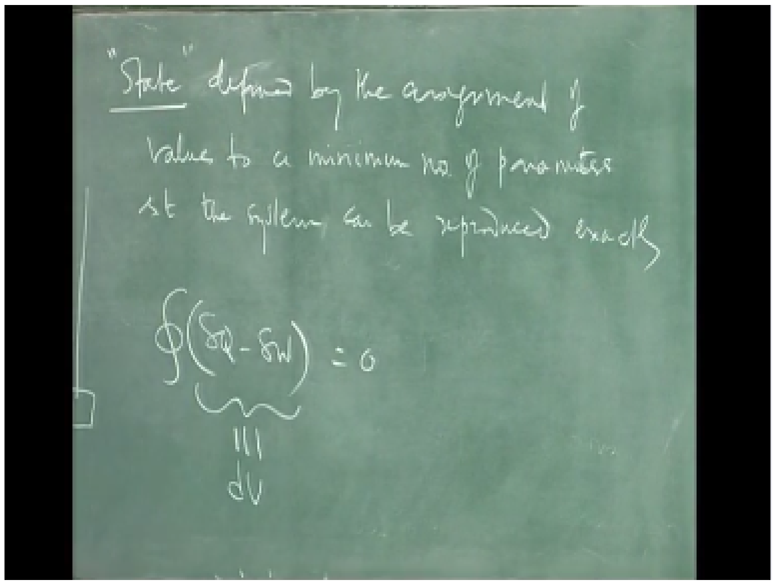


In thermo dynamics we do not worry about the containership we are only interested in the system say water; if I was interested in the system shape then I have to specify the container and all its properties as well. So if your system is simply water then you have to give me only two variables for example, if it is pure water so this is an empirical quantity and state variables are simply these variables that you have to specify. So what this does is to say that u is a function of state, if I know the state I know the internal logic exactly because if I go over a cyclic path and come back to the state u returns to its original value.

And only a functional state can return to its original value because the functional state implies that it is not dependant on the history of how it got there. I could have got this water from Cooum, it could have collected it from rain water, but if it is finally pure water at 25 degrees at one atmosphere it makes no difference, may make an emotional difference to you if I ask you to drink it, if I say from Cooum and I say from rain you will drink one very happily and the other you will not, although all of us will be forced to drink very soon.

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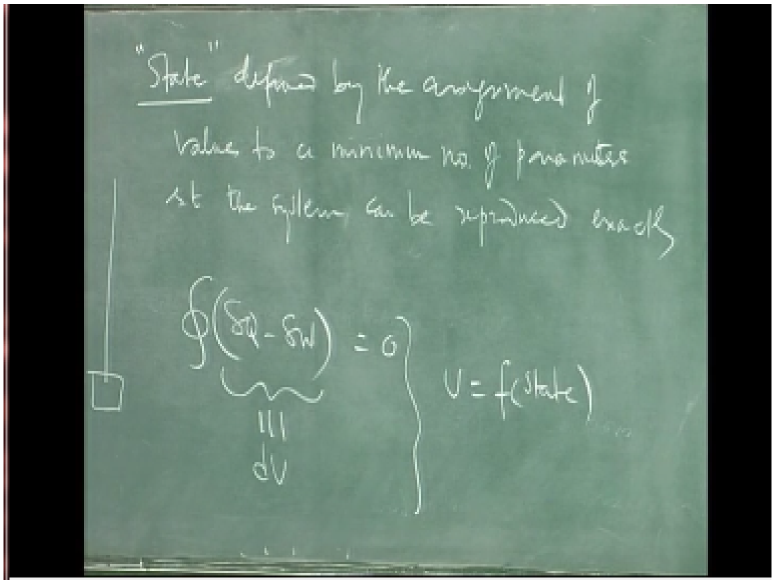


Recycled water, there is no choice but any case that is a different issue, that is why human beings cannot be modeled in thermal because they have a memory. If I describe this person then I can say what his state is, I can say he is so tall, he is so fat, he is so heavy and so on, all this I can specify but his emotional state cannot be specified in terms of just current variables and say how he was treated when he was 1, when he was 2, you know all that comes into play, the history of the, so when you say state variables and thermodynamics is confined to description of systems that can be described in terms of state variables.

That means I only talk about systems without a memory okay, if they have a very short memory it is okay, you can sort of draw gloss over it and say I will integrate everything and talk of properties over a five minute interval by which time he will forget, there are many organisms that forget, many biological systems are like that, they have such short memory that you do not have to worry about the  memory, but with human beings, with anything that have a long memory you have to worry, you cannot do thermodynamics of systems with memory.

So we have the state variables, I have this discovery of Joule and therefore he said u is a function of state, if you tell me the state there is a variable u which is uniquely fixed.

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