Thermodynamics And Kinetics of Materials

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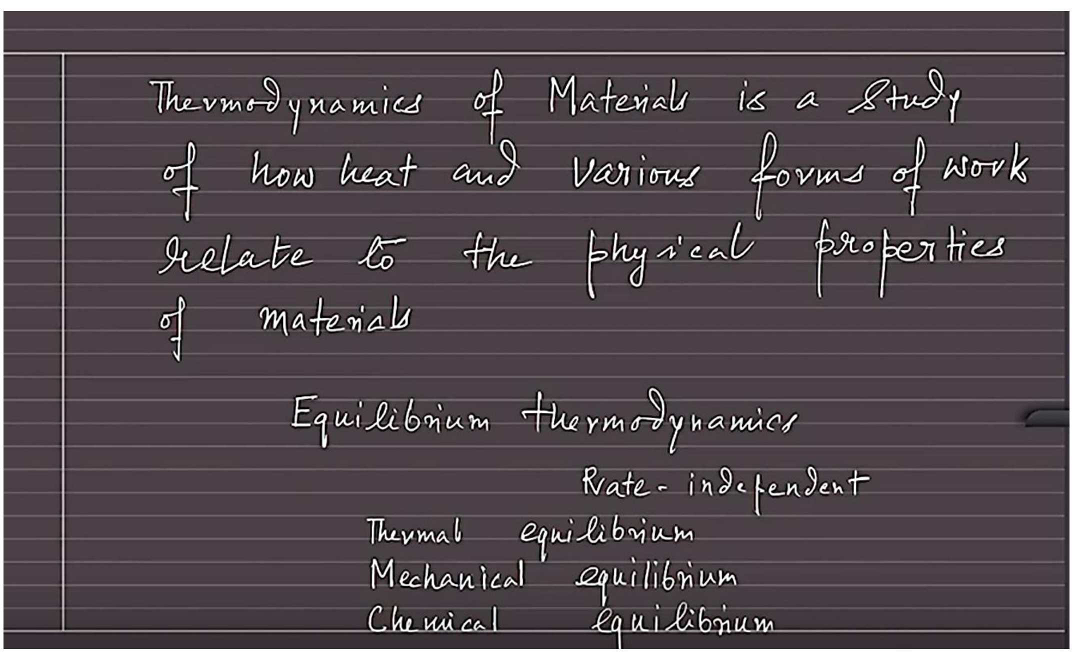
Lecture 1

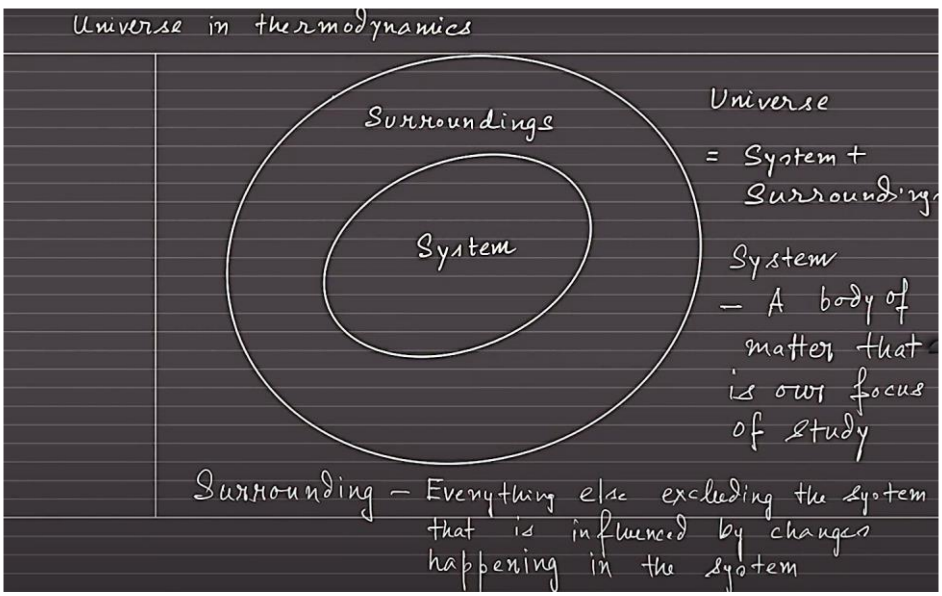
Basic Concepts

Welcome to the class on thermodynamics of materials and as you know, thermodynamics of materials is a study of how heat and various functions of work relate the physical properties of materials. By physical properties of materials we mean something like energy, entropy, heat capacity, thermal expansion etc. So, I will come to all these physical properties and how heat and work relates to that because as you know when we talk about thermodynamics when we talk about thermodynamic processes we always think of heat flow or heat transfer we think of mechanical work we think of various forms of work like mechanical, electrical or electrical work is possible, mechanical work is possible, chemical work is possible but basically there is a chemical reaction happening so that gives rise to what is called chemical work. So, or some phase transformation or phase change is happening all of these comes into the purview of thermodynamics of materials. However, these lecture series so initially we will talk about equilibrium thermodynamics which is basically when I talk about equilibrium that means this rate independent it does not depend on rate or time. So, it has nothing to do with time it basically tells whether some reactions are feasible whether a phase change



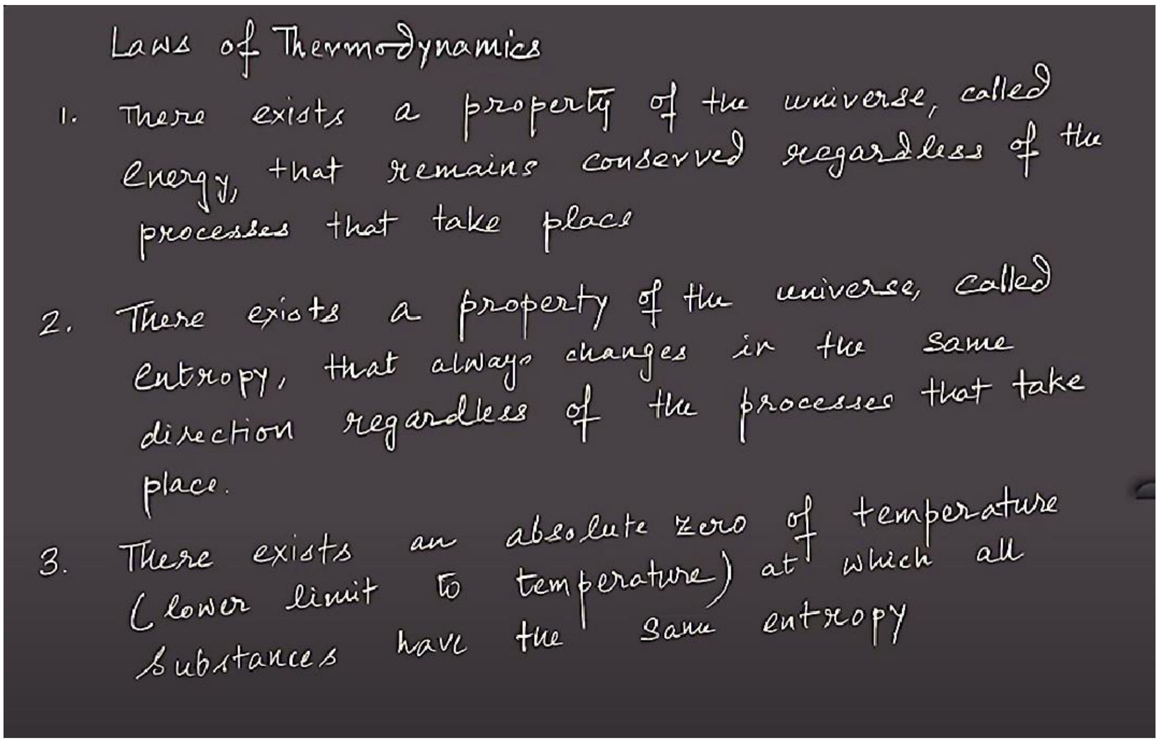
is possible and stuff it talks about equilibrium.

Now equilibrium what type of equilibrium does it talk about say for example thermal equilibrium when two bodies or a body itself is in thermal equilibrium or is it in mechanical equilibrium that means sum of forces is equal to 0 thermal equilibrium means basically there is no heat flow and then in the body means from one part of the body to another there is no heat flow. So, and then if a body is in thermal equilibrium and means basically it is at the same temperature everywhere and then there is also chemical equilibrium where we will invoke or define something called chemical potential and we will tell that chemical potential again the chemical potentials are same for all species across different phases. So, I will come to all of these one by one. So, first before we go there we will tell that often I will use something called a body of matter and this body of matter I will refer to the which is of the focus of our study and that body of matter that is the focus of our study I will call it system.



So, I will call it system. So, system is the body of matter that is the focus of our study. So, this is basically I am focusing on some portion of matter and in that portion of matter we are looking at different thermodynamic processes and as a response to this thermodynamic processes how the condition of the system will change and also when the condition of the system changes as a result of thermodynamic processes in it the system also influences everything else and that is the surrounding and surrounding basically means everything else excluding the system which is our focus right system is our focus but everything else excluding the system that feels or that is influenced by changes happening in the system. So, if there are some changes happening in the system and that affects the surroundings. So, basically it is like a region of influence for the system.

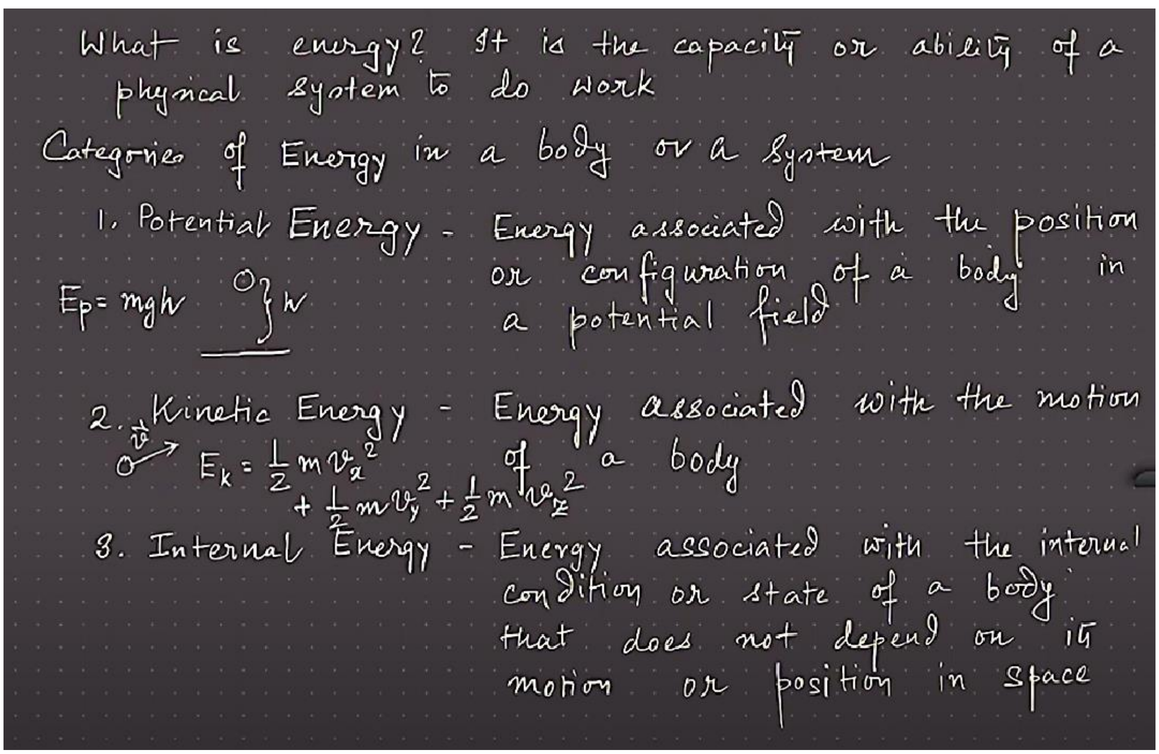
So, in the system something is going on. So, that system is our means focus of study right. So, we are studying the system and we are also seeing if there is anything happening in the system does it influence the surroundings. So, surroundings is that region which gets influenced by the system. So, as a result when I talk about universe in thermodynamics.



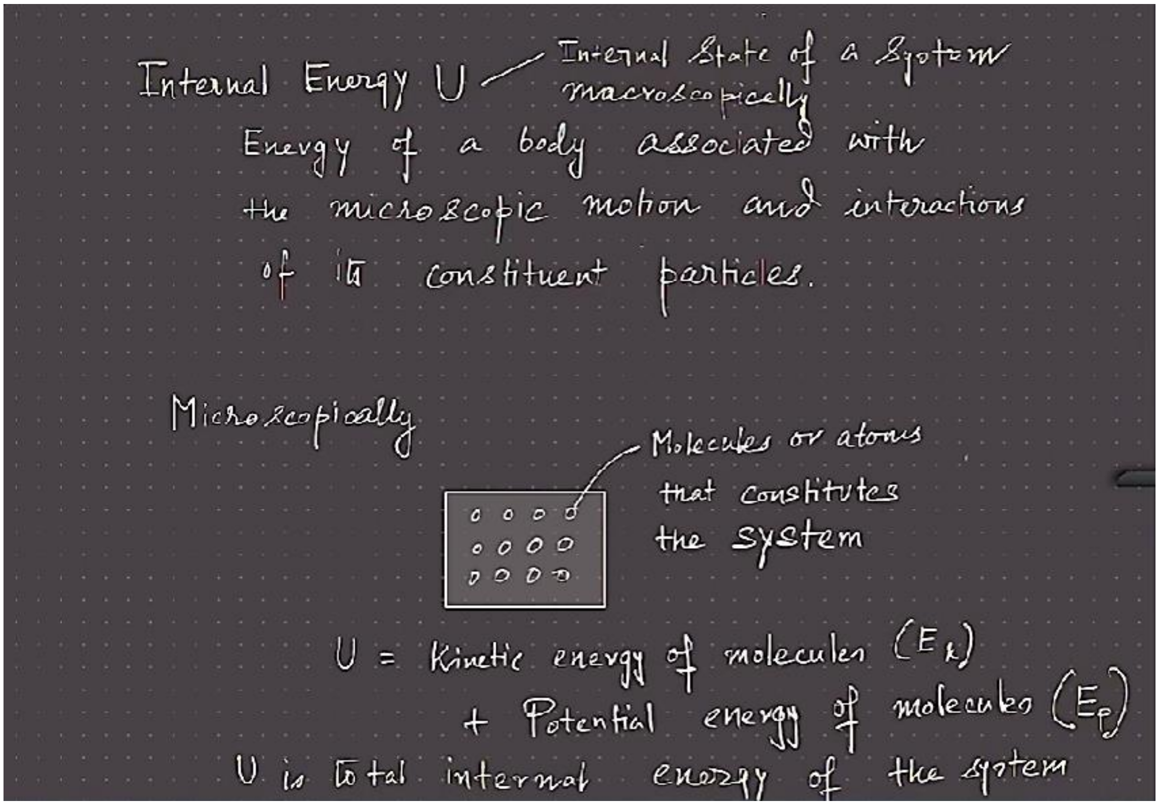
So, universe basically means system and surroundings. So, system and surroundings together basically make the universe. Now, when we talk about universe we talk of properties some properties of the universe and these properties of the universe define the thermodynamic laws. For example, as you know that there is something called first law. First law is nothing but a principle of conservation of energy.

So, energy is a property of the universe. So, there exists a property of the universe called energy that remains conserved regardless of the processes that takes place within the universe right. So, regardless of the processes that take place within the universe. Another thing I wanted to I forgot to mention that between the system surroundings a wall or a boundary and this is very important I will come back to that and I will come back to the properties of the boundary and this boundary or wall is something that defines the condition within the system as well as the condition of the surroundings. So, it is a boundary that separates the system from the surroundings and across the boundary you can have energy transfer different types of energy transfer like heat transfer or mechanical work transfer or chemical work transfer and so on.

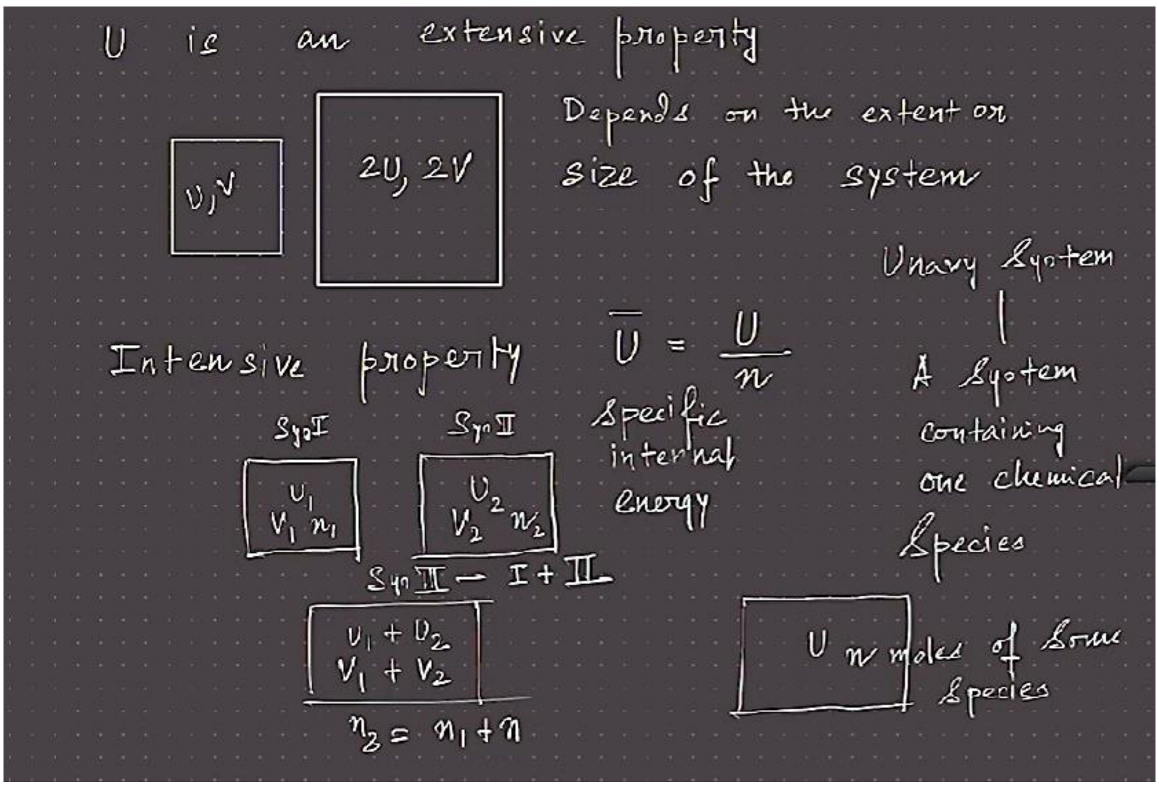
So, now as I told you first I defined energy as a property of the universe that remains conserved or constant regardless of the processes that take place within the system or within the universe. Again there exists another property of the universe which is called entropy that is the second law that always changes in the same direction regardless of the processes that take place basically entropy sets directionality of a thermodynamic process. So, it basically tells you that entropy decides whether a process will move in one direction or the other right. So, basically it gives the directionality of the system directionality of a process and it really does not have any conservation in it. So, there is no conservation associated with entropy but entropy gives you the directionality right it means whether a process will be spontaneous or not.



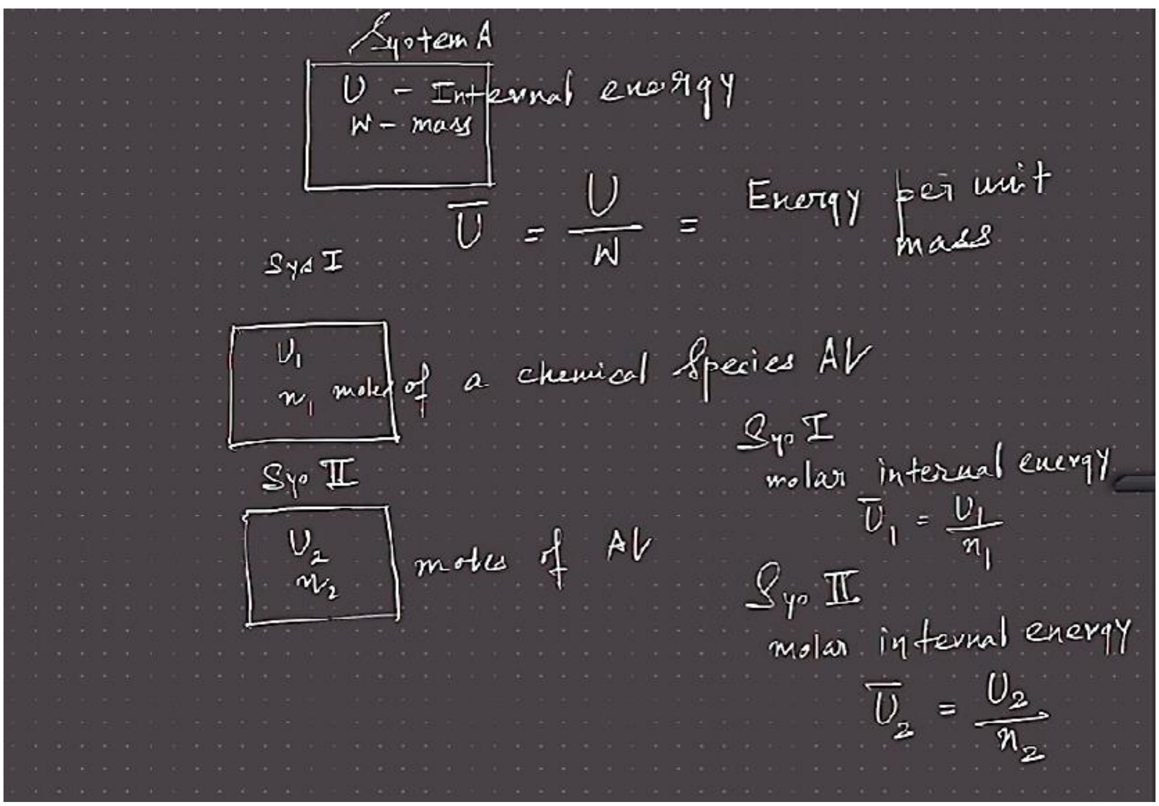
So, this is what entropy defines and this entropy again is a property of the universe that always changes in the same direction means either it increases or decreases regardless of processes that take place the entropy of the universe in general always increases and this is what we will see and we will see that if the entropy of the universe increases that is again a restatement of equilibrium right and then the final law that is the third law it tells about an absolute scale of temperature or and in that absolute scale there is a lower limit and this lower limit is called absolute zero of temperature this absolute zero of temperature is where all substances have the same entropy in other words all substances cease to have any entropy. So, entropy vanishes at the lower limit at the absolute zero of temperature. So, basically all substances we can also tell that all substances have the same entropy at this absolute zero of temperature. Now, what is energy? In general as we know like from the physics that we have learnt before that it is the capacity or ability of a physical system to do what right and the different categories of energy two categories we are already familiar one is potential energy, potential energy is associated with a position or configuration of a body in a potential field. For example, if I think of a pebble and I hold it at a distance h above earth's surface and this pebble is placed in the earth's gravitational potential field then this pebble experiences an acceleration due to gravity and this acceleration due to gravity is g and if the mass of the pebble is m then the potential energy E_p will be equal to m g h.



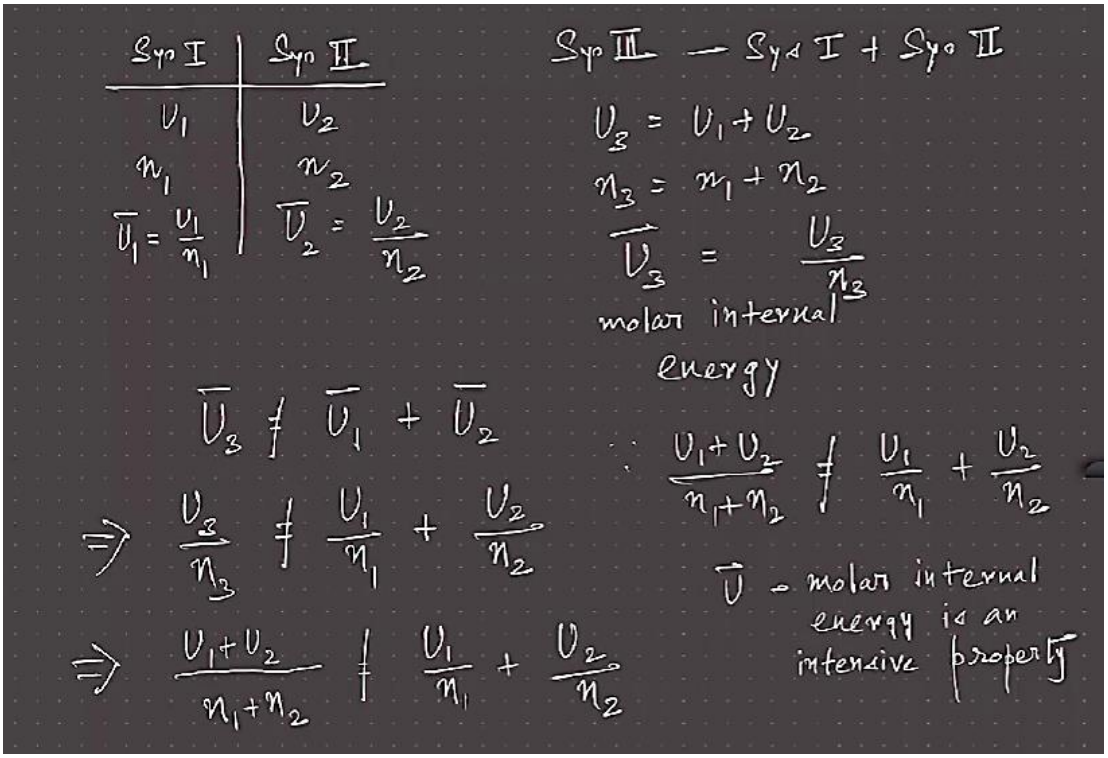
Now, let us assume that this I have taken this pebble and this pebble I have thrown and it has acquired some velocity then once it has velocity it has momentum as a result it has kinetic energy and the kinetic energy of this pebble will be moving in certain direction with some velocity V then in the three dimensional space basically in the three dimensions right we are three dimensional so we can write that E_k will be half m V_x square plus half m V_y square plus half m V_z square right where V_x, V_y, V_z are the x, y and z components of velocity field in a reference frame right in a given reference frame Cartesian reference frame and then there is another category of energy which is called internal energy this internal energy of a body or a system is the energy that is associated with the internal condition see there are these internal condition or state of a body or a system and it does not depend on its motion or position in space say for example I take a body and the body has a potential energy the body has a kinetic energy the body also has an internal energy this is this internal energy is the energy associated with the internal condition of the body it does not depend on any external condition of the body means basically whether it is placed in a potential field or whether it is moving with certain velocity



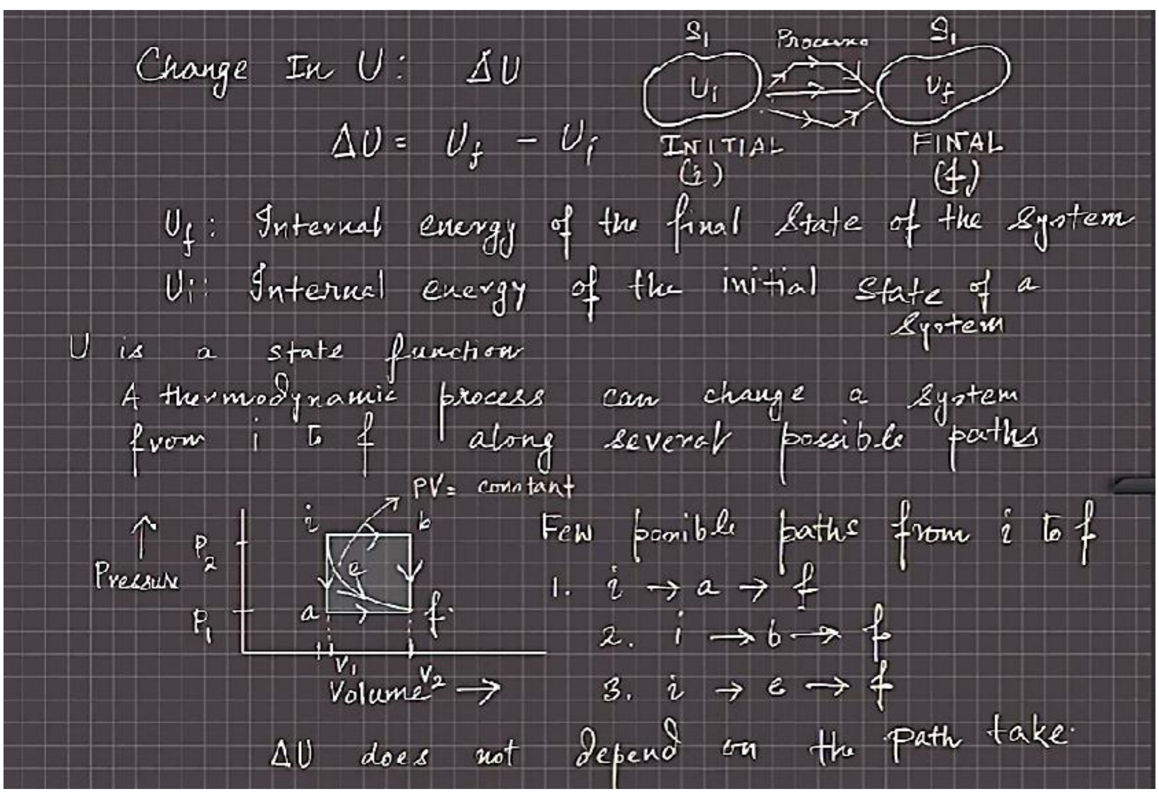
the macroscopic body has an internal energy this internal energy origin is basically microscopic because the body of matter or all matter is composed of atoms right atoms or molecules these are the building blocks of matter so these atoms or molecules are often in microscopic motion right they are in microscopic motion and they are also interacting with the other atoms right all these atoms that are there is like an assembly of atoms which is the body has constitutes comprises of a lot of atoms and these atoms are interacting with each other and these atoms are also moving right they are in there may be translational motion there may be rotational motion there may be vibrational motion right vibrational kinetic energy and all of these all of these microscopic motion and this microscopic interactions basically result in the internal state or condition or the internal energy of the body so basically you have body or a system right body is comprised of atoms these tiny particles called atoms or the building blocks called atoms and these atoms are moving then they are interacting right and all of these like interactions and forming bonds for example this is one like different types of bonds are formed and that means they are interacting there is some force between them of these atoms and then they are also moving right they can move there can be translational motion there can be rotational motion of these atoms and there can also be vibrational motion see all of these put together is giving you the internal energy of the body. So that is the idea so here we have written say for example here we can as you can see here that we are showing the body and this body is composed of molecules atoms and the internal energy which is macroscopic right so it is macroscopic but it is a macroscopic thermodynamic property right it is a macroscopic thermodynamic property but this is the outcome of all these microscopic interactions and microscopic motion like kinetic energy of molecules that comprise that comprise body and potential energy of molecules that comprise the body so this gives you the total internal energy of the system of the body.



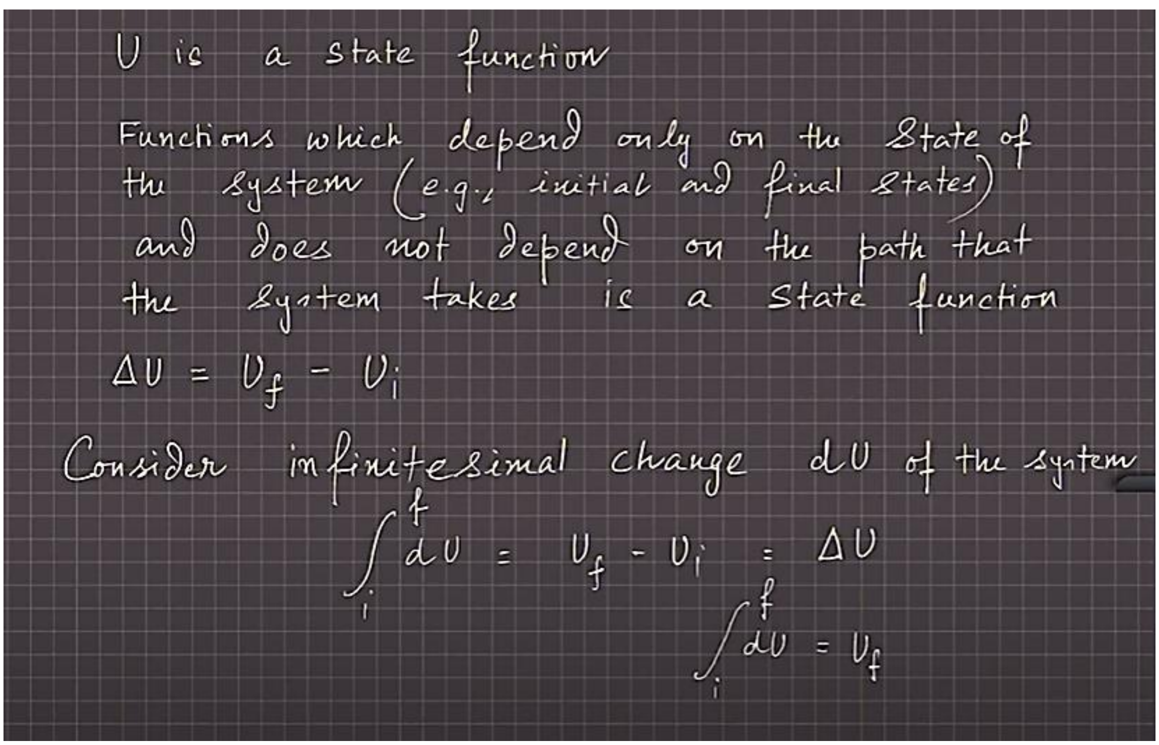
Now one very important thing that I have to tell you that this total internal energy which is a property of the body right which tells you the internal state or internal condition of the body is an extensive property that is its value it depends on the energy depends on the extent or size of the system for example let us consider this small system that we have with the volume V and internal energy U now I say increase the extent or size of the system by 2V right I increase it by 2 times the volume has increased then the internal energy also increases by a factor of 2 so it depends on the extent or size of the system so if I have say for example one system say let us call it system 1 and another system 2 and I have U_1 is the internal energy of system 1 and this is U_2 then basically I have if I combine these two systems and make a big system say call it system 3 which is 1 plus 2 there the internal energy will be U_1 plus U_2 similarly the total volume is an extensive property for example if system 1 has a volume of V_1 and system 2 has a volume of V_2 then the total volume when I combine these two systems is V_1 plus V_2 right so these are extensive thermodynamic properties and similarly if I think of like you have say I think of a unary system, unary system means a system containing one chemical species only, one chemical species it can be a compound, it can be an element, it can be gas, it can be solid, it can be liquid so one chemical species right so for example say water okay so here I have say n_1 so these are two systems each contain water and I have n_1 here I have n_1 moles of H_2O means water molecules and here I have n_2 moles of H_2O and I combine them together to form the system 3 and here the number of water molecules will be just additive right here for n_3 which is the number of water molecules of the system 3 it will be just n_1 plus right so the total internal energy, the total volume as a whole and mole number, mole number is the number of moles of a particular species these are all extensive quantities remember what is an intensive property?



Intensive property means it is opposite of extensive that means it does not depend on the extent of the system, it does not depend on the extent of the system for example $\overline{U}$ that we have used here this $\overline{U}$ is basically U by n n is basically the say for example n is the number of moles, n is the number of moles of a species and so basically I have a system let us consider a system whose internal energy was U and it contained n moles of species now if I tell $\overline{U}$, $\overline{U}$ is basically a specific internal energy specific internal energy means it is internal energy per mole of the species right so it has n moles of certain species of some species and what we are telling is $\overline{U}$ is U by n which is a specific internal energy or molar internal energy similarly I can basically give another example say for example I have some U_i has changed to U_f now what we are basically interested in is understanding this ΔU or change in internal energy when I go from one state which is say for example U_i is the initial state so this is the say the initial state and this is the final state so we are interested in the difference in energy when I go from say initial state to a final state so basically I have a reference state with respect to the reference state how much of the energy has changed if some thermodynamic processes have acted upon the system this is what we are interested right so in such now you see one very interesting thing I will write that U is a state function energy is a state function that is it depends only on the state of the system right so ΔU depends on the final state and the initial state right it does not depend on what type of path these processes have taken to go from U_i means I to F so basically you have



gone from initial which is basically I that you have gone to final which is F now whether your process went this way whether the process was like this or whether your process was just like that means whatever processes have happened like heat transfer has happened say some mechanical work has been done or mechanical work has been done by the system itself or it has been done on the system so the processes can take various paths for example it has taken various paths and it has finally reached like this type of a path it has finally reached in another case one process was there so it is like sum of three processes and in another case there was only one single process by which you have gone from U_i to here in another case you have gone through some other group say for example you have gone like this so you went like this and then you went like this irrespective of whatever processes whatever paths this process have taken the ΔU that is a change in internal energy depends only on the final state and the initial state so the internal energy in the final state minus the internal energy in the initial state basically gives me the change in internal energy therefore U is a state function so basically a process a thermodynamic process that involves heat and work transfer can change the system from I to F along several possible paths for example I will give some few possible paths here in this PV diagram so I have P in the y-axis or pressure in the y-axis and volume in the x-axis and let us assume that we are talking about internal energy of a gas and the rate of a system that contains a gas and I am telling that I am going from I to F across three different paths say for example the first path is from start with I, I go to A which is basically we are telling of see as you can see this is volume axis this is the volume axis and this is the pressure axis along volume axis if I go from I to A this means my volume is constant but my pressure is dropping from P_2 to P_1 right my pressure has dropped from P_2 to P_1 but my volume remains fixed so these processes where volume iso-volume means the volume is changed is called an isochoric process right it is a iso-volume process is called I think it is called as a isochoric process and then if I am telling wrong then you can find out what it is and let me know and then from A to F so I am going from I to A which is an iso-volume so I have maintained the volume to the same I have only there is a pressure drop right during this process there is a pressure drop from P_2 to P_1 and but the volume remains the same now you go from A to F where basically the volume has increased from V_1 to V_2 when you go from A to F but you have kept the pressure at P_1 so you have held the pressure at P_1 and the volume has expanded from V_1 to V_2 and you have now gone finally from I to A to F there is another process for example say you go from I to B okay where basically the volume has increased from V_1 to V_2 and this again isobaric process because the pressure is maintained at P_2 and from B you have gone to F again this iso-volume or isochoric process where there is pressure drop from P_2 to P_1 so this is another possible path that we can think of there are infinite number of possible paths but I am just talking about some three possible paths so basically I think of another possible path which is slightly curved path where basically along this curved path we are maintaining so along the curved path that is I to E to F or I to E to F we are maintaining that pressure at the product of pressure and volume so along I to E to F we are maintaining for example that P times P equal to constant now if I assume the gas to be ideal so PV as you know equals to nRT and I am telling n is constant say R is universal gas constant and I am telling the temperature is constant then PV is constant basically denotes an isothermal process so IF is an isothermal process by which you have gone from I to F now you see there are three processes or three possible paths by means that I have shown here there may be more possible paths like you can have an adiabatic process you can have many many different processes or different pathways through which you can go from like go from the state I to state F however the delta U does not depend on whatever paths or whatever process whatever was what was the sequence of processes or whatever path has been taken it depends on U_f and U_i so basically it depends on the value of U here and the value of U here that is all so it depends on that and if it knows U_f and U_i it just takes U_f minus U_i and it gives you delta so it does not depend on the path taken it does not depend on the path so we can call that U as a result is a state function right it depends only on the state of the system it only depends on the internal state of the system it does not really depend on that for example it depends on the initial and internal states but it does not depend on the path that the system takes and therefore it is called a state function so delta U equals to U_f minus U_i.



Now as I told ΔU equal to U_f minus U_i which is basically like a macroscopic change in energy we can also think of an infinitesimal change for example there is an infinitesimal change du right here we have written there is an infinitesimal change du and now I am integrating du from the initial state to the final state what I get is U_f minus U_i.