Thermodynamics And Kinetics of Materials

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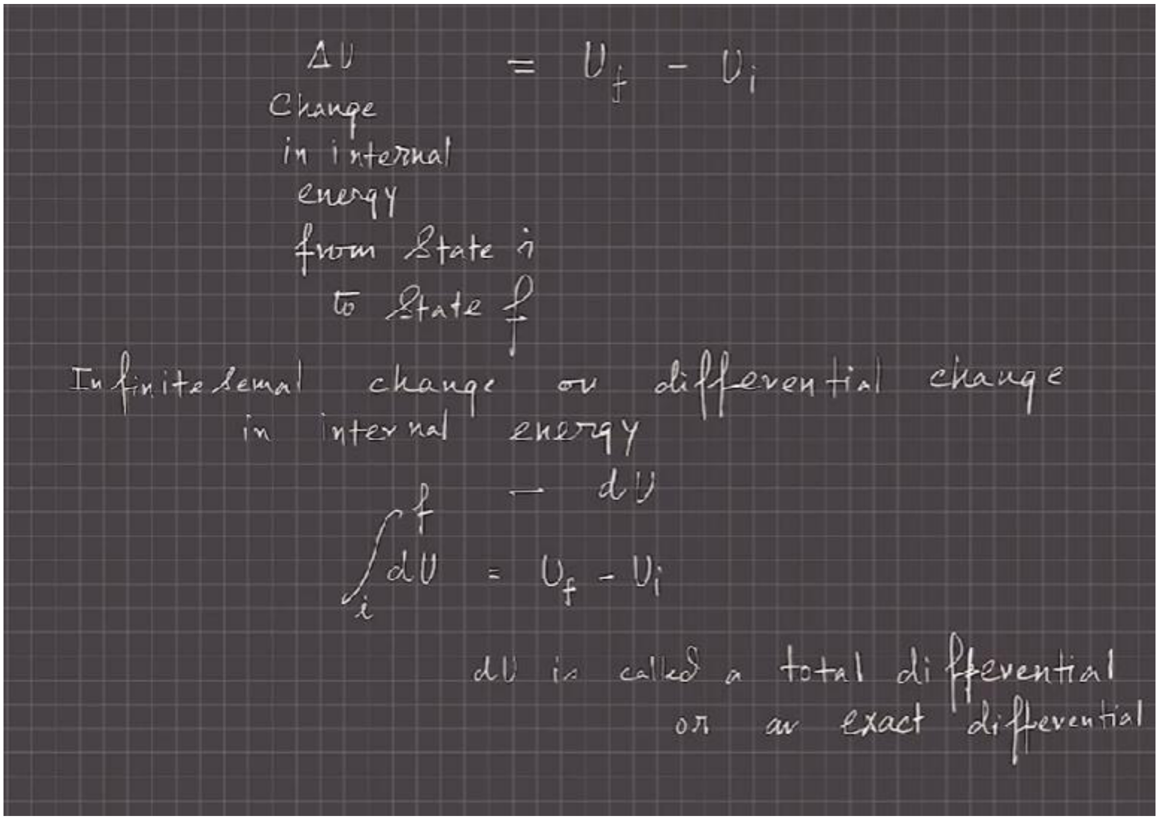
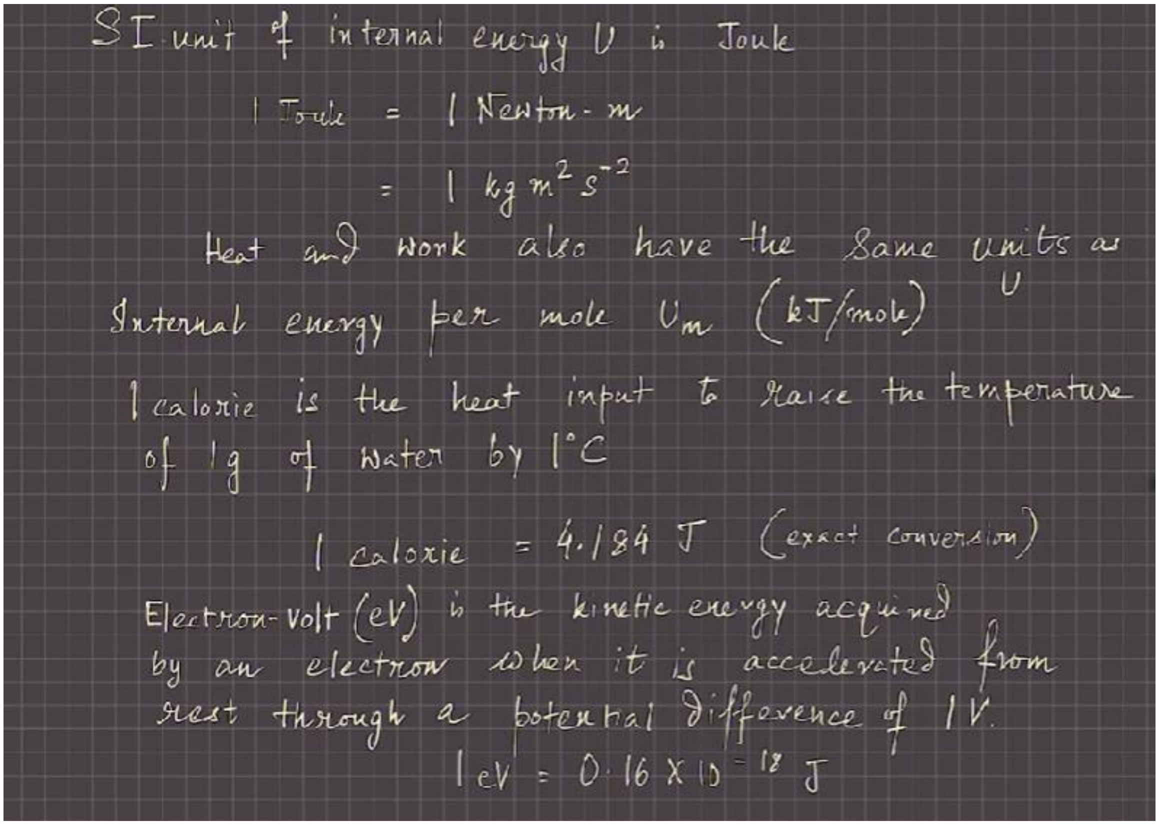
Lecture 2
Energy, Heat and Work - I - Part 1

Now, as you understood now, the Δ that U is a state function right, we discussed that with the state function and we tell that ΔU that is a change in internal energy depends only on the final and initial states U_f minus U_i. Now, I can think of an infinite similar change right, an infinite similar change in the internal energy or we can call it like a differential change in internal energy which is denoted by dU. Now, if dU is a, dU is a differential change then if I tell, if I integrate dU so the total differential and if I integrate dU from states U_i to U_f basically the integration will basically give me Uf minus dU right. Now, this dU is called total differential or an exact function, this is a very important so the state function property is very important from Mx because it gives you, so since U is a state function you can write it as a total differential or an exact differential and these exact differential properties exploited at various times and used at various times and this becomes very very important in quantum graphs right. So, it becomes very important to understand or it is a very useful tool which if you have a state function you can express it as a total differential and you can using this total differential or exact differential properties you can derive many useful relations that you will see later right. So, another thing that I wanted to tell you that you have to be very careful in thermodynamics about units right for example, in general we will use throughout this course SI units.

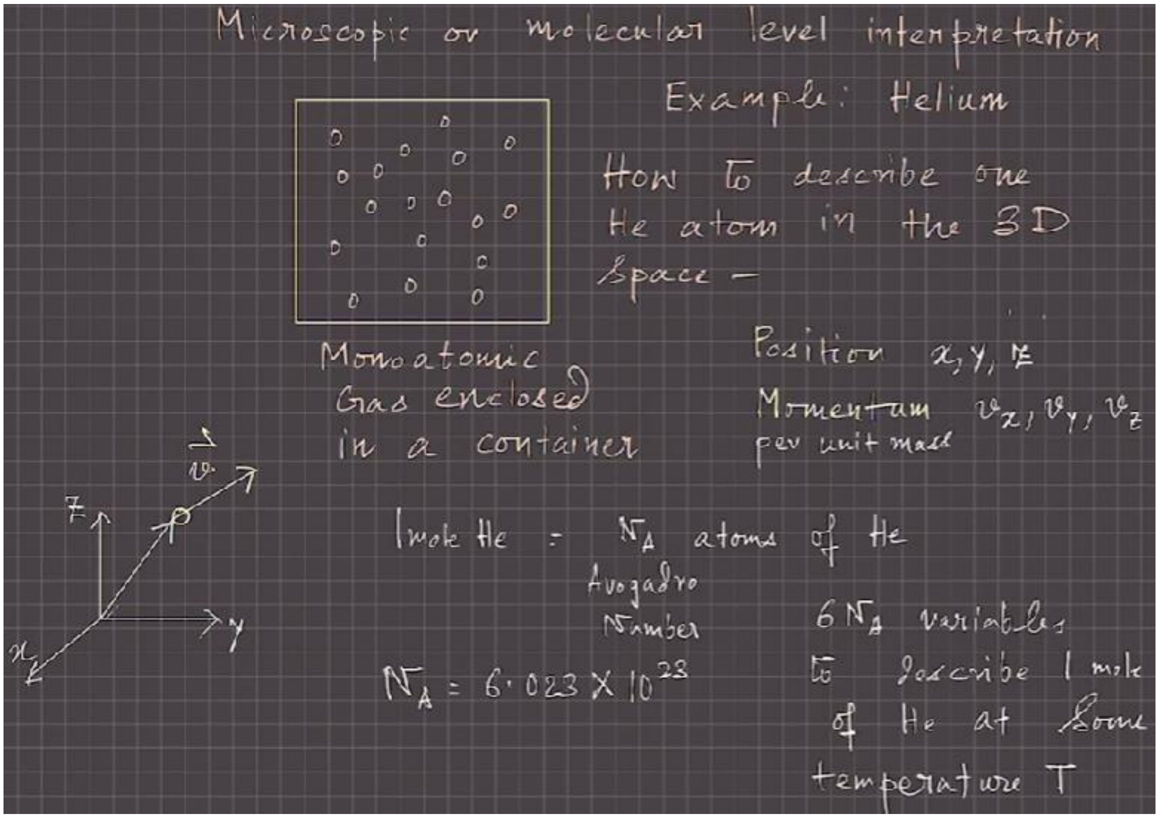


So, SI units are like Joules say for example, internal energy SI unit of internal energy is Joule and Joule as you know one Joule is basically equal to one Newton meter right Joule is the unit of energy Joule is the unit of work, work is like force times displacement and force as a unit of Newton and you have like and for length for distance the unit is meter. So, one Newton meter is one Joule and one Newton is nothing but one Kg meter square per second square right because it comes from Newton's law force equal to mass into an acceleration right and then heat and work right have the same unit as energy have the same units as energy and what is the unit Joule right. So, heat the unit of heat is Joule we will take the unit of work as Joule. So, basically all of these units we have to be very consistent and we are using SI units, but many a times same problems sometimes people use this British units and sometimes they use this CGS units so called CGS units.



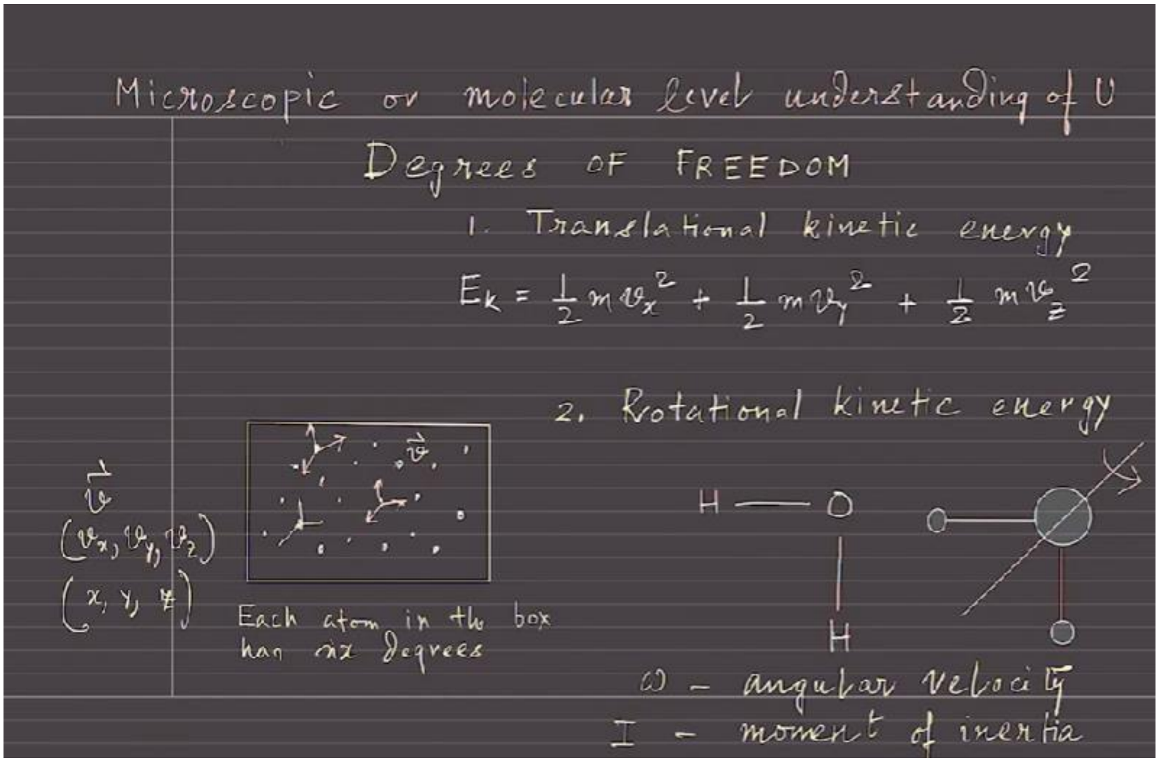
For example, calories still are very popular unit for heat input right and one calorie is defined as a heat input to raise the temperature of one gram of water by one degree Celsius right. So, it is one calorie is the heat input to raise the temperature of one gram of water by one degree Celsius and one calorie is nothing but 4.184 Joules right it is an exact conversion. You can think how is it derived you think about it a little bit that it is one gram of water one degree Celsius you want to raise it by one degree Celsius and get and what you define is one calorie and you will see later why this is an exact conversion or you can yourself also work it out. Now electron volt is another very popular unit of energy and electron volt is basically when you express it some we generally express energy per Kg or energy per mole, but if we want to express energy per atom then electron volt is the unit of choice and electron volt is the kinetic energy acquired when electron heat is accelerated from west to a potential difference of one volt.

As you can see one electron volt is basically energy per atom. So, you see one electron volt and what is the relation between electron volt and Joule you can definitely you can understand that there is some where Avogadro number coming in because one electron volt equals to 0.16 and comes in as 18 Joules right. So, it is the energy acquired or kinetic energy acquired when electron is accelerated from rest through a potential difference of one volt right and if the relation between electron volt and Joules is this that is like 10.16 and comes in as 18 Joules or 1.16 and comes in as 18 Joules right and we also have discussed this molecular interpretation of internal energy, but one very interesting thing that we have discussed is if I have this microscopic or molecular level interpretation or understanding of internal energy then is it possible to use some or find some average energy and find U in terms of that average energy and this average energy is basically coming from statistical mechanics ok. So, it comes from statistical theory of matter and means where we are describing matter in terms of particles. Remember in thermodynamics that is a very interesting thing in thermodynamics macroscopic thermodynamics we use we use properties like pressure, volume, temperature say for example, volume we think of one liter of water we do not tell that one liter of water contains how many molecules of water and how are each molecule behaving of water behaving and stuff right that is not impossible to describe, but we just tell one liter of water and immediately we will understand what I am asking for right it is all a macroscopic description of matter not really molecular description because if it is a molecular description as you know say for example, I have this one mole of helium atoms enclosed in a container ok and this is a three dimensional container so it has a volume and we have one mole of helium atoms one mole means Avogadro number of helium atoms right and this is a mono-atomic helium is a mono-atomic gas and it is enclosed at you can liquefy helium, but we are assuming that it is in a gaseous state currently we are considering it in a gaseous state and you can liquefy helium at a very low temperature, but here we are looking at it as a at a room temperature and we are telling that this mono-atomic gas is enclosed in this container which has some volume right. Now if I have to describe each atom in this mono-atomic gas then basically I have to know the position of each atom and the momentum of each atom in this three dimensional container. Now if I want to know the position as you know from three dimensional coordinate geometry you require to basically specify three coordinates right x you have to tell you have to specify x for each molecule you have to tell or each atom you have to tell x, y and Z.

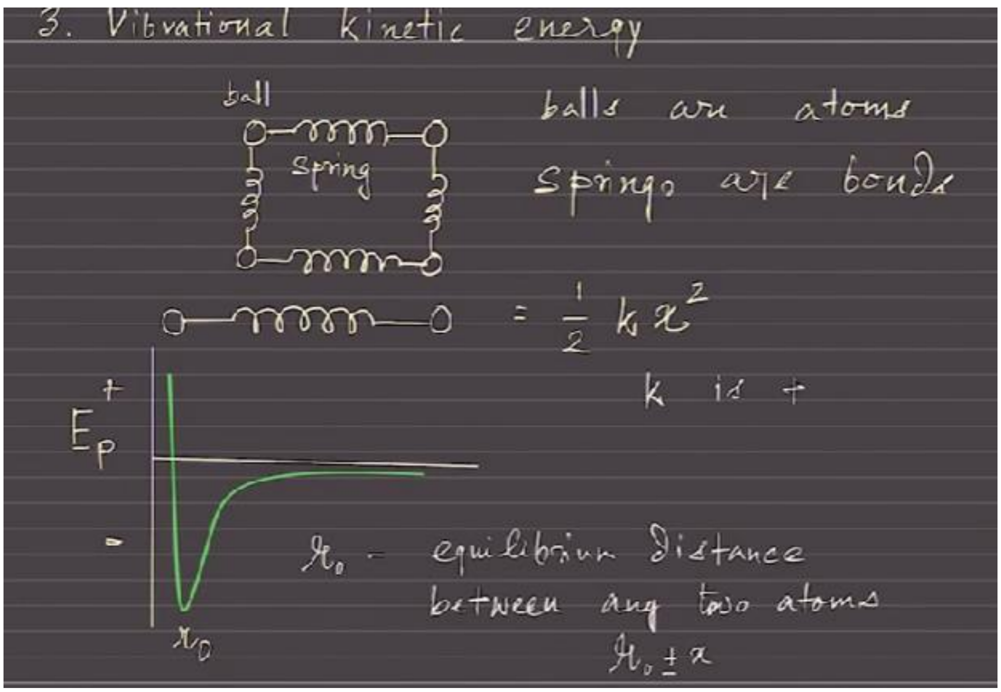


Now if I tell momentum let us assume that all helium atoms are the means that is a fair assumption that all helium atoms have the same mass right and we are telling that if it has the same mass m then I have to specify the momentum, so momentum basically or if I tell momentum per unit mass, momentum per unit mass is let us call it momentum per unit mass which is basically the velocity. So we have the position which is x y z the three coordinates and you have momentum per unit mass which is like 3x, 3y and 3z. So if you have one mole or N_A which is Avogadro number one mole of He which is equal to N_A atoms of helium, so this is the momentum per unit mass where N_A equals to 6.023, as an approximation I am telling 6.023 then but 3 there may be some more values in the you can go to 4 or a fifth or sixth decimal places you will have some numbers, so I am just using up to 3 decimal places 6.023 and then but 3. Now you have these many number of atoms of helium in this box let us assume now in this box for each of these atoms I have to define these three positions, type three position of coordinates and the three components of velocity like 3x, 3y and 3z. So basically I require or it requires basically if I want to describe it at the molecular or microscopic level or the atomic level basically we have to describe 6 N_A positions of the 6 N_A positions, so basically like 6 N_A variables right, so you have 6 N_A variables to describe or required to describe one mole of helium at some temperature, so this is the number of variables temperature right, you require 6 N_A variables which is like a very huge number of variables on the other hand if I just tell one mole of helium that chamber contains one mole of helium it adds some temperature

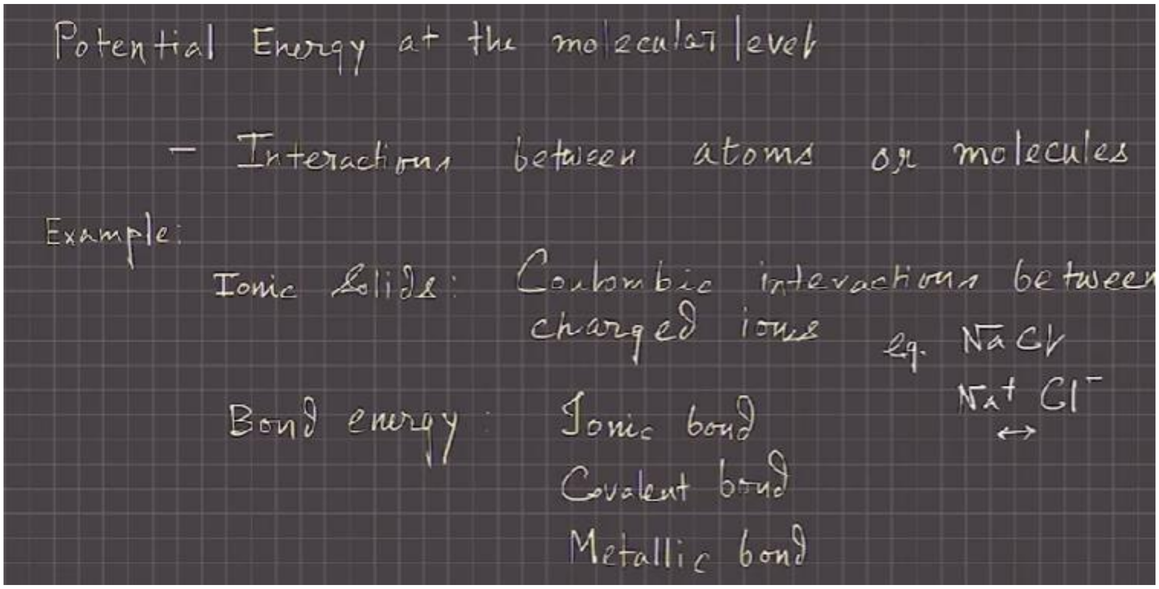
T I specify the temperature I tell the mole number right how many moles of helium are there is inside I can also specify the dimensions of the



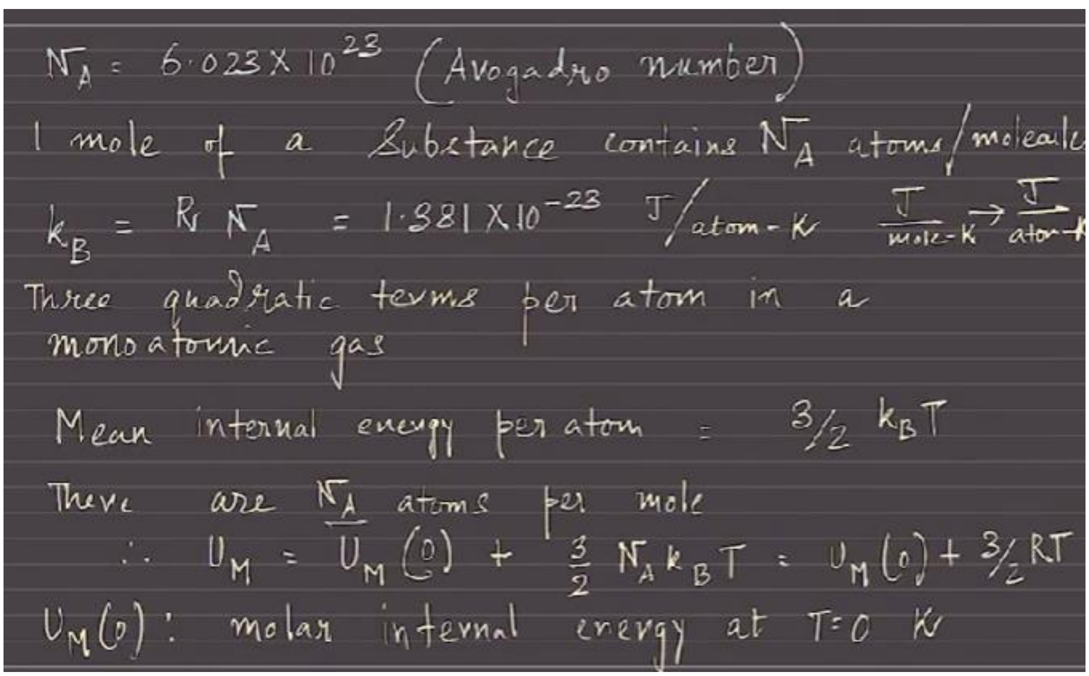
container once I have done that that is good enough means I do not really require this molecular level description of helium like if I require such it is impossible to describe because it is like you require to know the instantaneous position and velocity of 6.023 into 10 to the power 23 atoms which is impossible right, so that is a problem but this basically gives you one very interesting idea so if you see these atoms are basically moving around right and it has something called translational kinetic energy so for each atom I can tell of mass m the translational kinetic energy is nothing but half m moles of helium V_x square plus half m see the V_x, V_y, V_z can be different for each atom right but basically you have like V_x for all these N_A atoms, V_y for all these N_A atoms and V_z some values of V_x, V_y, V_z so basically if I know that then I can write these are my this is my translational kinetic energy right so basically what I am trying to say is that each of these atoms will have this different degrees of freedom like 6 degrees of freedom if I tell that it can be like more degrees of freedom even so if I think of like translational kinetic energy or but for example if I take a here we are talking of monoatom but if I think of diatomic molecules like hydrogen or if I think of water molecule right water molecule contains H right and 2H and 1O right so 2H and 1O and if I tell that see there are so it can basically rotate right it can basically rotate then on an average I can tell that about some axis and I know the moment of inertia so I then it will be like we are adding another term it is the rotational kinetic energy which is half I omega square where omega is the angular velocity right so you have half I omega square so this is called the rotational kinetic energy now another thing if you have if you assume these atoms are interacting and then you can think of these atoms are like balls you can assume these atoms as balls and they can act like springs and say for example as you can see here this is a plot of a potential energy and we are telling that at a given temperature R_0 is the equilibrium right R_0 is the equilibrium distance between two atoms so R_0 is the equilibrium at a given temperature distance between any two atoms and this is the difference between two atoms means equilibrium intermolecular distance or inter atomic distance but see at a given temperature at some temperature there will be always atoms they will always be displacing from their equilibrium position slightly displacing from equilibrium position say for example they are displaced by say R_0 plus x or R_0 minus x now that is so and spring and you know that this is spring and these are like two balls and if you look at the restoring force for example and you are thinking of now simple harmonic motion right so about the mean position so about the mean position you are displaced by an amount x so you have half k x square where k is the spring constant



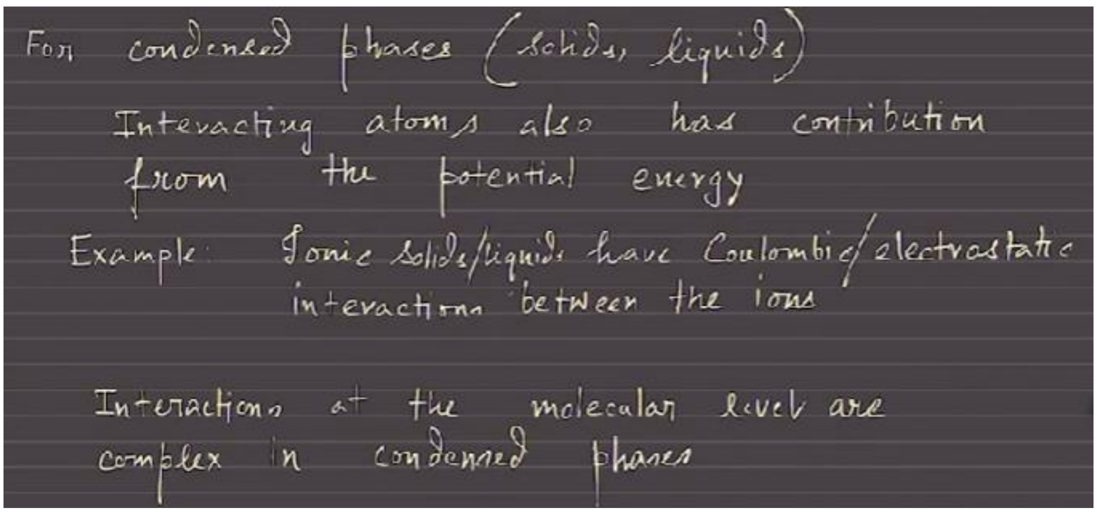
and it is related to the bond that forms between these atoms like the spring represents a bond between the atoms so k is related to the bond energy so k is the spring constant so if you can see then there is a vibrational kinetic energy so all these things basically constitute the degrees of freedom at the microscopic level now at the microscopic level from the classical mechanical point of view so again you have also potential energy at the molecular level right if you have an ideal gas then the potential energy is not there because there is no interaction between the gas molecules but if you think of a real gas or if you think of a condense matter that means condensed phases like solids or liquids then you are having interactions between atoms and molecules which give rise to different types of bonds right ionic bonds covalent bonds and metallic bonds and say for example ionic solids you have say like sodium chloride you have sodium ion and chloride ion one is positive and another is negative and there is a coulombic interaction right and electrostatic interaction between these ions right so if you think of example one example is like k NaCl so you have like Na plus ion and Na plus ions and Cl minus ions and then there is a electrostatic interaction or coulombic interaction again bond energy so there are different types of bonds that can form like ionic bonds between ionic solids then



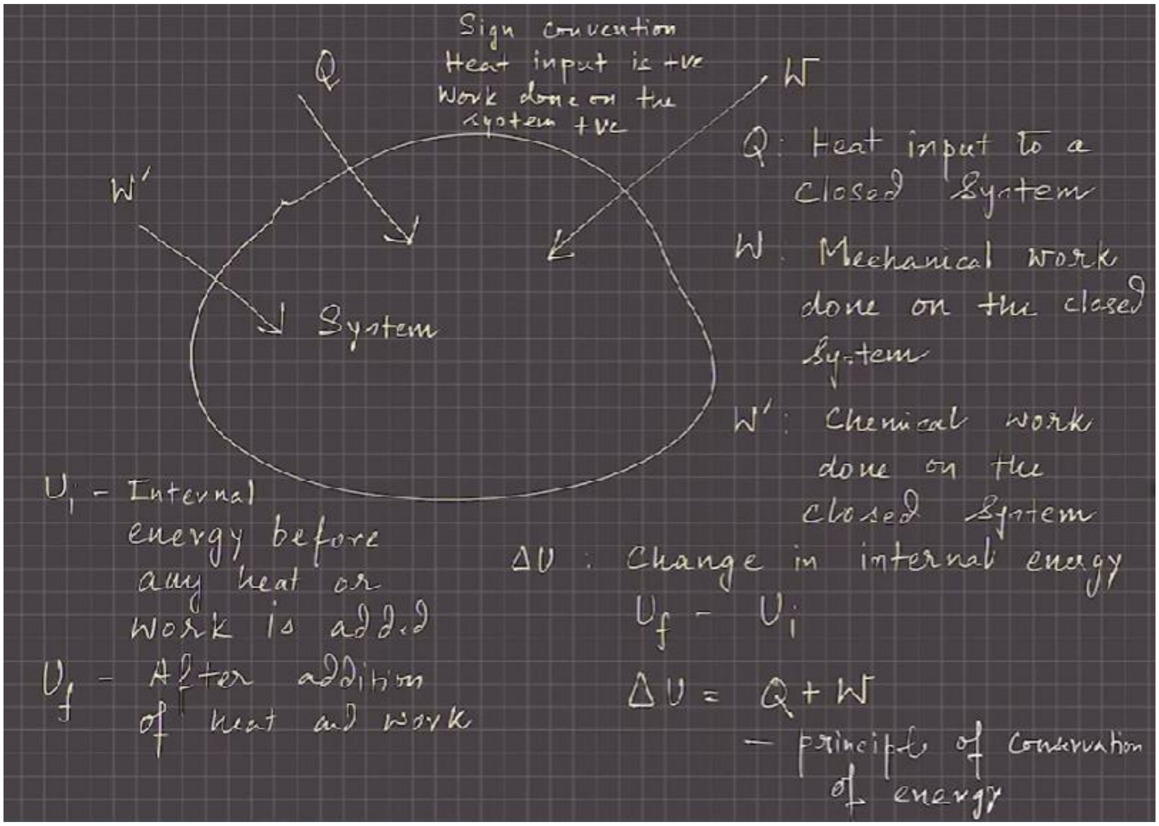
there can be covalent bonds like where you have all these different types of hydration and say for example bonds between carbon and carbon and hydrogen and carbon so or polymers and then basically you have metallic bonds like in aluminum say for example in aluminum all electrons are delocalized so basically atoms are the ion the atom cores are embedded in a sea of electrons right these electrons are delocalized so you form some fundamental bond so in each of these bonds that form again I am not discussing this, this will be discussed in some courses on physics of solids ok the details of it will be discussed but I am telling that this will give rise to this bond energy and this bond energy again can have you know it can be a very complex polynomial you can represent it with a very complex polynomial or some function now all of these are happening at a microscopic level but if all of these are happening at a microscopic level for example for a monoatomic gas I can tell you that if we apply an equipartition theorem which is coming from classical mechanics what it states is that if you have an assembly of particles that are equilibrium at a temperature T that means that they are equilibrium at a temperature T means the mean temperature for this assembly of particles is T right the temperature is T is held at a fixed temperature T everywhere the temperature is same the average then in such a case the average or mean value right the average or mean value of each particle is equal to each quadratic contribution now quadratic contribution to energy is something like I omega half I omega square or half mv square this is like a quadratic contribution so each quadratic contribution right it can be from this different types of kinetic energies and also it can be from potential energies right because if there is interaction between the atoms or molecules now all of this so for example if I take a monoatomic gas ideal gas and we are talking about monoatomic so you are not considering any rotational kinetic energy and there is no interactions and there can be some vibration of kinetic energy but assume that it is mostly translation of kinetic energy then because yeah you cannot have vibration of kinetic energy because you know there is no bond formation or no interaction so as a result you have only the translation of kinetic energy and translation of kinetic energy means there are three degrees of radians right v_x, v_y and v_z so each of these right each of these quadratic contributions the average or mean value of each of these quadratic contributions for all these atoms is the same and is equal to half k_B right where k_B is the Boltzmann constant and Boltzmann constant is nothing but universal gas constant gas constant it is R sorry for the mispronunciation so the universal gas constant R is equal to N_A . N_A is the Avogadro number which is basically JB and k_B is Boltzmann constant so it is as you can see N_A is the number of atoms so k_B is 1.38 into 1.3 Joules per Kelvin and it is also basically power atom right



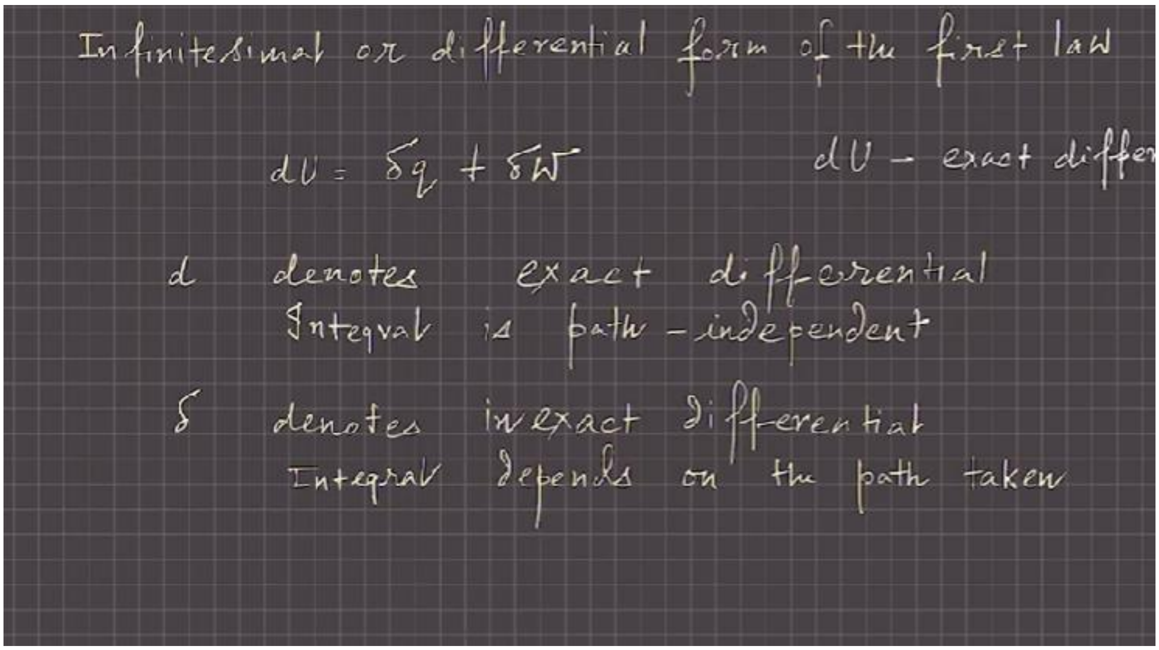
for example R is Joules per mole Kelvin and this is like k_B is Joules per atom right so you have k_B which is Joules per atom right now you have three quadratic terms per atom in a mono atomic gas and so if you add them then you see the mean internal energy per atom for this mono atomic ideal gas is 3 by 2 k_B right and then if you have total one mole of atoms which is like the Avogadro number of atoms right this Avogadro number of atoms per mole then we can write U_M which is like the molar internal energy is equal to $U_M(0)$ so this is $U_M(0)$ is the molar internal energy per mole so this is like we have T equal to 0 Kelvin plus 3 by 2 and 3 by 2 k_B T is per atom right so 3 by 2 into N_A into k_B and N_A into k_B is nothing but R, R is the universal gas constant and so you get $U_M(0)$ plus 3 by 2 R right so that is your internal energy of a mono atomic ideal gas which has 3 degrees of freedom because there is no interaction between the atoms so you have 3 degrees of freedom because of the translation of kinetic energy right if you think of a molecule say for example of atom in molecule which has also this rotational energy then you add another half k_B T now if you also consider vibrational kinetic energy you can add half k_B square so it can become like 5 by 2 k_B T in some cases it can come like if you also consider quadratic terms that come in the potential energy can be like 3 k_B T or some k_B T right so basically per atom the mean value right and it comes from equimetric equi-partition theorem of specific mechanics right.



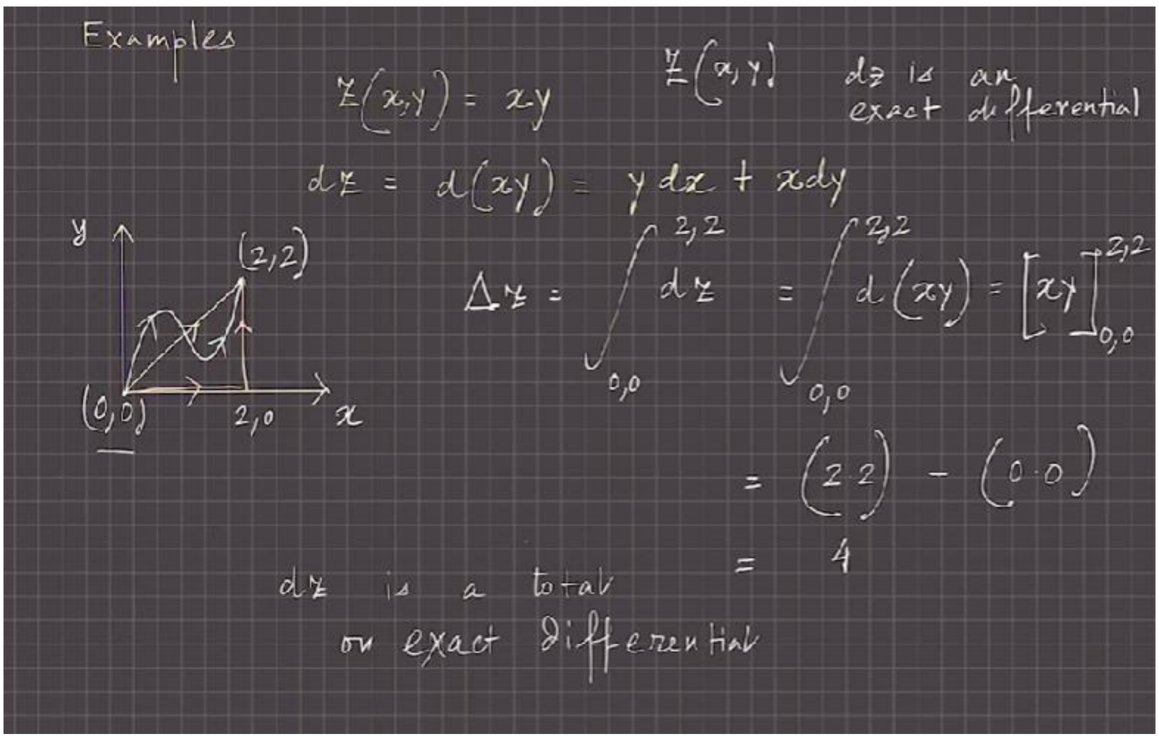
Now note that for condense phases whether it is solid or liquid the interacting atoms the potential energy of the interacting atoms always have a contribution and for example in ionic solids is like coulombic interactions between the ions and then there is metallic bonding in metals and but one thing to remember it is not very easy say for example there are some simple potentials that can describe interacting atoms in real gases however interactions at the molecular level become very very complex when you consider condensed phases this is something that you should always take a note of ok so that is the idea so again I go back to the first law because I want to use this definition of internal energy and I want to incorporate it into the principle of conservation of energy right so what it tells is that energy can either be created or destroyed right there are various forms or various restatements that we can use of the internal energy right so energy can either be created or be destroyed but can be transported or converted from one to another and the total energy of the universe is constant so there are many ways of restating the same right this principle of conservation of energy right and if we know that then there is something very interesting that can be written we all know but I want to write the differential form and I want to tell because I have already defined something called an exact or total differential I have told that if you have this total differential or exact differential you can integrate between initial and final states right without thinking of the path right I have not defined exact differentials



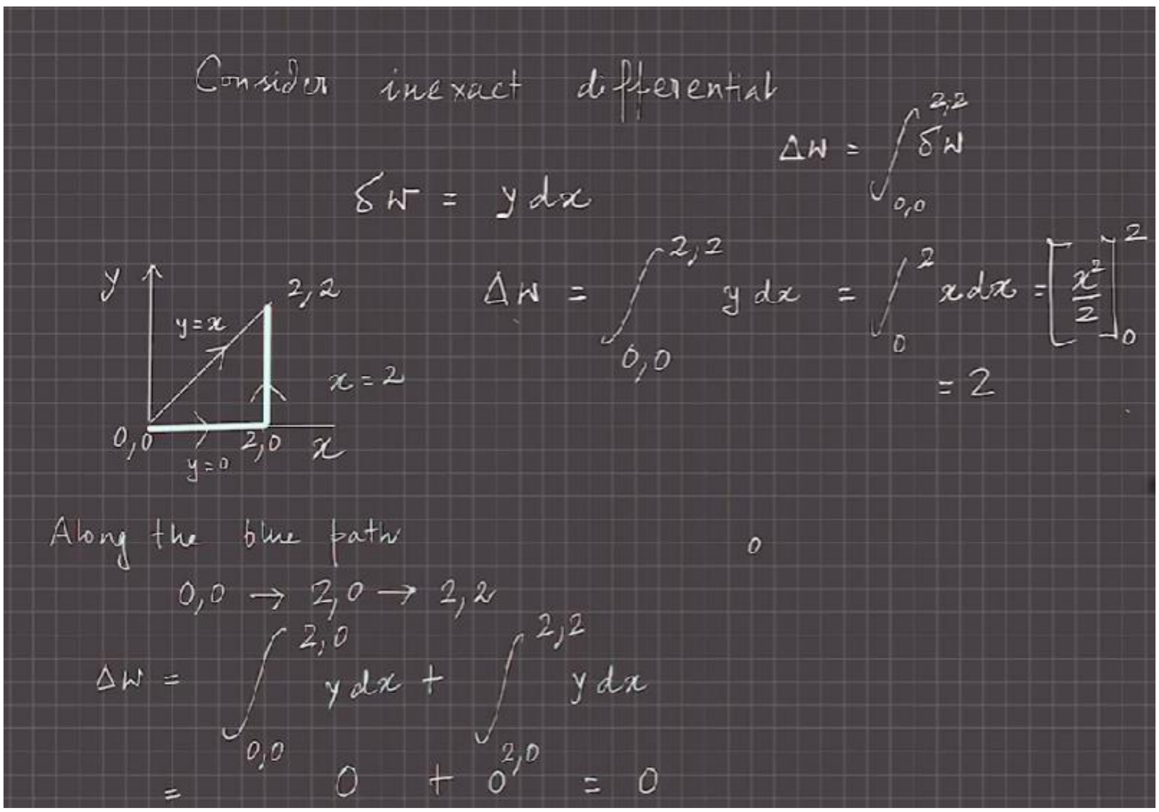
I will come to that and I will also give an example of what is the difference between exact and exact differential because exact differential depends on the path but before all of these I have to first restate first law of thermodynamics in a simple mathematical form so remember in these cases so basically there are various books like I have mentioned at the beginning of the course say for example the book by Richard Swalin that you can use as a textbook and the book by Gaskell and then Robert D. Hogg's book and there are various other books that are there and each of these books use different sign conventions when it comes to stating the first law right so sometimes we use a convention we use different conventions so sometimes you will see I will come to that so here what convention we are using is very simple so as we know now the molecular interpretation of internal energy so we will be very we will try to be as consistent as possible and what we are telling is if there is a heat input to a system then basically you are adding to the internal energy of the system right you are increasing the internal energy of the system so as a result heat input to a system is positive similarly if I am doing some mechanical work on the system again you are basically this mechanical work is tending to increase the internal energy of the system as you can understand because you are bringing the molecules closer there may be more interactions by forcing the atoms nearer you can increase the interactions or you can basically add to the internal energy right increase the internal energy so in both cases heat input as well as work done on the system we are taking means wherever internal energy is bound to increase of the system bound to increase say for example if I am doing work on the system or compressing the system for example or I am adding heat to the system I am exciting the molecules to the system I am adding to the internal energy so in such cases we are telling that all of these



are positive so heat input to the system is positive work done on the system is positive while work done by the system against the external pressure is negative according to us and heat projected by the system to the surroundings is going to be negative right so basically Q is the heat input so if we have Q as the heat input to the closed system and we have W which is the mechanical work done on the closed system now one very interesting thing that we will mention soon that there are different types of systems like this is closed and you have isolated so there are various categories of system are open so we will define it shortly but first let us restate first law in a simple map form so you have Q that is entering and we are assuming heat input to the system is positive work done on the system is positive work done can be mechanical work it can be chemical work or some other form of work and then with all of these things that come in what happens is your system was in an initial internal energy of U_i it has changed to U_f and as I told you that internal energy before is U_i means at a reference configuration is U_i and after addition of heat and work it has become say for example U_f then the change in internal energy is what matters the most and change is Δ U and ΔU is nothing but Q plus W according to and it is a closed system so Δ equal to Q plus W is the principle is according to the principle of conservation of elements or according to first law. Now if the system say for example the system is moving and the system has some position or some special position in a potential field I can also add all of those so we can think of like Q plus ΔU equals to Q plus W and Δ U is like change in internal energy but we can think of also adding change in potential energy change in magnetic energy and stuff but we are basically considering a closed system where ΔU which is a change in internal energy is equated to Q that is the heat input to the system and W and both of them we have assumed to be positive but it is not really matter so that is what I was just about to say whatever side convention you use if you are consistent does not really matter the relations do not change right. So the infinite similar differential form is where it becomes interesting now as you can see dU I defined as an exact so dU so dU when I am using dU so I am telling that this is the total differential dU is the exact differential.

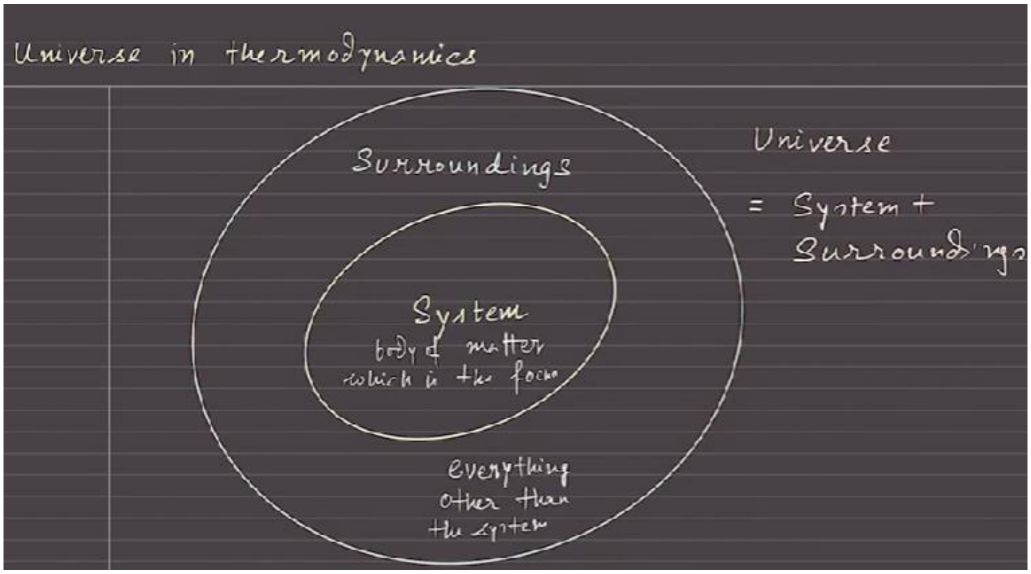


However heat input or heat transfer or work done generally basically these are basically path dependent functions like work done or heat input these are all path dependent functions so as a result δQ and δw we are using δ see we are not using d but we are using δ this denotes in exact differential where the integral depends on the path dependent see in this case the integral is path independent right we could just integrate like this dU I to f and that was like U_f minus U_f right but here you cannot it depends on the path taken right we will give an example of that. For example if I tell that there is a function z of z of x and y such that P_z is an exact differential that means integration of dz does not care about the path that is being taken right and let us assume that z xy is nothing but x times y and we have this is y axis and this is the x axis and I am plotting say I have the value of x and y to be 0, 0 and I have gone to something like 2, 2 right 0, 0 to 2, 2 and the value of z xy is x times y right. Now I have taken different paths right I have taken different paths to go from 0, 0 right this 0, 0 coordinate is the origin in 2, 0 say for example I have taken a path like I go from 0, 0 to 2, 0 then from 2, 0 I go to 2, 0 here I have taken a path like this like a path right it is almost look like a sine wave type of a path again I have taken another path which is just like directly going from 0, 0 to 2. So, 3 paths I have to be limited one is this one, one is this one and the other one is this and the other one is this right all these 3 paths are there but what I told the initial point was 0, 0 and here is 2, 2 and we are telling dz so dz basically is dxy right so dz because z xy cross to xy so dxy, dxy means y dx plus x dy. Now I want to know so if I know dz I want to integrate dz right I want to find Δ z that is change in z this is the Δ z, Δ z is nothing but integral of z from 0, 0 that is the initial step to the final step which is 2, 0.

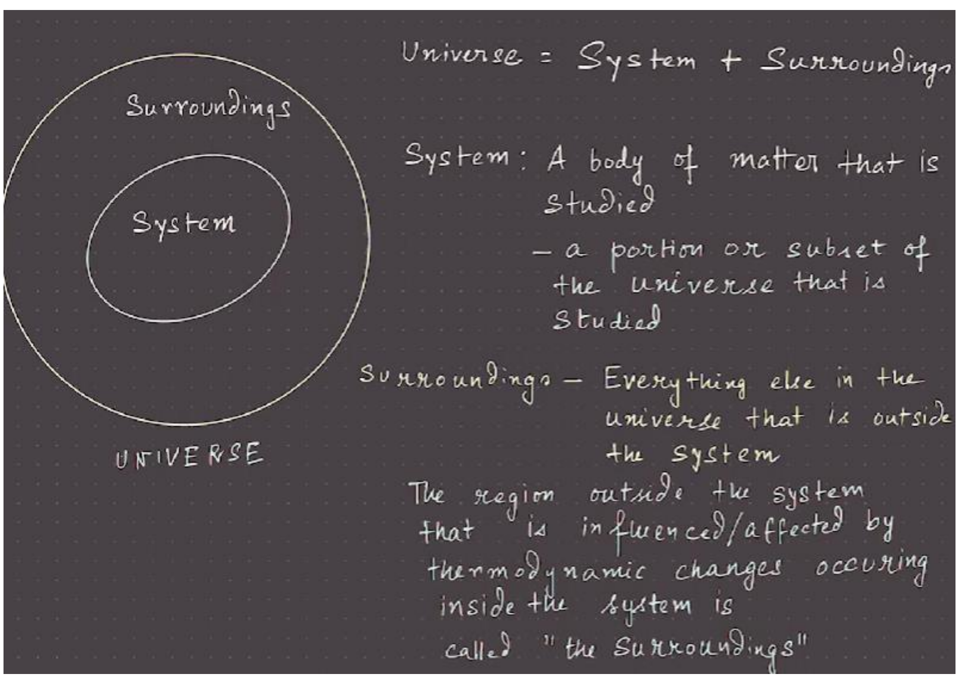


Now you see z is nothing but xy so I can write dxy which is coming from 0, 0 to 2, 0 and that means I am just using xy I am putting the limits and the limits are basically the initial position and the final position 0, 0 and 2, 2 and this becomes 2 times 2 minus 0 times 0 which is equal to 4 so dz is the total or exact position. So you can see that whatever path has been taken when I did the integral of dz I just looked at the initial position and the final position I did not look at whatever path was taken to achieve this final position from z starting from 0, 0 right and I so whatever be the position taken as you can see Δ z just depends on the initial and final steps and we thought I will separate both. Now look at an inexact differential let us assume that we have an inexact differential which is given by δw cross to y dx so again you have this coordinate system y versus x and now δw I have given as y dx now you see I am asked two paths one path is like when going from here to here directly along the diagonal and another path is like I put 0, 0 to 2, 0 and from 2, 0 I go to 2. Now if you see when I go from 0, 0 to 2, 0 my equation is y equal to 0 and when I am going from 2, 0 to 2, 2 my equation is x equal to 0. Now so this is the blue path and this is the say for example the yellow or diagonal path so this δw is the first path which is along this path if I have to find out δw the δw is the amount of work done or means it can be like δw is nothing but the integral of δw is nothing but integral of δw and there I am again giving some these are my initial and these are my final products.

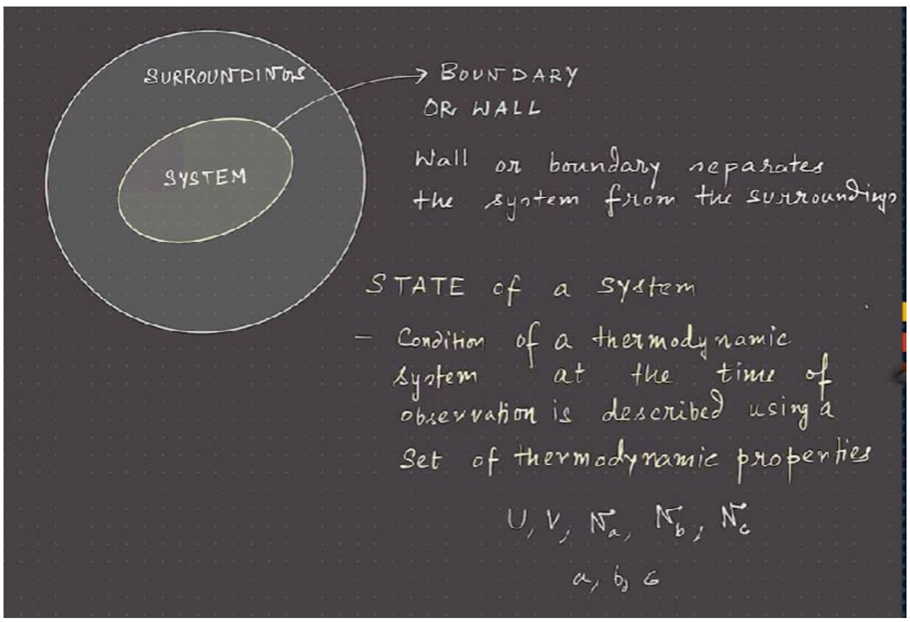
Now this is what I have written δw is y dx so I will write y dx and it is going from 0, 0 to 2, 2 now y is nothing but in the first case when I am going along a diagonal the equation is y equal to x right so instead of y I have to x and this becomes x dx and now the x values are 0 and 2 so I just get 0 and 2 and x dx is x square by 2 and 2, 2 and 0 to 2 we took the limits and I get a value of right. Now let us look at the blue path so I go from 0, 0 to 2, 0 from 2, 0 I go to 2, 2 and now I am looking at finding δw which is again integral of this small δw right this is the upper case and this is the lower case δ right so you have this triangular Δ and then you have this δ here this is the small δ so if I have that now I am integrating along the path right so I go from 0, 0 to 2, 0 now 0, 0 to 2, 0 what is the equation y equal to 0 and I put y equal to 0 here so this integral this value is 0. Now I go from 2, 0 to 2, 2 now in this case the equation is x equal to 2 whatever be the value y x equal to 2 so if x equal to 2 that means dx is constant so right if x equal to 2 then dx is constant right and so this value also goes to 0 right so you have 0 plus 0 is 0 so in one case you got a value of 2 when you are travelling along the diagonal in the other case when you took another path we get a value of 0 right so basically this is an inexact difference this is an example of an inexact differential where the integral of this inexact differential depends on the path taken right so that is the idea.



Now as I have told before that there is this universe and this universe is basically the system that is the system that we are focusing on that body of matter the system is this body of matter which we have which is the focus of our step and this is everything else everything else means everything other than the system. Now I could have made it as big as possible but I have kept it small enough so that what I am telling is this is my system this everything other than the system that is influenced by the changes in the system if the system is changing because of some process then what is the region of influence and that region of influence the surrounding and together.



it forms the universe this is something that we are clear and we also talked about there is a boundary in the system in the surrounding which you can call wall or wall and this boundaries property determines how heat transfer will take place from system surrounding or how what transfer will take place various works where transfer will take place from system surroundings right whether it is a chemical work whether it is a mechanical work how will it take place is based on the property of the wall that separates the system from the surroundings right so this we already know that the region outside the system that is influenced or affected by the surrounding changes of the inside the system is called the wall right and this boundary or wall so that is the I told you that is one of the most important things to consider because this wall and boundary basically will give you the physics of the process right it separates the system from the surroundings and what is state of a system we know it is the condition of the thermodynamic system at the time of observation which is described using a set of



thermodynamic properties right the state of a system can be given by a set of thermodynamic properties for example I can give the state of a system in terms of U which is the energy then V which is the volume and mole number of different species like A, B, C these are basically A, B, C are the components right A, B, C are the components that are doing the system so all of these thermodynamic properties basically describe the condition of a thermodynamic system at the time of observation.