

hello my name is dibakar dhara i belong to chemistry department of iit kharagpur and i will be teaching you the unit on thermodynamics

so if in this lecture in a probably in the first two lecture first two hours of this unit we will talk about an essential concept and definitions and then heat will talk about introduce the concept of heat work energy and internal energy and then we will talk about first law of thermodynamics and then we will go in the calculation of work heat and different processes for an ideal gas and we will talk about enthalpy and heat capacity and we will then talk about determination of experimental determination of ΔU and ΔH

we will come to those terms in a minute so this is just a basic outline of the first two lectures and obviously we will move to other lectures ah i will show you the content of the other lectures when it time comes now let us begin with some pictures you know you know this is now its a winter time here and you can see people are trying to get some heat just burning some leaves here

so it what is happening here is the chemical energy stored in this leaves the basically reacting with oxygen and getting burned and in that process it is producing some heat and of course some light also will be there

so in this case the chemical energy is convert getting converted into heat energy and light energy in this picture you see cars are running and most of the cars still run on fuel petroleum or diesel and what happen in this case the petroleum petrol or diesel get burned in the engine and as a result you this mechanical energy the car starts running

so this is the example where chemical energy is getting converted into mechanical energy now of course you can argue that there are cars nowadays which run some battery

so this is just a picture of one battery and

so what happens battery waiting basically because the chemical reactions in the battery electrons are pumped in this outside circuit

so as a result you get electricity

so in this case you get your basically getting electrical energy from chemical energy if it is a rechargeable rechargeable battery then you can

charge it again by applying electrical energy from outside and getting back the chemical reaction

so basically while charging you are converting electrical energy to chemical energy and while

discharging you are ah basically converting the chemical energy into

electrical energy

so these

basically are examples to show you or convince you that ah probably you know already all these

things that energy are interconvertible

so you can actually convert one form of energy into the other

form and thermodynamics is ah thus the part of science which deals with ah the interconversion

of energy and in broad sense it deals with macroscopic systems and in this unit we will talk

about only the systems which are at equilibrium and the properties of systems which are at

equilibrium which means will deal with only equilibrium properties of this of the systems

in this in in this unit now thermodynamics was first formulated by physicists and engineers when

dealing with the efficiency of steam engines but it is it is of extreme importance or immense help

for both chemist and biologist you know while on one hand it basically explain or deals with

the energy output from a chemical reaction on the other hand it basically forms

the basically helps in explaining or answering the questions which are center or at

the heart of biological sciences like for example how the energy gets transmitted

through the biological cells or how the large macromolecules get assembled within a small volume of cells

so these are the the main questions the biological science poses also had to be answered by from the knowledge of thermodynamics

so basically you know that

thermodynamics is a very important subject and we should learn thermodynamics so if we just write once more that and in this unit as i said we

will be dealing with equilibrium systems and will will not considered systems having very

few molecules will be talking about systems which have great number of many molecules so

this thermodynamics is does not apply for systems which has very few molecules but

it applica it is applied or applicable only on systems which are large number of molecules

so if we just write we will talk about systems containing large number of molecules

so on that we are talking about the macroscopic macroscopic system not a microscopic systems we are talking about macroscopic systems now we

have used this terms quite a few time or talked about this um terms systems now obviously what is

systems or what is a system system is ah the part of the universe which is of our interest our interest means which is of our interest in

that moment for for example if i ah take a beaker if i just take a b car and put some water

in it and we consider this is the system so

so the beaker with the water

water in it is consist of is made us make the system and everything outside the beaker is what we call surroundings

so basically is when you are doing a say we are doing a reaction in a round bottom flask we the flask containing the round bottom flask ah the reactants and the products are basically our system and everything else which is not belong to the system we call surroundings and systems could be of ah different types the main three types

of system we will talk about is ah open system open system where a system can interact or exchange matter and energy surroundings

so basically open system can exchange we should write exchange here can exchange matter and energy with surrounding

so the example we talked about the beaker or say a conical flask if we can draw a conical flask here and we are taking some reactants here and this is this is not tied properly it is open then it actually can exchange the matter the molecules which in the system which

are in the system and of course it can exchange energies with surroundings

so this is example of ah open system if we consider our own body myself as a system then obviously we exchange a matter and and energy with surroundings

so if you consider a human body say open system example of open system obviously second is a closed system in a closed system the system can exchange can exchange energy with surroundings but it cannot any matter with surroundings

so basically if i had this ah conical flask can we just leave it properly air tight

so that no molecules can go in and out from the system then this system cannot exchange with any matter with the surroundings but because it can exchange energy with system and surroundings

so that would be the example of a closed system the third system we will talk about is an isolated system obviously is the third third category where no exchange of energy and matter is allowed between the system and the surroundings obviously a closed system which or other way it is an isolated system which is obviously has to be a closed system because its does not allow the matter to go in and out probably reverse is not true all closed

systems are not ah isolated systems

so basically all isolated systems are closed system but not all ice closed systems isolated system and will mostly in in this unit we will mostly deal with the closed system one may once once more closed systems are systems

where the the system is not allowed to exchange matter with surroundings but it can exchange

energy with surroundings and system is separated from the surroundings by what we call walls or boundaries

so basically we can write a system is separated from surroundings by various kind of walls walls or you can call boundaries as well

so what are the different types of boundaries or walls first is first type is a rigid or non rigid non ready is nothing but movable boundaries if i have say a cylinder with a piston a gas with a piston now this can be this boundary if it is not fixed if piston is not fixed anywhere here the volume of this gas can change by movement of this piston so in this case this piston surface is the boundary between the system and the surroundings which is movable so that case will call this as a non rigid boundary or movable boundary if this is fixed if i fix it somewhere like i can put a screw here in this case and we can make this piston fixed here so that this is now this has the piston has now become non movable and obviously these boundaries are or walls are fixed so they are not movable either so in this case the volume of this system cannot be changed it has a fixed volume so in this case the boundary we call this as a rigid boundary so if the boundary is movable by which it can change the volume of the system then we call this is a non rigid boundary or wall and if the boundary between the system and surroundings is not movable which means that the volume cannot be changed the systems volume cannot be changed by changing the position of the wall in that case the boundary of the wall is called rigid boundary the second type is called permeable or impermeable obviously if this boundary has say this piston is porous which means the gas inside is allowed to move out to the system or the gas or something from outside can come inside the system through these boundaries then we call this boundary as permeable boundary and if the boundary does not allow any exchange of matter between system and the surroundings then we call impermeable boundary so obviously this is case if it is a system is surrounded by a impermeable boundary then obviously its a closed system because this does not allow matter to move in or move out from system similarly if it is if the system is surrounded by a permeable wall then obviously the system is a open system because the matter can exchange between system and surroundings the third type we call we are talking about these are walls is adiabatic or non adiabatic non-adiabatic is sometimes called diathermal or diathermic walls as well now in this case if the boundary between system and surroundings allows exchange of heat between system and surroundings then we call that is a non adiabatic or diathermal boundary which is basically in this case the boundary consists of thermally conductive material but if the system is surrounded by a boundary which does not allow any heat exchange between the system and surroundings then we call

the boundary or the wall as a adiabatic wall adiabatic wall is very difficult to achieve in practice ah the most close example we have those flash thermo flask where we have actually a double walled ah boundary with ah nearly vacuum inside

so basically that prevent almost prevent exchange of heat between system and surrounding

so that you can keep your drinks or whatever material in the thermal flask at higher temperature or a lower temperature for long time

so that is the closest

example of adiabatic boundary we have now obviously adiabatic boundary will not allow something to permit the matters to go on out

so adiabatic boundary will the system surrounded by adiabatic boundary or walls has to be closed system and system surrounded by impermeable walls has to be closed system also if the system is surrounded by permeable boundary then its open system and if a system is surrounded by all three like a system which is surrounded by rigid impermeable and adiabatic walls then what we call it it cannot exchange because rigid this by moving the boundary in and out by changing the volume we can

exchange energy we can exchange energy either by heat changing the like exchanging heat between system and surroundings

so if you are closing the system with rigid and adiabatic that means there is no exchange of energy possible and of course if you are impermeable boundary then there is no question of matter being passed

so in this case matter and exchange matter and energy is prohibited for exchange between system and surroundings as a result we call this as in an isolated system

so as a an isolated system would be surrounded by rigid impermeable and adiabatic boundaries

so we talked about system and we talked about walls now how do we describe a system now a system when you describe a system you have to specify the values of several properties like for example if i want to describe a system we have to specify the equilibrium pressure equilibrium temperature volume composition

so these are the sum of the properties the values of which the values of which need to be specified or mentioned then only will be able to describe the system and once we do that we call that say state of the system

so state of the or thermodynamic state of the system is specified by or described by specifying the value of the properties of the system and as

i told the beginning that in this case will be in this unit or in this thermodynamic course we will

be only dealing with equilibrium properties so when you talk about pressure temperature volume

composition we are talking about the equilibrium pressure equilibrium value of the pressure

and equilibrium value of the temperature equilibrium volume of the system and

so on
so if we have two system
so i have a water here a bottle of water ah in
this case which i have say 25 degree centigrade and i have a volume or mass is
i know what is
the mass and i know what is the temperature i i know what is the pressure
inside now if
i have another bottle which has have same amount of water with same amount of
volume and
temperature is same pressure is same then we call that these two are of same
thermodynamic state
so basically thermodynamic state if i consider this as a system then the
obviously
the bottle outside will be the boundary and to specify this ah system or
describe this i have to tell how much amount of what is the amount of water in
it
what is the temperature what is the pressure and obviously if you mention
these three the
fourth one the volume will obviously be linked with the forth
so we do not always need to
specify all the volumes because sometimes they are linked with each other for
example if you know that ideal gas they are linked with the the the pressure
volume temperature and the number
of moles are linked with this
so if you know three of them n t and v then you will be knowing
able to know the fourth one
so you do not have to mention all the time all the thermodynamic
properties because some of the value of the sum of the thermonic 40 properties
can be obtained
from the relations between them and these are called the relations between the
thermodynamic
properties are called an equation of states now these states or this value this
properties
are called also state variables what is state variable what are state
variables for example the values of
pressure volume temperature you do not have to if you mention what is the
value that is enough
so we do not have to tell the history you know how the pressure is achieved
or how the volume is achieved how the temperature in this case is reached it
does not matter the
history of the system it will only the present value with dictate the system
or describe the
system
so these are called state variables
so if i take again the bottle of water and talk about
the pressure inside is one atmospheric pressure temperature is 25 degree
centigrade and volume and
so and
so so i do not need to mention that whether the water was obtained from
melting ice or water
was obtained by condensation condensing the vapor it does not matter as long
as i mentioned
the the present value of the temperature volume pressure then this system is
fully

described which means that these are called state variables

so the very the the value

of the state variables do not depends on the history of the system it depends on the present

value only

so these are called state variables we have some other ver some other classification of variables one is extensive extensive variables or extensive parameters another intensive parameters or variables now extensive variable variables depends on the size of the system which means if you double the size of the system

the the the value of that variable will double for example the volume if i increase the size

increase this mass if i have this water bottle again if i increase the or double the amount of

water keeping the pressure temperature same then the volume of the water will be double

so volume

in this case is extensive quantity or extensive parameter how do you call or equal and basically

the total volume of this bottle can be obtained by summing up the volumes of each part of this

bottle

so the value of any extensive variables can be obtained by summing up the value of that

particular variables in all part of the system on the other hand intrinsic variables they do not intensive variables do not

depends on the depend on the size of the system generally the value of intensive variables

are obtained at any point of the system if i want to get a temperature of this

water log water then i can measure the temperature on the top or i can measure

the temperature at the bottom it should get the same value of the temperature

so it does not

matter i have a half bottle of water i have a full bottle of water temperature would be same

so in this case the the value of temperature in this case it does not depend on the size of

the ah system now some systems may contain different phases what is call phases see if i talk about one term density what is density is extensive quantity or x intensive quantity always obviously density of ah system will depend on what will depend

on the size or it will depend on it will not depend on the size of the

so if

i talk about what is the density of water in this bottle it obviously does not depend on the

size

so density is in intense insane intensive variable property now if i add some sugar in

it keep on adding whatever at some point of time the water will get saturated and there

will be sugar lying on the bottom of this bottle

so obviously this the system will have

both water and the sugar which is ah in the bottom lying on the bottom

so now if i want to find out density in different parts of this system then obviously there will be different value for like in the solution there will be one value and the sugar which was lying which is lying on the bottom of this bottle which will have different value so in some cases if the system does not have same value for all the intensive variables across the system then we call that as a heterogeneous system obviously pure water will be homogeneous because the value of density of all the intensive variables value of all the intensity variables same across the system but the example i have i just given you where some sugar molecules are sugar are lying bottom of the bottle after the saturation is reached then you will have different value of density in the solution and the sugar sugar so though this example of heterogeneous ah heterogeneous system and the solution part and the sugar part will con will we mention a different phase so there is one phase which is the solution of sugar in water another would be the solid sugar phase so thats a heterogeneous system contains more than one phase and if the ah system is contains only one phase basically ah the the value of the all the intensive properties are same across the system then we call is a homogeneous system so i just ah gave you example of two types one is a heterogeneous system and homogeneous system so we know what is the thermodynamic state of a system now if we change if we say if we so we have a state one values are say p_1 one t_1 one v_1 one with some n is the value of number of moles amount of substance and we change to we change the value of say pressure and temperature p_2 and t_2 and say we volume also and without changing the number of moles so if you change it will be a new state of that system and how the change is brought about that is called process in a process by which the state of a or thermodynamic state of a system is changed and there are many different types of process possible and i will just try to name few of them for example we can talk about isothermal process isothermal process where temperature is fixed throughout the process all the time not that the initial temperature and the final temperature is fixed isothermal temperature is isothermal process is the process where temperature is fixed during entire duration of the process ok not that only initial temperature is same as the final temperature similarly isobaric process in this case pressure is fixed throughout the process again its not only the initial pressure and final pressure is fixed the pressure is fixed during

entire process isochoric process where volume is fixed throughout the process
now if there is a process where the state one is getting changed to state two without any heat exchange that means the system is surrounded by adiabatic wall
so there is a process going on inside the system which means the system will and there will no heat exchange between system and surroundings in that case we call that process as adiabatic process
adiabatic processes are the processes where adiabatic processes take place in the systems surrounded by adiabatic wall obviously there are other names like cyclic process where the initial state and the final state of the system is same
so there are many other possible names which will come across when required
so we talked about different processes what you know what is a process and then we talked about isothermal process isobaric process isochoric process and adiabatic process now let us come back and talk about the system we discussed earlier let us talk about again that cylinder with a gas and a piston this we consider a frictionless piston so that when it moves there is no friction associated in the walls
so there is no energy exchange during the friction of the piston and the system now how many different ways the system can exchange energy with surroundings say this is a diathermal wall
so we can exchange heat and this is a movable piston now if I place this system in a bath which is slightly higher temperature then heat will come in mean there will be heat exchange between surroundings to system
so heat will come in as a result the volume will get expanded so there is two type of exchanges possible one is heat exchange between system and surroundings and second one we are talking about the volume change and we call mechanical exchange mechanical exchange is nothing but the exchange of energy between system and surroundings because of the movement of the boundary between system and surroundings now if I consider that this is fixed now this boundary is fixed not movable or rigid boundary and then again we heat it up in that case there will be no volume expansion or no volume increase
so in that case only heat exchange is happening between system and surroundings in the third case if I have say this wall is a adiabatic wall which prevents any exchange between system any exchange of heat between system and surroundings and this is movable
so if I change the pressure just apply more pressure than inside then this piston will move in volume will decrease
so there

will be exchange of mechanical exchange we call there is a work the surroundings is working on the system and if the pressure outside is lower than inside then the system will move up i sorry the piston will move up volume will increase and we call that the system is working on the system and there is a mechanical energy exchange mechanical exchange between the system and system and surroundings this the work due to the the volume change also sometimes called pv work which is nothing but the mechanical energy exchange as explained here we call work exchange as well so work exchange happen the energy exchange between system and surroundings energy exchange between system and surroundings happen as work when the non rigid wall move due to difference in pressure inside and outside the system similarly energy exchange between system and surroundings happen as heat i am not writing that again ok i can write that energy exchange between system and surroundings happens as heat earlier it was work now it is heat when there is a temperature difference between system and surroundings so basically we now know that a system and surroundings can exchange energy by two process two modes one is work another is heat system and surroundings can exchange energy between them either by work what comes when the movable boundary moves and the system and sound can exchange energy as a heat when there is a diff temperature difference between system and surroundings now we talk about the energy of the system you know we are talking about the energy of systems now what are the different types of energy a system have obviously if i have a macroscopic object which is moving maybe i ah i will give you one more example of heat exchange and work exchange before i come to the type of energy let me just give you one again i have a piston here and in this case i have urea i am doing a reaction here within this cylinder so beginning i have urea this urea and oxygen and i keep this is in a say in in a water bath outside and once the reaction is done if this is having a movable boundary then because of you have no more number of the volume of the gases increases the volume will now increase maybe i will draw here plus water here liquid water here and you have this is placed in a water bath now in this case the system is doing some work on the surroundings because of the volume expansion plus there will be some energy exchange between the surroundings which is the water bath here and if you can measure the temperature before and after the reaction in the surroundings which might know with a very sensitive thermometer we will see there is a temperature change in the water bath here now if i do the same reaction with a fix piston so there is no volume changes allowed in this case water then what we will see this case that there is no exchange of energy as a work but in this case the temperature difference between the system and surroundings or ah the temperature change you

will observe

in the surroundings in this case water will be higher compared to the first case

so my drawing

is probably is not ah good here but anyway what i am trying to say is that i am doing a reaction

burning of urea inside a cylinder with a movable piston and that the container is kept in a

water bath now because there is a the volume of gas is increasing if this piston is movable

then it the volume of the system will go up which means there is exchange of energy

between system and surroundings as work and there will be exchange of heat between system

and surroundings and there will be change in temperature in the surroundings here in the water

bath if you do the same reaction in fixed volume where the piston is fixed then there will be no

exchange of work next no exchange of energy as work between system and surroundings in that

case the difference between the initial and final temperature in the surroundings will be

more compared to the last case ok

so basically we now know that the two ways

system and surroundings can exchange energy one is heat and the other is one is heat and another is work now what

are this different energy in a in a system if you just talk about say this pen it is not moving

so the macroscopic

kinetic energy of this pen is zero and if we though it its in a height maybe in a

table

so there is some bit of potential energy gravitational potential energy but thats also we can neglect

so you are talking about and if there is no

external field from outs applied from outside then there is no potential energy either

so in this case if i instead a pen i am taking a beaker or a

conical flask where i want to do a reaction generally it does not the beaker or conical flask

does not have any macroscopic kinetic energy or potential energy then what is the energy reaction

medium a chemical reaction median will have the energy is from the molecules which are presents

which are present in the system and that energy is called internal energy the internal energy is basically the energy due to the molecules present within

the system and what

are those energies which are associated with those molecules i will just explain in a minute

so as i said if i just have a conical flask ah and we talk about a process from state one to state two

so and if i tell k is a macroscopic kinetic energy then Δk is zero obviously before and after

both kinetic energy is zero

so so k is macroscopic and only changing the state of the system there is no change in macroscopic kinetic energy if you do not apply or change the potential from outside then the macroscopic potential energy v is also zero

so there is no change in macroscopic quantity of kinetic energy or potential energy

so what could be the change between say state one thermodynamic state one two thermodynamic state two there could be change in internal energy if you express internal energy as u then the change would be Δu

so if i want to find out total energy change of the system for going state 1 to state 2 would

be given by daily total energy Δk is total change in macroscopic kinetic energy macroscopic potential energy plus Δu and obviously as we mentioned the type of system

chemical system we will be dealing with in this unit or generally we deal with in thermodynamics

these two terms are zero

so the total change is equal to the total change in internal energy

so basically now nodes will be focusing on when you talking about the change in total energy of a system will be focusing focusing mainly on the change in internal energy not any other energy of course now the question you will ask what is

internal energy

so internal energy u which is due to the molecular motions plus inter molecular interactions

so you consist of you know the translational energy of the molecules

so molecular

translational plus rotational vibrational and electronic energies of the molecule plus relativistic rest mass energy m raised c square of the electrons and the nuclei plus the potential energy of interaction between the molecules

so this

lecture i will stop here and in next lecture lecture 2 i will continue from our discussion about internal energy

so we just take this slide and then page and will continue in the next lecture ah more about internal energy you