Chemical Principles 2
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Module 4
Lecture 24
Second Law of Thermodynamics

In this module we are going to start talking about Second Law of Thermodynamics. So this is pretty exciting because we have finished the first law of thermodynamics in which we have seen (energy conservation) energy is conserved and we have seen how different forms of energy go from like one form to another form. How one form of energy goes to like from work to heat and heat to internal energy and things like that. So only thing that is not answered in the first law of thermodynamics is that whether the change will be allowed or not, whether a conversion of heat to work will be allowed or not or whether this conversion will be fully used or not.

So second law of thermodynamics is going to add a new thing a new rule to the change of method or change of different forms of energy and that is we are going to learn in this particular modules which is going to go on like now or several modules. We have divided into two parts (first part) in the first part will we are going to deal with the classical approach to second law of thermodynamics which is you now typically taught in undergraduate courses however since more and more books are coming up with molecular approaches that means they are trying to understand (know) this laws of nature from atoms and molecules.

We also going to adapt the molecular thermodynamics approach to complement our understanding of second law of thermodynamics and in general thermodynamics. So thermodynamics basically is a like second law of thermodynamics is everything thermodynamics itself as will see. Once we understand that we can get all other forms all other laws as a corollary to this one however ofcourse we have mention the 0^{th} law of thermodynamics as a foundation to the second law because we had to define the temperature using 0^{th} law of thermodynamics similarly first law of thermodynamics which talks about conservation of energy that is already you know isn't known from other fields as well.

However the second law of thermodynamics as we will see is unique and it will give us a handle to understand when one thing will actually change from one form to another form. Before we start that I am going to start with some quotations for the second law of thermodynamics as people have now mentions the great scientist have mentioned over the time.

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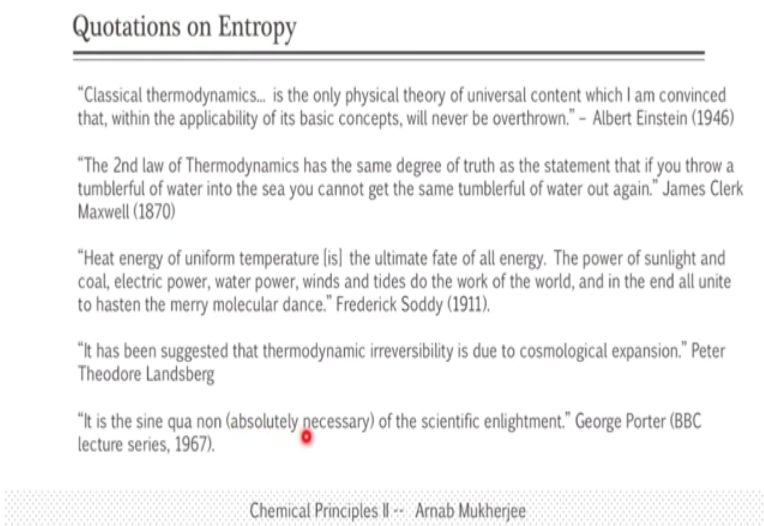

The first one is by Albert Einstein who says that the classical thermodynamics is the only physical theory of universal content which I am convinced that within the applicability of its basic concepts will never be over thrown that means we have seen that timing again that there is a theory which is proposed and then ofcourse that is modified or (you know) made that anything like that over the time right.

For example, Newton's equation of motion, we now know that, that is only an approximation to underline quantum mechanical concepts. So however he says that the thermodynamics is such thing that pretty much will be solid and not going to be over thrown you know for a long time. Second one, second law of thermodynamics has a same degree of truth as the statement that if you throw a tumblerful of water into the sea you cannot get the same tumblerful of water out again by James Clerk Maxwell what that does mean? So you take a bucket of water let us say you specify in that bucket all the water molecules you number them or you color them let us say you tag them by somehow and put it into sea and try to collect back the same, you can do the same you can take colored water a mug of colored water put it somewhere a pond or something and try to get back all the colored molecules that you have, will you get back ever?

See if you cannot get back ever that thing the truthfulness in that in the fact that you cannot get it back is of the same degree of truthfulness as a second law of thermodynamics. If you cannot get it back and if you agree that you cannot get it back then you basically agreeing to the fact that second law of thermodynamics holds ok. Third one heat energy of uniform temperature is the ultimate fate of all energy. So we talked about energy conservation energy to work, work to heat, heat to energy and all sorts of thing energy to energy, solar energy to chemical energy, chemical energy to other energy, we talked about all that right but then where we are heading?

We are heading towards a direction where everything will be heat energy and the power of sunlight and coal electric power, water power, winds, tides do the work of the world they do lots of work we use solar energy to do work, we use electrical power to do work, water power to do work we have shown some examples of that during our demonstrations and in the end all unite to hasten the merry molecular dance. So the merry molecular dance meaning the jiggling and wiggling of atoms and molecules under the heat or temperature that is there. So basically everything is going to go all the energy that we have talked about whether it is energy of the sunlight or do the work or whatever we eat food at the end everything is going to go into heat energy and it is just going to just change the motions of the molecules at the end that is our fate of all energy that is what talks about.

This is very interesting I put it there because it has been suggested that thermodynamic irresistibility is due to the cosmological expansion. Now again this are the quotations from different people. You may not be able to connect it right now but at the end of the course or at the end of our discussion of the second law of thermodynamics you will understand all of that. (this course) what it means is that the fact that you know the people believe that we are now in the expansion phase of the universe some dark theories right they said that the universe will expand and contract and there are many-many different theories available but this is the I think the theory by Roger Penrose or Stephen Hawking that says that earth will be expand and then contract.

So right now we are in expansion phase cosmological expansion and the fact that we see things irreversible things that we see there that happens irreversibly due to this expansion and this is the from George Porter's video so which was BBC lecture series in 1967 he also has very nice half an hour video on the thermodynamics this thing I suggest all of you to see that and where he mentions that is the sine qua non or scientific enlightment that means it is absolutely necessary knowledge for any scientific you know understanding that one might have be it like biology, chemistry, physics every subject you will find that the application of thermodynamics will be essential or especially the second law of thermodynamics.

In order to understand what is second law of thermodynamics we are going to talk about some changes so as we said before that thermodynamics gives us the room to say that whether the change will take place or not whether it is a change of matter, change of phase, change of state, change of anything for that matter, whether that will happen or not that depends on the rules you know that is govern by the thermo dynamical principles so we are going to talk about few of the changes.

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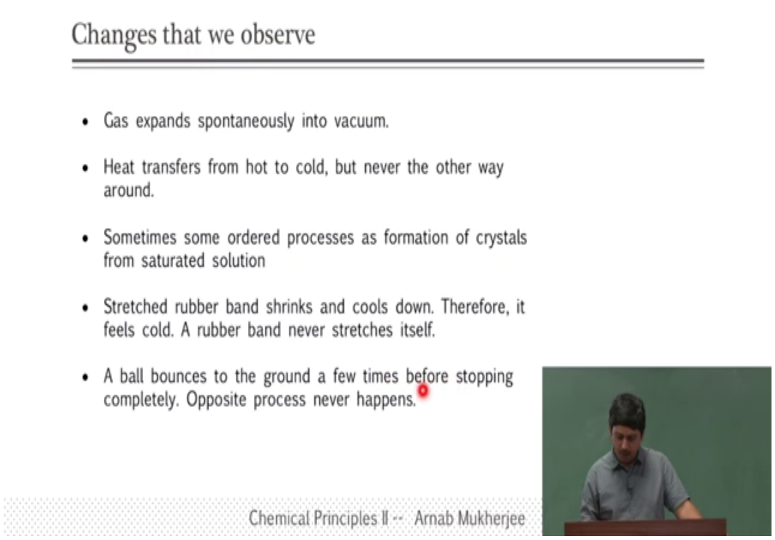

One change is that the gas expands spontaneously in the vacuum right like if you let us say you put gas in a container try to give some color to that and then open the container, what do you expect the gas will expand? So therefore it is a natural process we see that everyday and that does not bother us you know even the child sees that does not bother the child quite happens right, it is quite natural because you see that everyday around us maybe don't understand that but for example you light an incense and what happens the smoke that comes out it will fill the room it is quite natural for us to see that, that is a spontaneous change that we absorb. Let us talk about one more heat transfers from hot to cold we see that always even in our class 7^{th} standard experiment I think remember that we had to show that you know heat transfers to a metal or something and then we put wax on one side of the metal and heat by other side so that side will be hot work side will be cold and the works will melt which means the heat transfers from hot to cold.

It is quite natural that when you put your hand in a boiling water you feel you know hot because the heat transfers from boiling water to your hand similarly because we are ofcourse you are colder than the boiling water and you will touch an ice you are hotter than the ice therefore the heat will transfer from your body to the ice and therefore you will figure sensation of cold so heat transfer form hot to cold is quite natural phenomenon for us to absorb. However we have seen that we have refrigerators in our house where the temperature of the refrigerator is colder than the that of the room so there the heat actually transform from cold to hot we will discuss that, why that happens that (())(10:57) spontaneous thing.

So we are talking about on the spontaneous ranges spontaneously heat transformed from hot to cold, hot to cold again in terms of temperature hot is high temperature cold is lower temperature. Sometimes some ordered processes as just formation of crystals, crystals from saturated solutions also happens so you can see a order for example we see that we see the trees grow right this is an ordered process. We see many ordered process around us. So it is not that only wee see the something that spontaneously happen will go to some dis-ordered or chaotic nature. Many things for example when we build a house or a tree grows or soils actually combine together in organize form making you know an organisms.

They are all ordered processes this ordered processes may tell us that spontaneously happening and therefore it might be going against the natural process however there are things that are round that which will be getting more of dis-ordered nature. For example stretched rubber we will show you a demonstration very simple one so when you stretch it, it is not a spontaneous pressure you have to really do the work right. However when you release it, it is a spontaneous the strings it doesn't shrink beyond this it will sshrink to a particular optimum line it will not go below that. So a stretched rubber shrinks and cools down. Now you try this, you have this balloon you stretched it in a first you touch it here you see the temperature or (())(12:40) is fine, stretch it, touch it, release it and touch it.

You can try that and you will see that when it spontaneously comes back it will get cool down, when you stretch it you will get heated up and spontaneously cool down. Another thing you can do here is that you can put in your finger, stretch it, this works very well, release it. you will see that you fingertip becomes colder so this a very standard experiment and what you are going to learn later is that it is a demonstration of (())(13:19). It is getting cooler the reason again will explain later but again the here what we are talking about is that a spontaneous process of an extended rubber to normal form that is a spontaneous process that happens.

A ball bounce to the ground a few times before stopping completely and opposite never happens so when you drop the ball is very natural for us to see that right and nobody is going to associate you know like initially any theories behind it, it is ok gravitational attraction therefore this following down I understand that gravitational attraction lets it to fall down to the ground. However the energy of this particular ball remains conserved right because initially it is the full potential energy gets converted to kinetic energy when it touch the ground it has highest kinetic energy and therefore it can bounce back should bounce back to same level right but it does not. So the first law of thermodynamics does not prohibited to not come back to our hand.

Neither any rule or physics will tell you that why should not come back it is perfectly reversible process that it goes down and comes back to your hand there is no problem associated with that yet you do not find the things come back to our hand and you call that an inelastic collision right. If you ask them ok why it does not happen you said inelastic collision, what does it mean? What does an inelastic collision means and why this processes are inelastic? What is the nature of this thing that makes it inelastic? So we will talk about that you know later so the point is that it is not that the fact that it doesn’t come back is has anything to do with forces.

So force that pulls the ball we will have exact an opposite forces when it hits the floor and therefore you should have come back to a hand however it does not come back because we know that what happens there is a loss in the energy and how that loss happens and why that loss happens that is what we are going to talk about when we discuss about second law in more detail.

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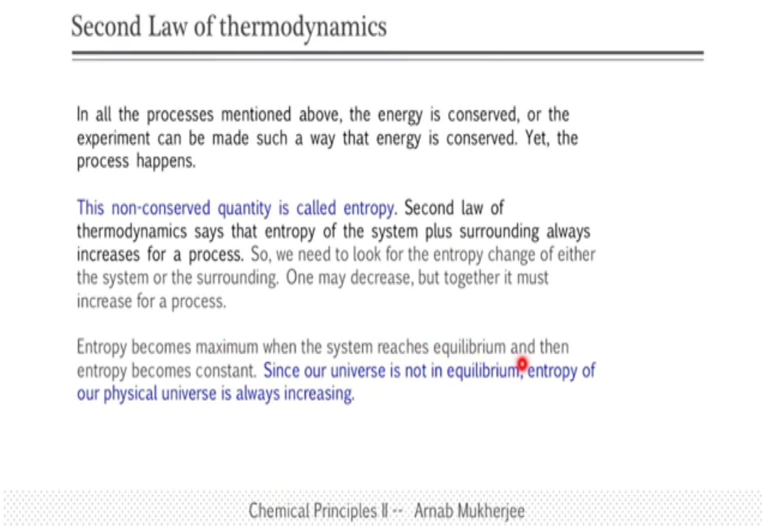

So in all the processes mentioned above the energy is conserved as I said and our experiment can be made in such a way there energy remains conserved yet the opposite process never happens and this process only happens. This non-conserved quantity so in every this irreversible process which means when I talked about expansion of gas is an irreversible process I talked about the ball falls down to the ground and it does not come back that is an irreversible process and we are given some other examples in every case there is energy is always conserved in all those cases right that never changes because we had the potential energy got converted into kinetic energy then some of that got converted to sound energy and then heat energy and all that. So energy gets energy is always conserved however some quantity is non-conserved that is non-conserved when we are holding the ball versus now when the ball is again static on the ground.

There is something which is entropy that has increased in this process this non-conserved quantity is called entropy and second law of thermodynamics says that entropy of the system whatever system we have discussed about system and surrounding right, entropy of the system plus surrounding always increases for a process. Remember our discussion about system and surrounding, system was whatever we talk about like this ball and surrounding will be everything else in the universe except the ball. So when we talk about system and surrounding we are talking about the entire universe. So when you are holding the ball versus now entropy of the universe has increased.

In fact when we started the class and now the entire universe has increased in fact at every moment, at every second every minute entropy of the universe is increasing. So entropy becomes maximum when the system reaches equilibrium and we call that an equilibrium system, now what is that entropy? We have said that there is a non-conserved quantity unlike you know all physical laws things are conserved force are balanced energy you know total energy is conserved but entropy is non-conserved quantity and what is that, that is what we are going to study right.

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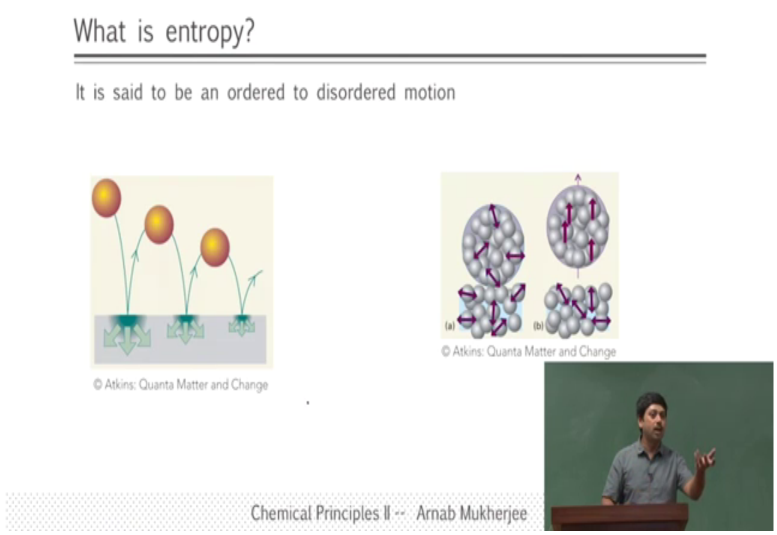

So it is normally said to be an ordered to disordered motions, so I have the ball, drop it and it bounces back two times right, bounce back two times. Each time the height was lesser and lesser and then its stopped and you see when it hit the ground that is there in the ground the particles, atoms of the ground, when it hit that it transfer some energy to the ground particle and then it came back again hit the ground again it transfer some energy to ground particle. Now when it hits the particle on the ground the atoms of the surface of the floor that energy again transfer to the next atom to the next atom to the next atom gets lost. It is like again putting water into the sea once you put it you can no longer get back, why? Because this water molecules now has gone into and mixed with the sea.

Unless they come back together and to your hand it will not happen that we get back the same thing right. So this is taken from Atkins, this two pictures you see here so initially this there are random motion so when the ball is falling down it has all the atoms of the ball is the direction of the you know downwards direction. One it hits that then it gets all oriented differently unless it come back altogether unless this the dissipation that has happened to the atoms of the floor it comes back together you are not going to get back the ball. If they decide that ok let us all the energy that we have been dissipated to the atoms of the floor come back in harmony together and pushes the ball back then it will come to our hand that the probability of that happening is extremely small.

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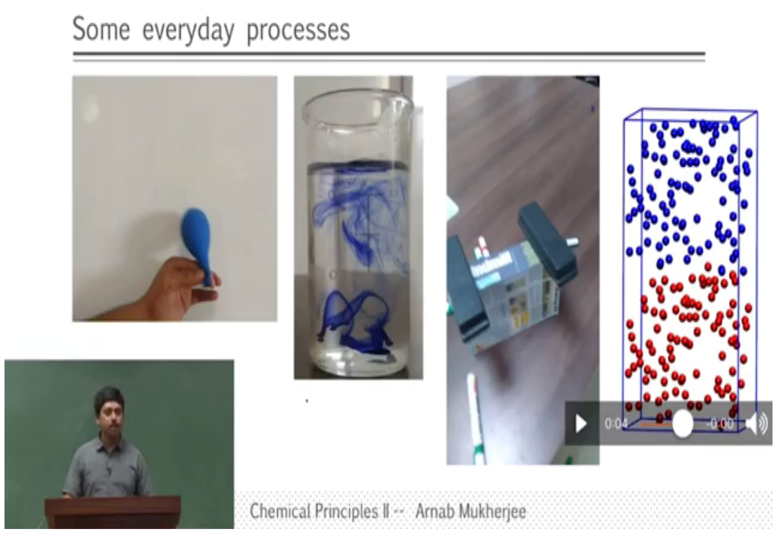

So now we are going to show some demonstration and see ok so now this is the ball falling to the ground and all that is very common to us right. Now I can put a glass and will break you don't see the opposite process happen. An egg breaking is very common phenomenon opposite never happens, do you imagine that the broken egg will you know combine together and come to your hand never right. However, in our real world it never happens but you can always make it make that thing happening in a virtual world, how? You can always take a movie of that and run it backward right then you can see the egg coming to our hand right.

But then you will know for sure the that is surely a movie running backward isn't it? You know for sure that's movie is running backward you know for sure that cannot happen in the real world. So here we are going to show you some movies and you have to tell that whether they are this movies are running forward or backward ok. So let us see if it runs, so what happened the air that was there inside that you know outside suddenly came into the balloon and swollen up the balloon see saw what happened? Swollen up the balloon, you know some air molecules decided to come inside the balloon and swell it up, why it happened in the real world?

Ok so in this those ink which is there in the water suddenly decides to (())(22:34) together and come to the hand, possible? This is an interesting where (I don't know how to) so run that again, so it starts all the you know all this pen there were like I scattered and they decide to come back and form a very nice (())(23:01) not possible right you sure about that right. Fourth one, this is a mixture of red and blue particles and that they are suddenly unmixed, possible? No.

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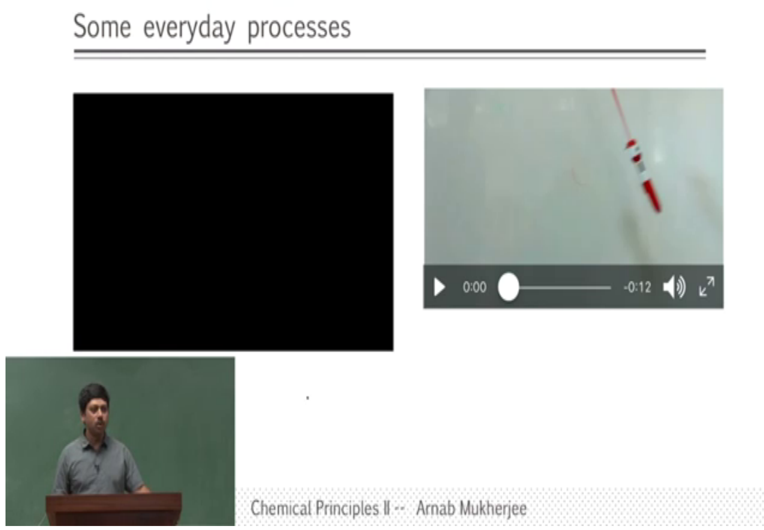

Now (())(23:23) is in the swing tell me whether the movie is running forward or backward? Will play it once more, is the movie running forward or backward? Ok, one more there is a pen here which (())(23:54) is trying to you know swing it and here it is, is it running forward or backward? Now you see suddenly that you cannot answer this right, is difficult, it is not obvious what has happened. If you take my picture walking on the (())(24:22) like this and run it backward will you able to tell whether the movie is running backward or forward if I take a movie and then run backward will you able to tell? Sure? Try that, try that, you take the movie and run it backward do it yourself and see whether you can tell that whether running forward or backward? If I drink the water very slowly I will drink it, I cannot spill it forget about the spilling ofcourse you can see that because here the water will be going out of the bottle right.

So I will not do that lets try that this one you will be able to see I am drinking I will be running forward backward but this one run it backward and you will see whether you can tell whether forward or backward not. If you do not see the water spilling from the bottle (())(25:48) slow enough will not be able to tell. Now why is that? Why in one case you could tell in another case you could not tell, either the movie is running forward or backward we don't I did not tell you which is that one but you are unable to decide. Now why is that? To understand that again you have to understand the error of time. So as I told you before that entropy increases a spontaneous process anything that is happening spontaneously increases the entropy.

So if you see something is not possible entropy must be decreasing in that and if you see that you cannot decide then the system is in equilibrium and entropy is not increasing because entropy is not increasing we didn't know whether the movie is running forward or backward because if the entropy would be decreasing then you will know for sure that the movie is running backward. In both those two examples the movie is running is backward but you will not guess it right obviously so those are examples an equilibrium processes and at that process change of entropy is zero. Ofcourse I do not claim that will exactly zero but will try to make it as closets as possible. It is not detectable by our understanding obviously. So what does that mean?

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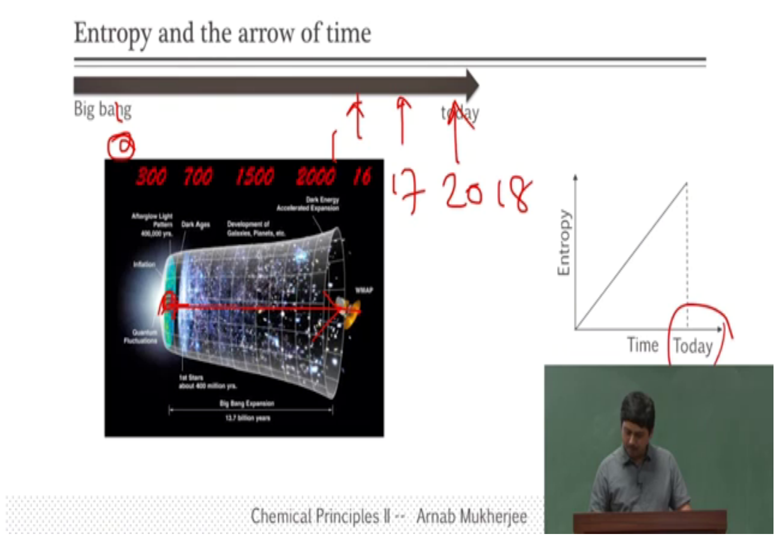

It means that, that at every instant as I told you before at every instant every point of time entropy must be increasing for all irreversible processes. All the reversible processes entropy is not increasing but all irreversible process whether it is braking of an egg or whatever falling from high to low and in all other processes you can name it chemical reactions as spontaneous process every process entropy is increasing, entropy of the universe is increasing and since the decrease is never possible which means that we can associate the entropy with the array of time.

So lets say we are here today so this is like 2018 right which means it is higher than 2017,2016 and you are going back and back and back to you know 0 1 BC and all that right. So where then at some point it must have started right. So at some point we could not go back further and that is our zero of time. So every year if you look backward in our past entropy must have been entropy of the universe must have been lower than what is today right because every process is irreversible is contributing to which means that will go back and back and back and some point you cannot go back any further and that is the origin of the time because time starts from 0, doesn't have negative value.

So the zero of time is as we understand we can say that the zero of the time is the big bang and then with time entropy of the universe kept on increasing till today which is here and that is what I (())(29:41) here today, so this is today and I put a linear line by just a schematic line I don't know whether this change is linear or not it may not be linear, it maybe be in-exponential or super exponential, we do not know that, at least I do not know that but it must be increasing monotonically increasing function of time. So therefore entropy is used as the array of time quite naturally because we know there are some point in you know in the past entropy must have been zero and that is associated with that time when the universe was just like a point and then the expansion happened and then (you know) kind universe we have with in a entropy and it is still increasing and the reason that it is increasing, can you tell me the reason that it is increasing? Why is entropy still increasing?

From whatever we discussed till now can you predict that why it is still increasing? Correct so it has not reached the equilibrium, if it reached equilibrium entropy would not be increasing and we will not see any change anywhere ok. So that is the beauty of it that our universe is not in equilibrium situation because it is still expanding, this expanding faster and we know that our entropy also increasing so therefore that is cosmological expansion thing came to the picture that because probably this expansion is related to all those spontaneous processes having to do with the increase in entropy. Now we know that entropy is increasing so it has it was lower before right now it is higher but where it will end then, it will keep on growing right.

So 2018 it is some value then 2019 it will be higher, 22 even higher and lets say 3000 or 4000 sometime it will be very high right but we know the lower value zero we know the higher value we don't know the higher value but we know what will have its higher value the fate of the universe I mean the future we can predict right you can predict that the entropy will be very high so high that no more changes will be possible and we know that again that another quotation that everything will go to merry molecular dance in which the all forms of energy will convert to heat energy at a constant temperature.

That means there will be no longer structures available as long as we have structure we have energy in a very closed form it is not dissipated you will learn later on that as long as you confine energy to a particular place your entropy is low, entropy will be high when it will be distributed spreaded so as long as you see structures, structures in the form of either building or tress or any organizations having to do with the lower value of entropy. So how is (())(33:11) entropy such that there will be no structure, no organizations that means no human being, no planets, no other thing it will be just a heat bath in which nothing will exists and that is the fate of the universe.

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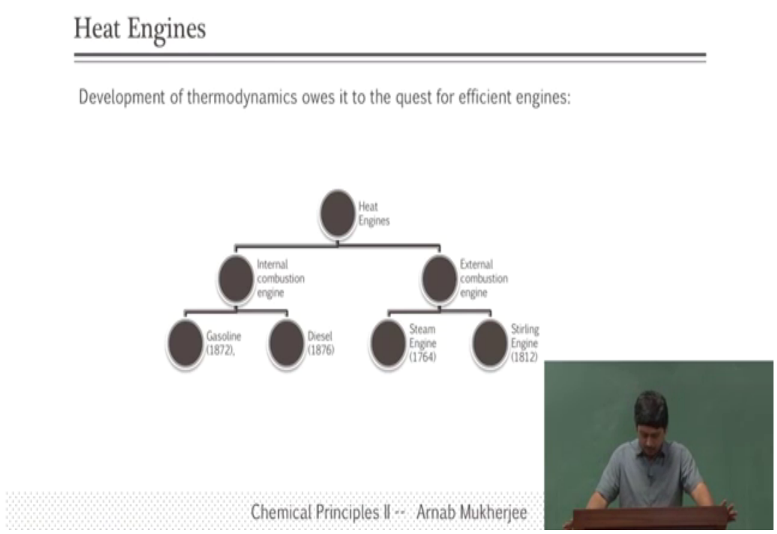

So now the beginning of second law of thermodynamics had to do with peoples idea to make an engine with better efficiency so talked about history of thermodynamics and there we may saw that around 1700, 70 years sometime we got same engine and then around you know so people were trying to make better and better and more and more efficient engines so efficiency of heat engines had great role to play in the understanding of second law of thermodynamics. We specify to do we already told you that what is the fundamental definition of second law of thermodynamics that the system and surroundings entropy is continuously increasing that is one of the statement of second law of thermodynamics.

However the same time you will see that, that has to do with also the efficiency of heat engines like it is kind of disconnected right in one case I am talking about the entropy of the universe you know continuously increasing another case I am talking about that thermodynamics limits the maximum efficiency of nay heat engines and this efficiency of engines rove the foundation of thermo dynamical principle and its started at the onset of this series of ideas that started with Sadi Carnot around 1824 very proposed something called Carnot engine and we define that what is the maximum possible value of the efficiency of the engine will be.

So it has to do with engines right, so an engine’s heating can be divided into parts one is internal combustion engine where the combustion happens inside the engine like car, trucks and all that which of two types like gasoline engine and diesel engine and there is external combustion engine where combustion will happen outside the engine like steam engine. So combustion will happen steam will produced and that steam will now push the piston and steam engine and sterling engines are example of external combustion engine. Will talk about this engines later in little bit more detail schematically. So this engines drove (the you know) the quest for efficiency of for this engines drove or gave rise to the you know second law of foundation of second law of thermodynamics.