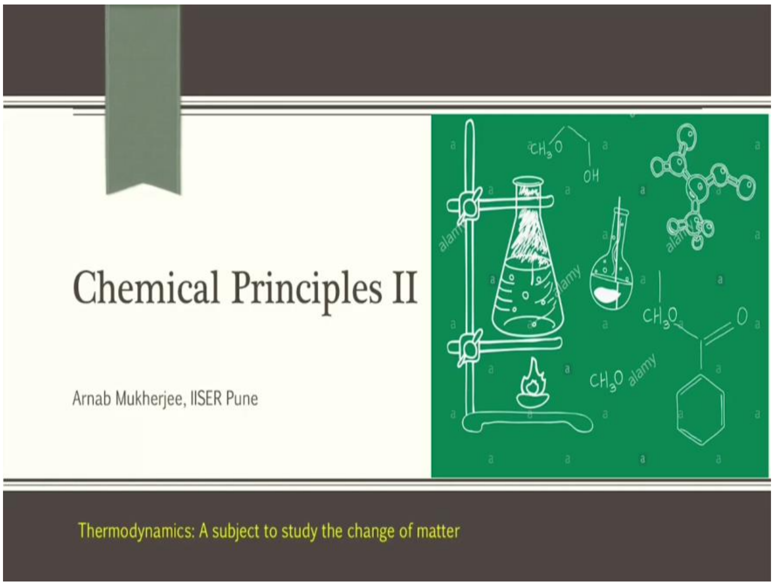
Chemical Principles II

Dr Arnab Mukherjee
Department of chemistry, IISER Pune
Indian Institute of Science Education and Research, Pune

Introduction to Thermodynamics

(Refer Slide Time: 0:17)

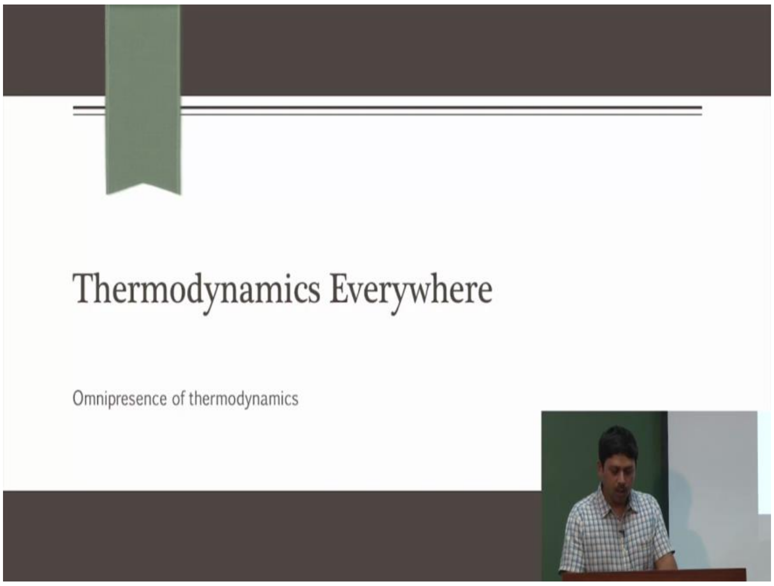


Welcome to Chemical principles II course. This is the course that is typically taught in the 2nd semester of first-year students at IISER Pune, and in this particular course we study the subject of thermodynamics.

So, why it is called chemical principles II is that, in the first semester we have chemical principles I where we study structure of atoms which typically gives us an idea about how to estimate the energy of the particular matter or how the matter is constituted of. For example: we know the hydrogen atom is constituted of proton and electron and the behavior of the electron gives rise to all the orbitals. And then in the 2nd semester we study chemical principles II where we see how matter changes from one form to another.

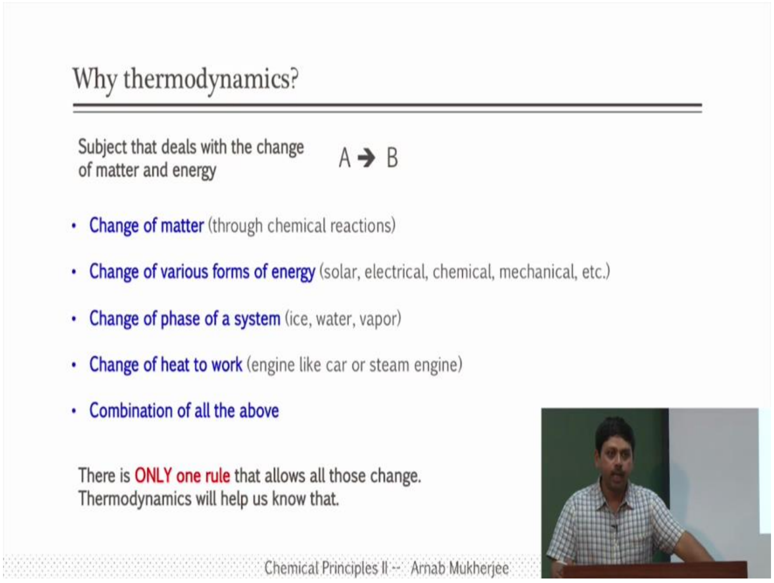
These transformations are governed by a different principle and these principle will tell us, for any process how the change will happen from one form to another, or how the change will actually take place. So, that's why we call that Chemical Principles II.

(Refer Slide Time: 1:41)



Thermodynamics is a subject to study the change of matter. So, you will see that thermodynamics is actually present everywhere.

(Refer Slide Time: 1:48)



We shall see some examples here. Let's say a process is going on where change is happening from A to B. Now any change will have a governing principle of thermodynamics behind it. I will give you some example.

Change of matter or chemical reactions: atoms going to molecules or change of matter where you are breaking something, that will be a change of matter, whether it is a chemical reactions or not. Any of these, if they involve a change of matter it has to be governed by thermodynamics. Further, the changes between various forms of energy, for example a change from solar energy to electrical energy or to chemical or mechanical energy etc will also be governed by a thermodynamic principle.

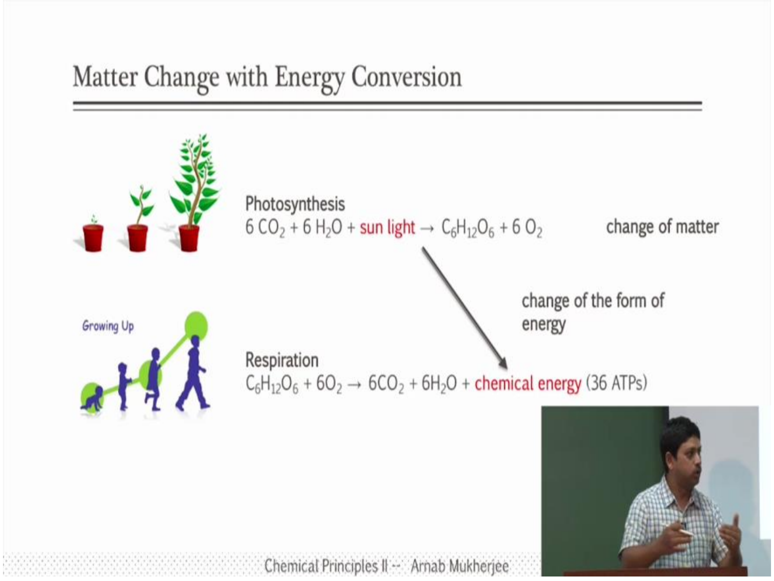
Change of phases are also governed by thermodynamic principle. For example, water has, as we know three phases: ice, water and vapor phase. Again the changes between these states will be governed by thermodynamic principle.

A lot of people have tried before to convert heat into work and vice versa. So, if I have not stated anything here that talks about the change that also will be governed by principle of thermodynamics. Only thing that we have to understand is that where and how this changes are taking place.

Some of the examples will be given here. Now all these changes, as it is said in accordance with “The Lord of the Rings” that there is only one rule that allows all those change. Hence, there is a law that rules every changes that happen and we shall see in this particular course that it is all about understanding that rule.

It is a very simple rule. But if you understand that rule we will actually have a grasp of all hose thermodynamic processes. When you will look at them, let’s say for example when you came to this particular class from your home, then you must have noticed a lot of changes. Lot of things that were there before and not there today or there in the morning and not now. All those changes, if you note it down, you may find an explanation for those changes when you study or learn this particular course.

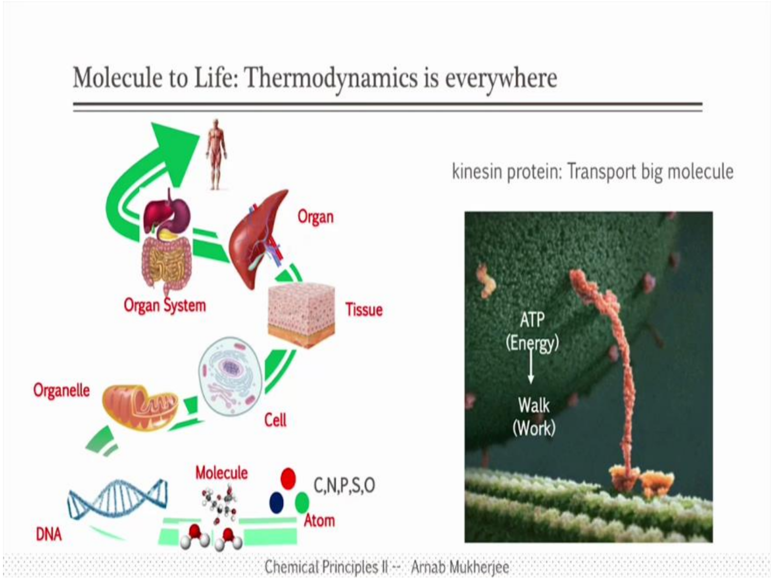
(Refer Slide Time: 4:32)



We will give some more examples here. Let's talk about photosynthesis. In photosynthesis, what happens is, as all of us know that the trees will absorb carbon dioxide and water, and with the help of sunlight it will produce glucose and oxygen. The interesting thing is that it is a change of matter because there is a chemical reaction happening. Carbon dioxide is a different matter, water is a different matter and glucose is a completely different matter. So there is a change of matter going on. Again this will be governed by thermodynamic principle. Interestingly, we know that same glucose is actually used by animals too and with the help of oxygen, it will produce carbon dioxide and water back. This is almost like a cyclic process. In the process, it will store the energy in ATP. So essentially, what has happened is that, from the sunlight, the solar energy has been converted to a chemical energy. Why we call it chemical energy will become clear later. However, right now you can take my word for it that the energy that was there in the sun has now been stored in the form of chemical energy.

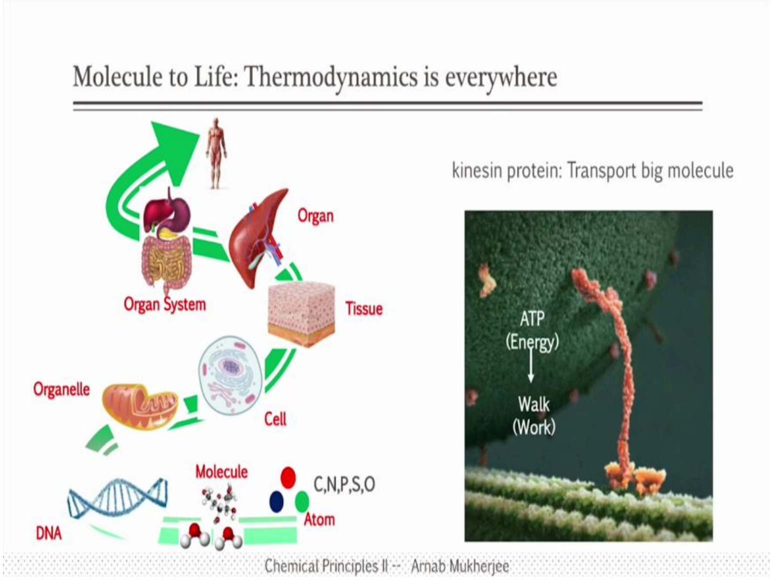
So, this change from one form of energy to another form of energy such as the overall change from solar energy to chemical energy is also a process that is governed by thermodynamic principle.

(Refer Slide Time: 06:12)



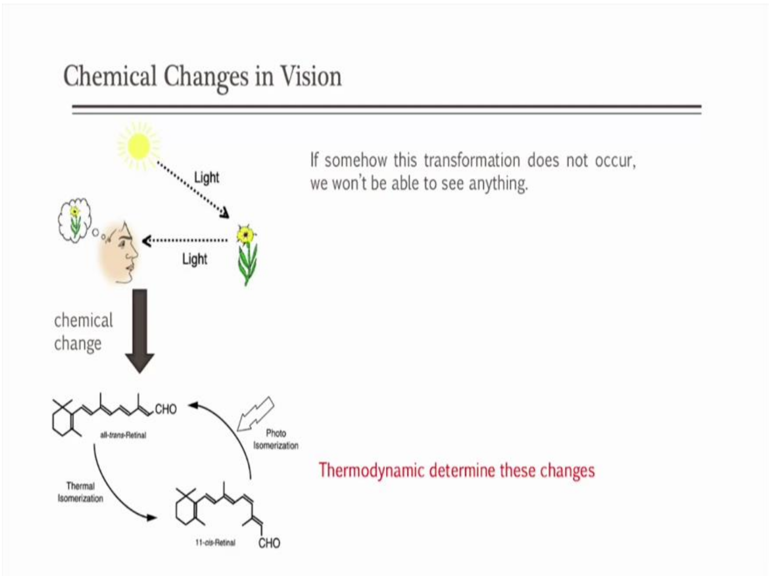
Now let's talk about the molecules of life. As we know, thermodynamics is everywhere. So let's talk about atoms. We know that common atoms like carbon, nitrogen, phosphorus, sulfur or oxygen combine to form molecules. These molecules further combine to form supra-molecules like DNA. Those supra-molecules assemble together and form organelles. These organelles remain in cell. Cells combine to form tissue, then organs, organic system and human beings. So, ultimately we are all made of these atoms and molecules. If we break down the cells, then we shall get the atoms finally. So, the parts that are there in our brains including or the ones that are enabling us to talk is made up of atoms. And these atoms combine to form molecules following the principle of thermodynamics. In our body, lot of chemical reactions are going on all the time. When we talk about biology as a different subject we see that at the end all the subjects actually will amalgamate together. Because we talk about biology, we will talk about biological systems. But inside a biological system there will be chemical processes happening, and these chemical processes will actually be governed by physical principles. Physical principles can be understood by mathematical equations to some extent.

(Refer Slide Time: 7:43)



We know kinesin proteins and the job of this particular protein is to carry a big load of nanometer size scale and this is shown using a cartoon work, where the particular system is taking the energy stored in ATP and performing a mechanical work, which is a walk. This work is being performed by this kinesin protein. So, this again as we said earlier will also be followed by thermodynamic principles.

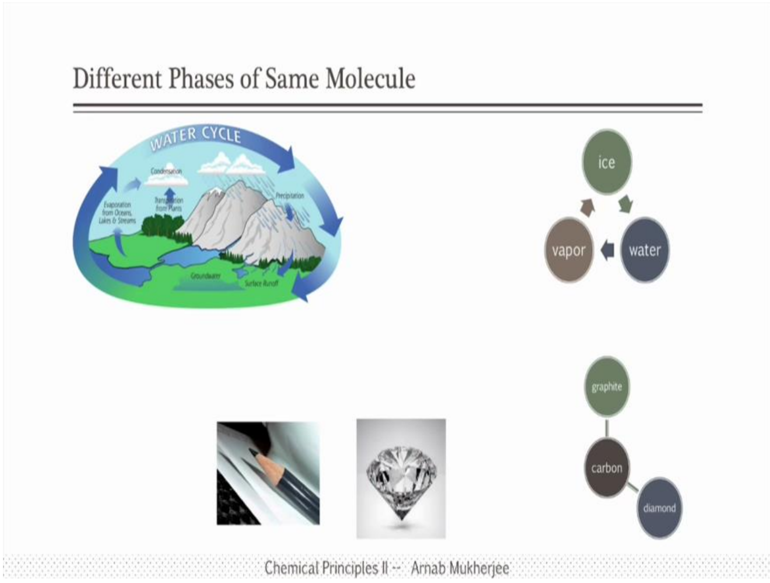
(Refer Slide Time: 8:25)



Now let's talk about another example. When we open our eyes in the morning, thermodynamic principle starts happening. For example, when light falls into an object and then comes to our eyes, a chemical change happens. In our eyes, all *trans*-retinol molecules photo isomerizes to *cis*-retinol. This isomerization can only happen because of the Photon that falls in our eye.

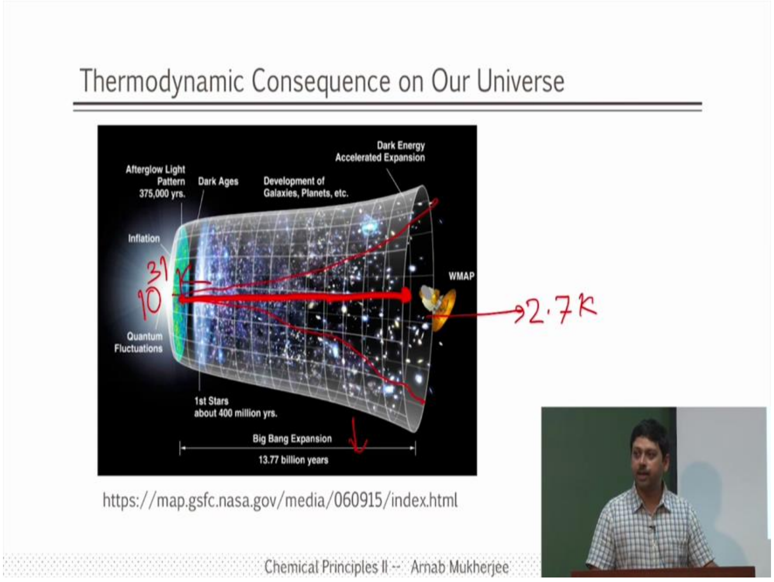
We cannot see all possible light through our eyes. We see only in the range of a visible light which is in 400 nm to 800 nm range. So, this means a particular frequency of light or a particular frequency of light only can activate this *trans*-retinol and form *cis*-retinol. So, thermodynamics determine this changes. So if let's say less than 400 nm light falls on our eyes which is also an electromagnetic radiation, yet it cannot activate this chemical transformation. Because this light cannot activate the chemical transformation one cannot see. So, that means even in our vision there are chemical changes happening and in that chemical change thermodynamics is playing a very important role.

(Refer Slide Time: 9:47)



We have seen different phases of molecules such as phases of water. In reality, water has many more phases but we will just talk about the standard three phases that we know. One is ice, another is water and the third is vapor. They are know to form a cycle. Now it turns out that one cannot just convert ice to water. It needs a particular condition. We all know these conditions. The vapor also requires certain condition. Therefore, certain temperature and pressure is required for one form of the matter to be stable. Now, let's talk about carbon. Carbon also has different forms: one is graphite which we have in pencils, another is diamond which is very different from graphite. Diamond is extremely costly. They form at a certain conditions. So, all these forms are allotropes of the same element: carbon. So, here matter is not changing but the phase of the matter or their arrangement in that particular molecule is changing, and consequently the physical properties, such as whether light will reflect from that or not. So these are the property of the matter and these properties of the matter is another subject. But the main point is that these formations will be governed by thermodynamic principle.

(Refer Slide Time: 11:29)

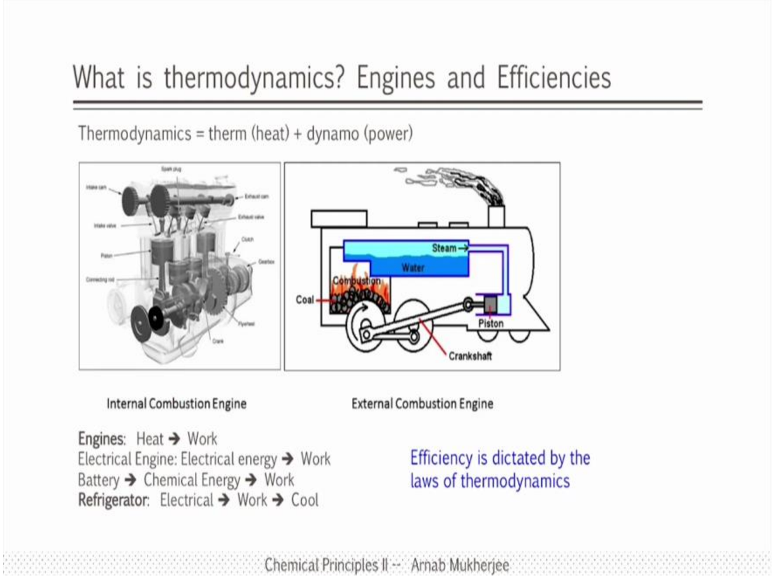


Now let's not talk about another very interesting subject. The thermodynamics have even helped for the existence of our physical universe itself. We know that our universe is approximately 13.7 billion year old and it is believed that it started with a big bang. According to this theory, at one point the universe was of a point size and then it expanded extremely quickly within 10^{-36} seconds to a larger form. Then it kept on expanding till this point that we are here.

Then it is believed that the temperature was 10^{-31} Kelvin during that time, at the time of big bang. So, it was only energy and nothing else. Now soon from that energy matter got created. So hydrogen and helium were the first two elements that got created just after the big bang. First of all, electron had to come, combine and hydrogen had to form. The process of expansion cooled down the overall temperature of the universe and right now the temperature of the universe is around 2.7 K. So, this expansion process is related to, as we shall see later on, is somewhat related to an adiabatic expansion. In adiabatic expansion the total energy remain same, what is happening is that, with the energy, when system perform work, then temperature reduces because system is using its own energy to do the work. A lot of other matters that got created during the big bang were due to explosion of stars and many other things. So, earth got formed around 4.6 billion years ago approximately. At that point, we had all the matters present. Conversion of energy to matter typically does not happen at normal condition like the earthly environment. In order to create any matter above helium, we need sufficiently high amount of energy, which is not present of course. So, currently scientists are trying to make matter in large Hadron Collider and in that too, they exist only for a very brief moment.

So the fact that it got cool down and the fact that universe has expanded from a point to this 100 billion light-years long universe has to do with the principle of thermodynamics, also. We shall come to appreciate this particular fact later on when we shall know more about thermodynamics.

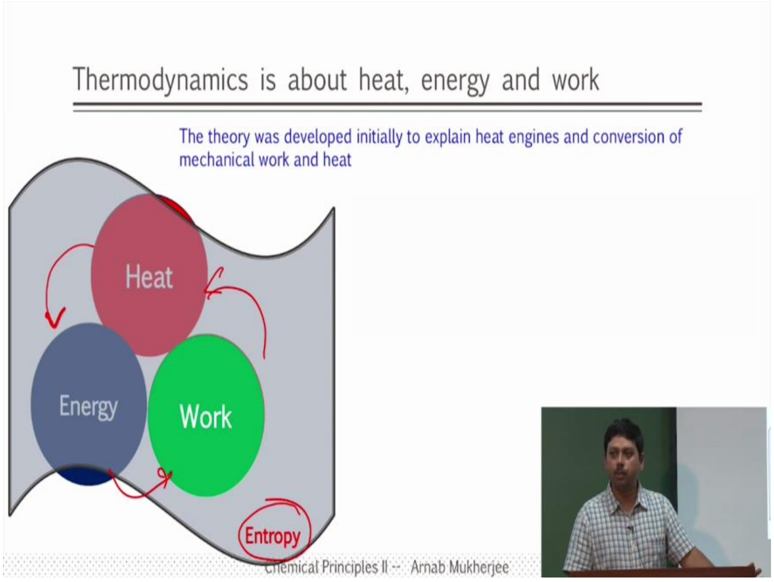
(Refer Slide Time: 14:57)



The subject of thermodynamics came into existence because many scientists tried to make efficient engines around 17^{th} to 19^{th} century. During war and many other things, they tried to make engines that will run with more efficiency like systems where we put some heat and then we shall get some power out of it. So, thermodynamics is basically *therm* plus dynamics: *dynamo* which is heat and power.

It is all about how to convert heat to power or heat to work and vice-versa. So, that's where the name thermodynamics actually came. Engines are basically converters of heat to work. So, electrical engine will convert electrical energy to work, battery will convert chemical energy to work, refrigerator will use electrical energy and do the work and cool the system. Refrigerator is typically the opposite one where we do the work and get the heat out. So, when we talk about engine there can be two types of engine: one is internal combustion engine which is there in our cars and another is external combustion engine which is there in trains with steam engines. In steam engines we put coal, we burn the coal, and the heat will make the water to vaporize into steam and the steam will put pressure on the piston. Then piston will do the movement. So, how much coal we need or how much heat we need in order to convert to work essentially depends on efficiency. So, the origin of thermodynamics came primarily at that point in search of a better engine. The efficiency of one particular engine again is dictated by laws of thermodynamics.

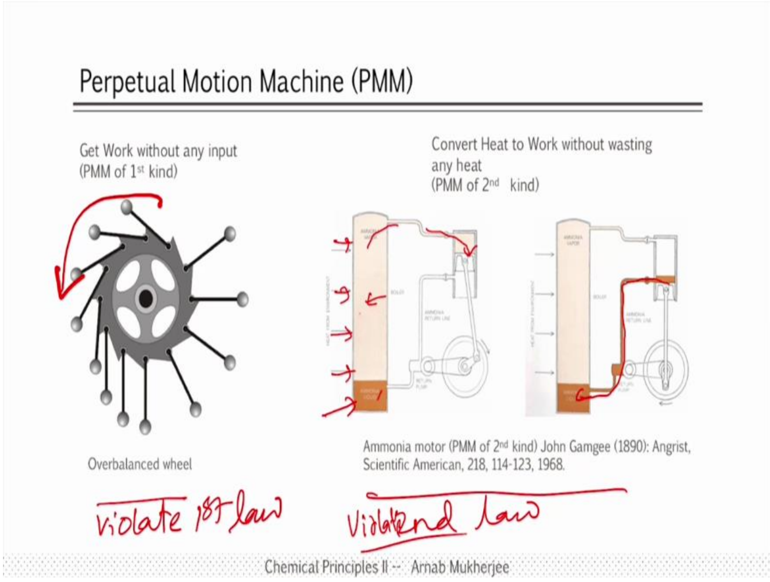
(Refer Slide Time: 16:59)



So then to summarize we can say that thermodynamics is nothing but conversion of heat to work to energy: these three things. So it will just go from one point to other and all other possible combinations. These three things, if you narrow it down to the smallest possible things, then we shall see that this principle is giving us a guidebook on how to convert heat to work, work to energy, energy to work, energy to heat. We are keeping heat and energy separate right now for a reason. We shall see that all these processes are in reality governed by something called entropy. So, this entropy can be thought of as a gatekeeper. So when the gatekeeper will open the gate anybody can go. So, when the gatekeeper entropy will open the gate for heat to be converted to work then only it will happen, otherwise it will not happen.

Thermodynamics is a term which is coined by William Thomson in 1854. He synthesized a subject of Carnot's motive power of heat and Joule's mechanical equivalent of heat and Clausius mechanical theory of heat into a subject called Thermodynamics. Right now we don't know about them but we will come to know about them as you go along the subject.

(Refer Slide Time: 18:29)



Another interesting thing about thermodynamics is that many people tried to make better engines at around 18th and 19th century. Here better means the most efficient engine is where you don't have to put any energy, and you get the work out of it. It is called Perpetual Motion Machine. So Perpetual Motion Machine is something where things will automatically happen.

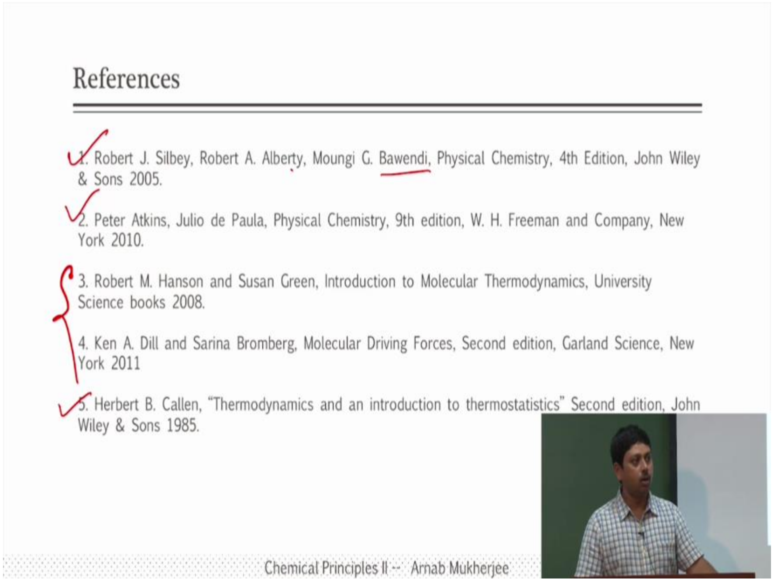
Example for a Perpetual Motion Machine is: let's say there is an over balanced wheel. So, this wheel is such that it will only rotate on one side and not on the other side. If we design something like that, imagine that if you can rotate the wheel in one direction you can get work done out of it and the way it is design it is supposed to move only in one direction. And therefore it will supposed to get work out of that. So, this is just one example.

Several others have tried to make Perpetual Motion Machine and ask for a patent. However, the US patent office has stopped taking application for such patents because thermodynamics says that it is impossible to make a Perpetual Motion Machine. In case where a Perpetual Motion Machine produces work without input, it will be called a Perpetual Motion Machine of first kind. However, there is second kind of Perpetual Motion Machine that is possible, hypothetically which will violate 2nd law of thermodynamics. Although the 2nd law of thermodynamics has not been discussed yet, still we can say that this kind of machine will give as much output as the amount of input without any wastage. This violates the 2nd law and therefore is not possible to make in reality.

An attempt to make such a machine was done by John Gamgee in 1890s which is called ammonia motor or zero motor. Here liquid ammonia at -33^{o}C is used and filled in a container. When this is exposed to sunlight, it vaporizes and forms ammonia gas, resulting in increase in pressure. This pressure will provide a push to an attached piston. Thus by providing only sunlight as an energy source, some work is getting done. However, in this machine, in order to get the liquid ammonia back, extra work will needed to be done. This was not considered in the original design. Hence this cannot be claimed to be a Perpetual Motion Machine. In case of refrigerators, external work is done to obtain cooling. Hence, without performing any work, it is not possible to pass heat from a low-temperature system to high-temperature system.

And John Gamgee did not think about that, okay! That is very unfortunate; he had to suicide later on. But he convinced and he got a patent for this. I think this is the, I…you know I am not 100 percent sure but this is the first and last patent that…that anybody got on Perpetual Motion Machine. But it never worked. In fact you will know, you will be convinced knowing thermodynamics that it is not possible to make a Perpetual Motion Machine.

(Refer Slide Time: 24:23)



The books that will be useful for this course are listed below:

1. Physical Chemistry by Silbey, Alberty and Bawendi and,

2. Physical Chemistry by Atkins.

These two books will be useful for classical thermodynamics part. For the molecular thermodynamics part, two books by Henson and Green, and by Ken Dill will be useful. Also the book by Callen, where thermodynamics has been discussed in a postulate based approach will also be useful.

Some demos for energy conversion will be discussed next. Examples for such energy conversions are present everywhere. For example, if we rub our hands together, heat gets generated. Here the mechanical energy is getting converted to thermal energy. The demos shown will show the following:

1. In one case, solar energy will be converted to sound energy;

2. In the second case, solar energy will be converted into light;

3. In other case, mechanical energy from wind will be converted to electrical energy where rotation of a fan will be used to switch on a small bulb;

4. In the final demo, mechanical energy from water flow will be converted to electrical energy. Here a fan will be rotated by flowing water and a light has been lit in the process.

In the final demo, conversion between chemical energy into mechanical energy will be shown. For this purpose, we connect two electrode to a solution and the electrodes are connected to a motor where a fan is attached. Now, in the liquid water where the electrodes are kept, some amount of glucose is added. However, this does not make the fan to move. Note here that it has been discussed that glucose is the main source of energy in the living cells. However, here the chemical energy of glucose does not convert to sufficient electric energy to move the fan.

Next, some amount of sodium chloride has been added to the solution. By addition of this, the fan is seen to rotate. Here, due to formation of ions by sodium chloride, the chemical energy from sodium chloride gets converted to electrical energy and this results in rotation of fan. All of these demos highlight the point that all processes are governed through thermodynamic principle.

However, in these processes, the amount of energy used as input and the resulting energy obtained as output are needed to be checked. These values will tell us the efficiency for these systems. Thermodynamics says that a machine with 100% efficiency is not possible. Therefore always in a process, some amount of work or heat remain unused. All such unused work or heat contributes to the change in entropy. Since in every process taking place in the universe, this entropy is getting accumulated, we can say that it is an un-conserved quantity. More on these topics will be discussed in the coming lectures.