Chemical Principles II

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History of Thermodynamics

In this lecture, a brief history on thermodynamics will be discussed. Unlike many other subjects like classical mechanics, thermodynamics has been developed by contribution of several scientists throughout more than one century. However, only in the 19^{th} century, the subject was actually formulated. We shall be discussing how the 1^{st}, 2^{nd} and 3^{rd} law of thermodynamics came into existence, out of which 2^{nd} law is the most interesting and intriguing. We shall see later that if we know the 2^{nd} law, then we can arrive at the 1^{st} and 3^{rd} law.

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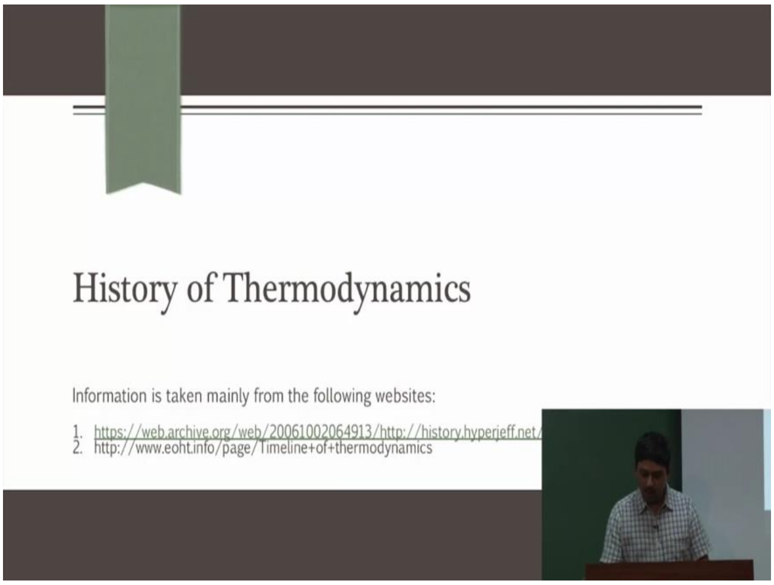

So we will talk about history of thermodynamics.

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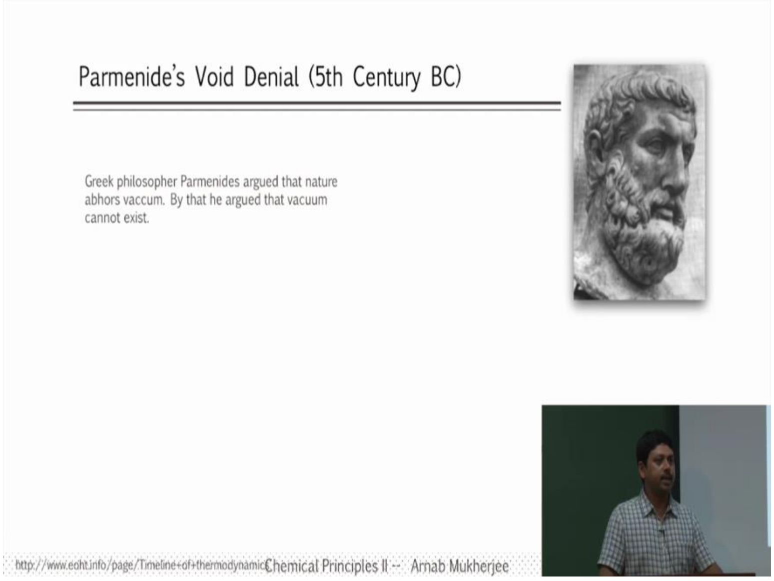

The history started with Greek philosopher called Parmenides who said that there cannot be any vacuum anywhere. It was said that nature abhors vacuum. Although this idea may seem trivial at this point, it was not the case in the 5th century BC. Later on, this idea of non-existence of vacuum has been used by others to make engines.

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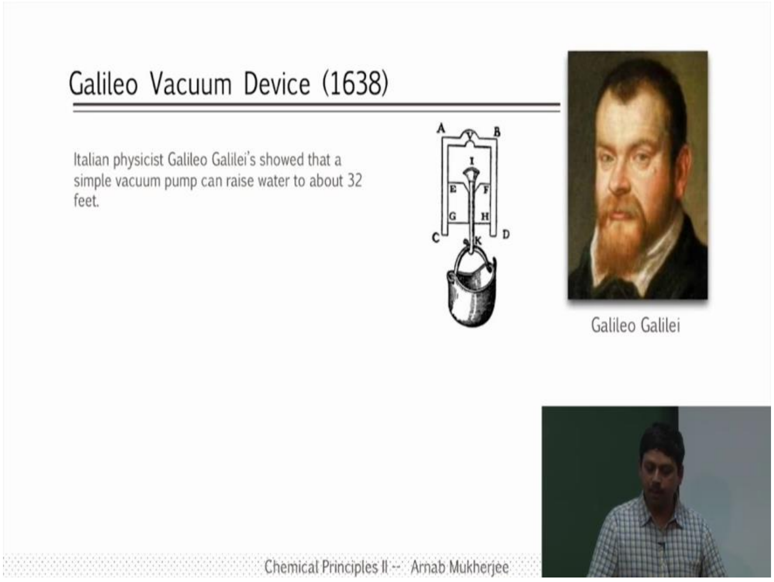

For example, in 1638, Galileo showed that by using a vacuum pump, water can be raised and water pump can be made.

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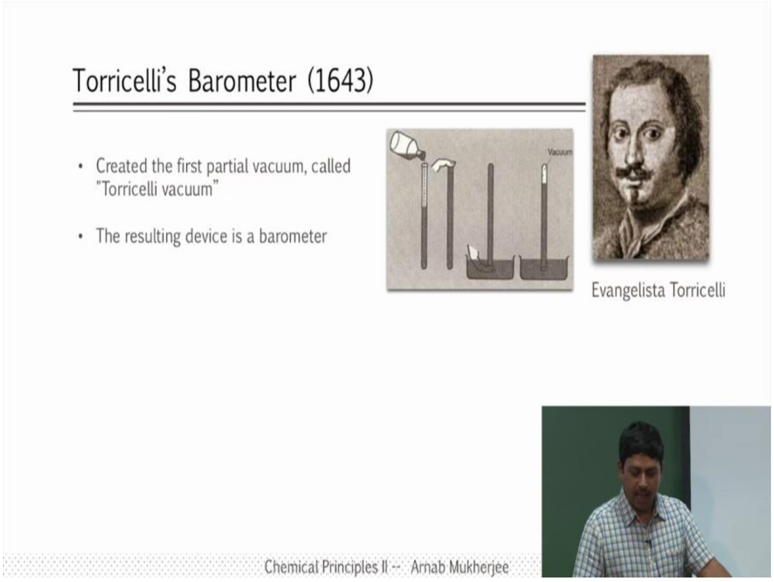

Later Torricelli tried to create vacuum by putting mercury inside a small tube. And then this tube was kept on mercury. When the mercury was removed slightly from the tube, he believed that a vacuum got created at the top of the tube. So, this is similar to a barometer where air pressure is measured. However, at the top of the tube, it is not actually a vacuum.

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Then a scientist called Guericke used demonstrated the power of vacuum by something called Magdeburg hemisphere. This Magdeburg hemispheres consist of two hemispheres. In his experiment, he used a vacuum pump to take out the air from inside of this hemisphere. Then he put the hemisphere and used 24 horses on both sides to pull the hemispheres. It was found that even with such power, it was not possible to separate the two hemisphere because of the vacuum that was created inside.

Here we will use a simple demonstration to show this. We shall create a vacuum here and show how hard it is to pull two hemispheres joined together by vacuum.

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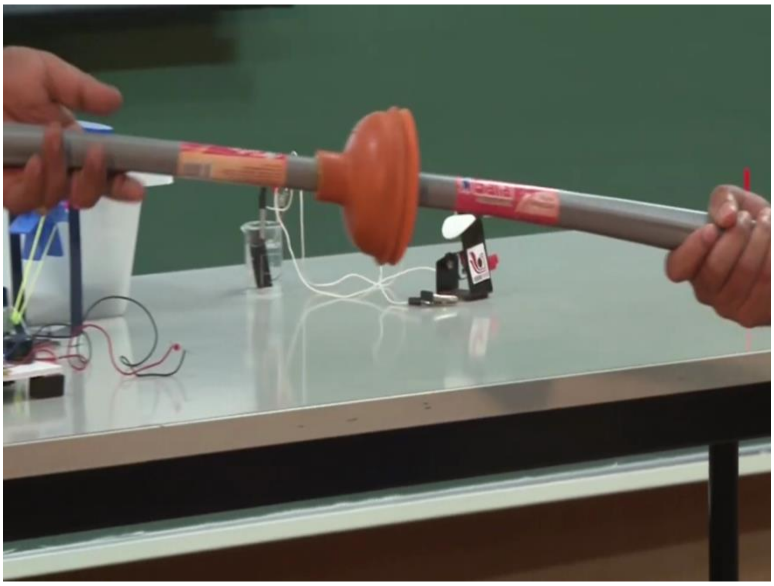

In this experiment, we can see that even when we apply strong force, still we cannot separate these two. This is because of the vacuum that has been created inside. However, this material can deform. Therefore it can bent and make way for air to come inside. That is why, unlike the Magdeburg hemisphere, this can be separated easily.

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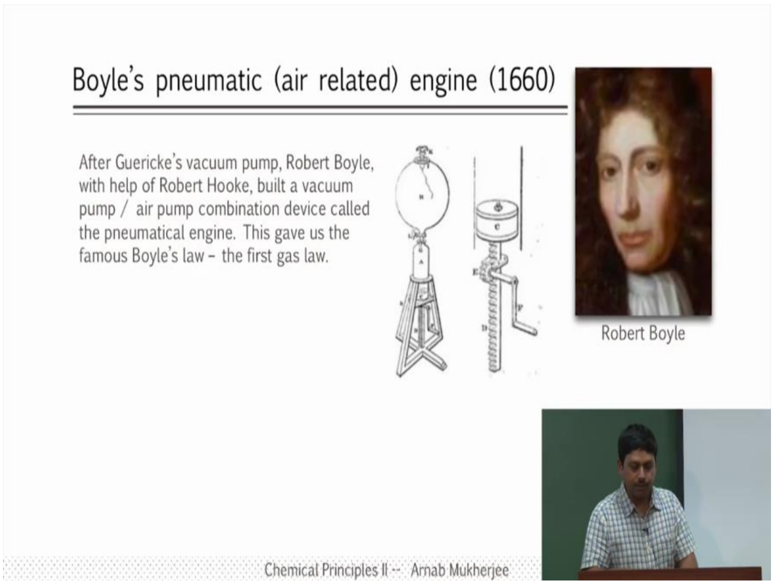

Soon after, Boyle, who gave the famous Boyle's law used a device called pneumatical engine to derive the Boyle's law. This law states that pressure is inversely proportional to volume. This relation was obtained using this particular engine in 1660.

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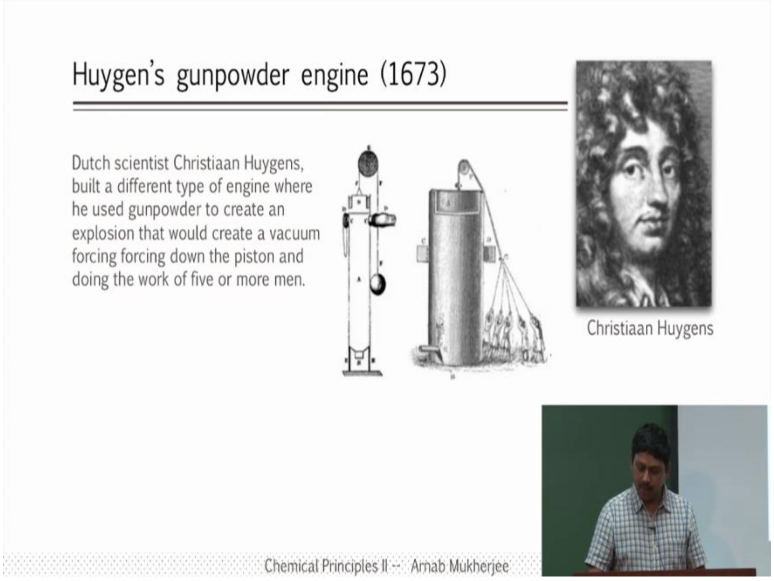

Few years later, Christiaan Huygen used gunpowder to create vacuum by explosion and using this vacuum, he could move a piston. This piston could be used to do work that is equivalent to work done by 4-5 persons.

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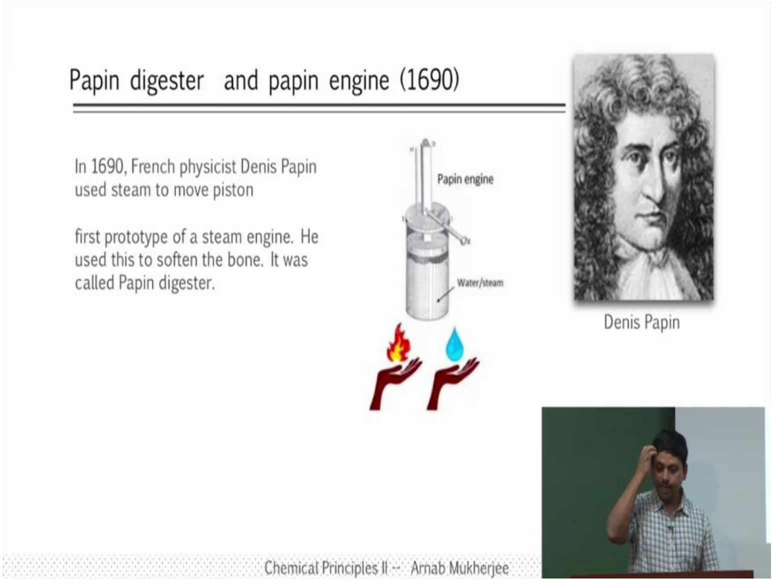

In 1690, French scientist Papin created a prototype of steam engine which is called Papin's digester. It is similar to a pressure cooker which is used to digest bones. It follows a two-step process: first it is heated to make it expand, then it is cooled to bring it back to its initial stage. In an engine, there will always be a cyclic process happening where the system must come back to its initial state after doing the work. This engine was very helpful in developing thermodynamics because later on Carnot used a better version of this engine.

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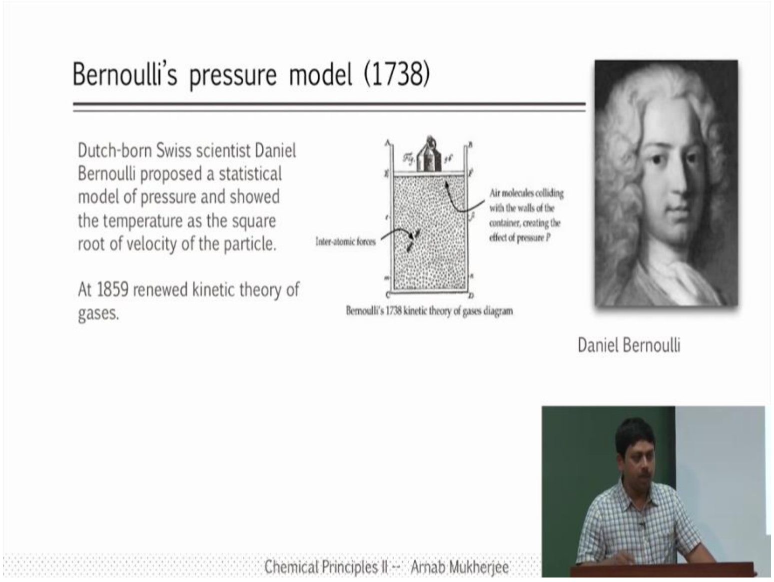

About 50 years later, Beroulli used a billiard ball model to talk about statistical description of pressure that the pressure is nothing but forces that is exerted by individual particles. Although he proposed this idea at around 1730, but it was totally forgotten for a long time. Later on Maxwell actually revived this idea and it gave rise to kinetic theory of gas. However Bernoulli for the first time was able to give this notion that ensured the temperature is actually square root of velocity, we will talk about this later on.

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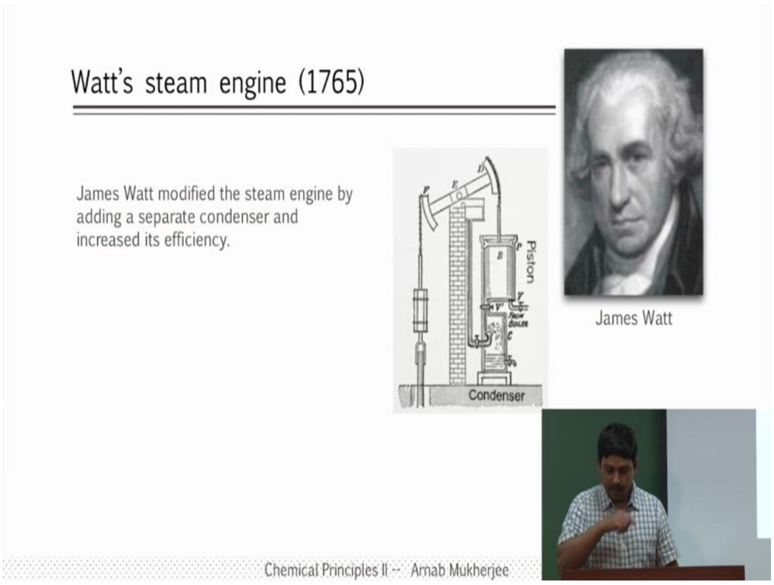

In the 18th century at around 1765, James Watt built a steam engine where he improved the idea of an engine by putting an extra condenser. In this way, the heated steam could be cooled much more efficiently and the engine could return to its initial stage much more easily. This improvement in the design made the steam engine much more efficient. Hence, this was James Watt made his contribution to thermodynamics and it is known as: Watt steam engine.

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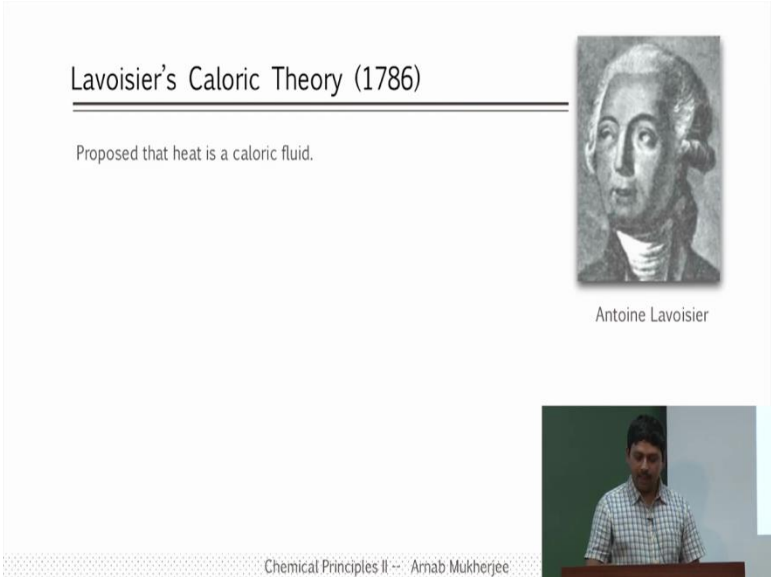

Around that same time, Lavoisier claimed that heat is nothing but some kind of a fluid called caloric fluid. This means when we heat something, for example when we heat water then that fluid goes into the water and heats the system. However, Lavoisier's caloric theory was disproven by Thomson.

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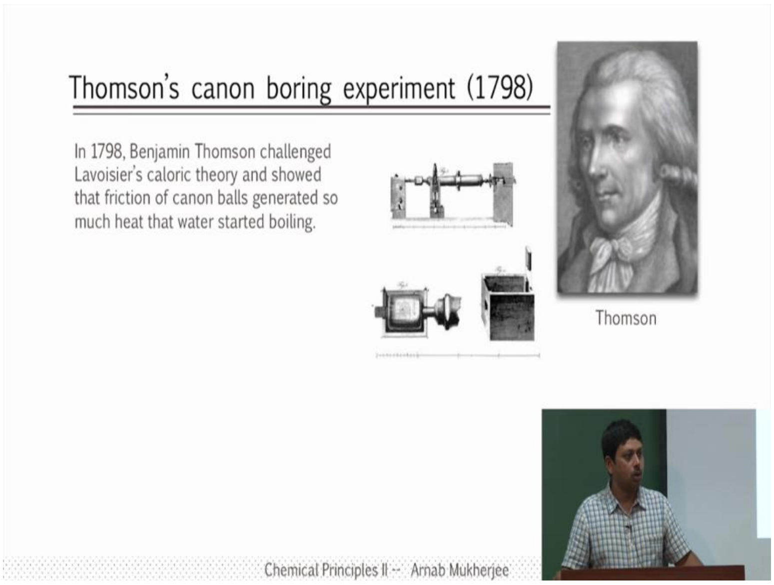

Thomson used Cannon boring experiment where he used boring. This means that he tried to make a hole with a cannon ball in a container filled with water. The process generated so much heat that the water in the container started boiling. Thus, he showed that this mechanical energy of boring can give rise to heat which means that heat is no longer some other fluid; it has something to do with particular mechanical work that was done.

He was the first to indicate the relation between mechanical work and heat. Although, right now it is very obvious but at that point of time it was a big discovery.

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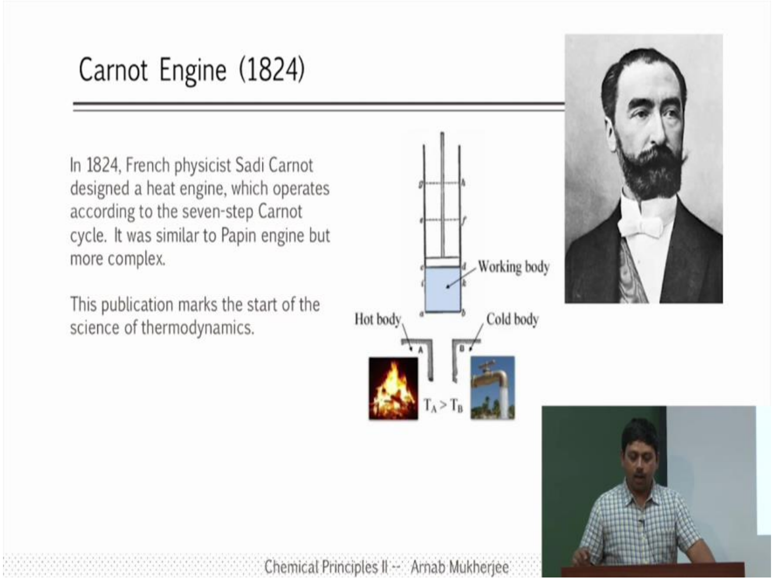

Then came Carnot engine in 1824 where the Papin's engine was modified to make a 7 step process. We will discuss about Carnot engine later on because it's a one of the most efficient engine possible, although it is the most efficient engine.

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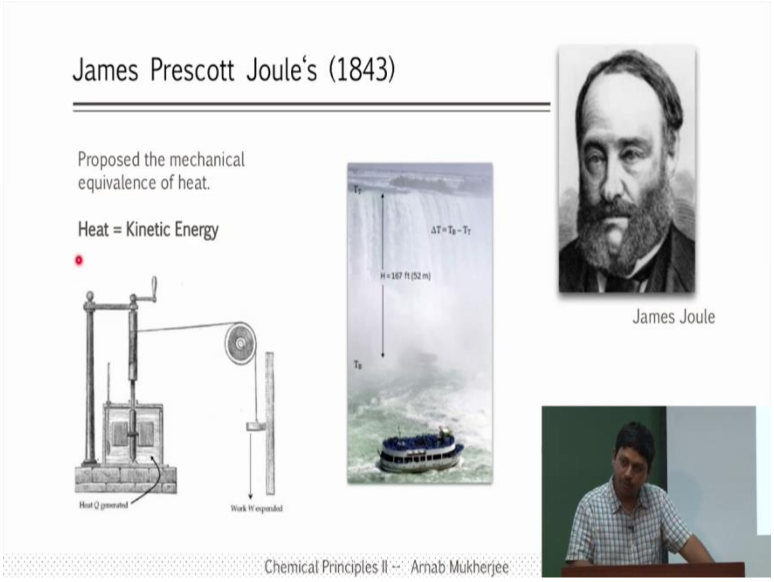

Later in 1843, Joules showed that heat is equivalent to kinetic energy. He used an experiment known as paddlewheel experiment which will be shown later on. He hypothesized that when a substance fall from a height, the kinetic energy gets converted in to potential energy. To prove this, he wanted to measure the temperature at the top and bottom of Niagara falls.

When the measurement of temperature was done on a normal day, it was found that the temperature is very similar at the top and at the bottom. However, when the measurement was done on a cloudy day, it was found that the temperature at the bottom is higher compared to the temperature at the top. The explanation for this is, because of the 52 meter fall, the kinetic energy of water gets converted to potential energy which causes the temperature change. This particular experiment is related to first law of thermodynamics which will be discussed later.

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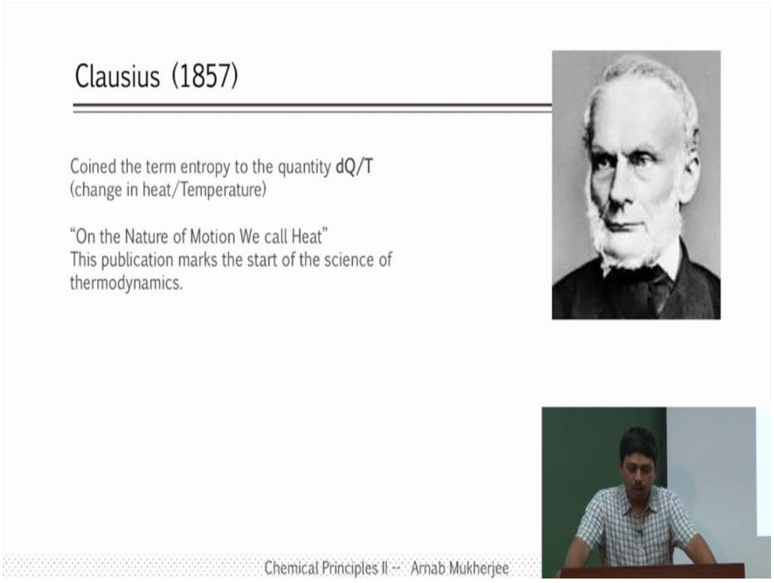

Clausius at around 1857 defined precisely a quantity: $\frac{dQ}{T}$,

Where dQ is the heat change and T is temperature. This quantity is defined as entropy.

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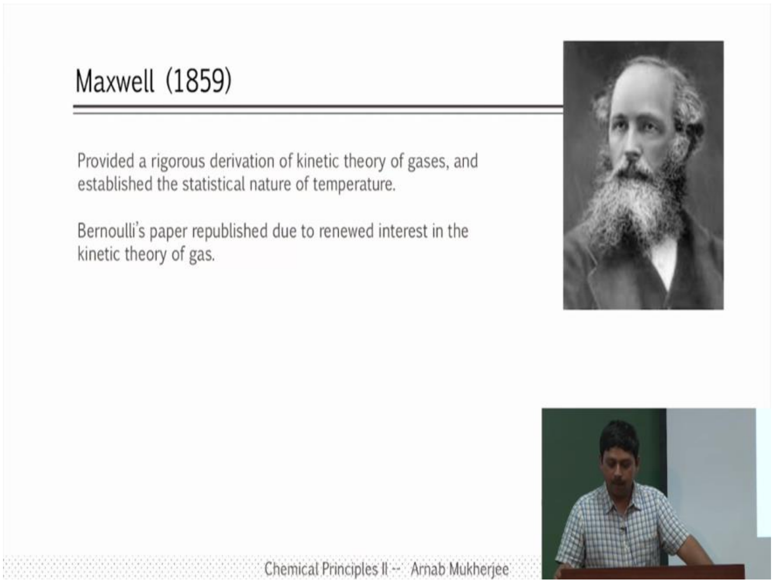

Then Maxwell gave rise to the kinetic theory of gases where precisely one can see the relation between the motion and the temperature that we normally associate with a particular system.

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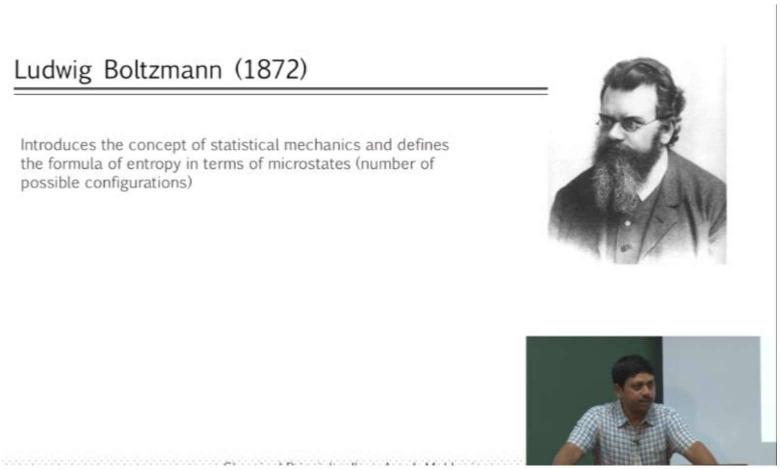

Later on around 1872, Ludwig Boltzmann developed formulation of statistical thermodynamics where all the observations that we have for a big system can be understood from the motions of individual atoms itself. This gave rise to a subject called statistical thermodynamics. We are going to also discuss a little bit of that.

There were several others who were not mentioned in the discussion. However, they also had important contribution. So therefore the importance of this particular theory is undeniable.

Einstein also had said that thermodynamics is one of the subjects that cannot seem to be overthrown so easily, it’s a solid theory.

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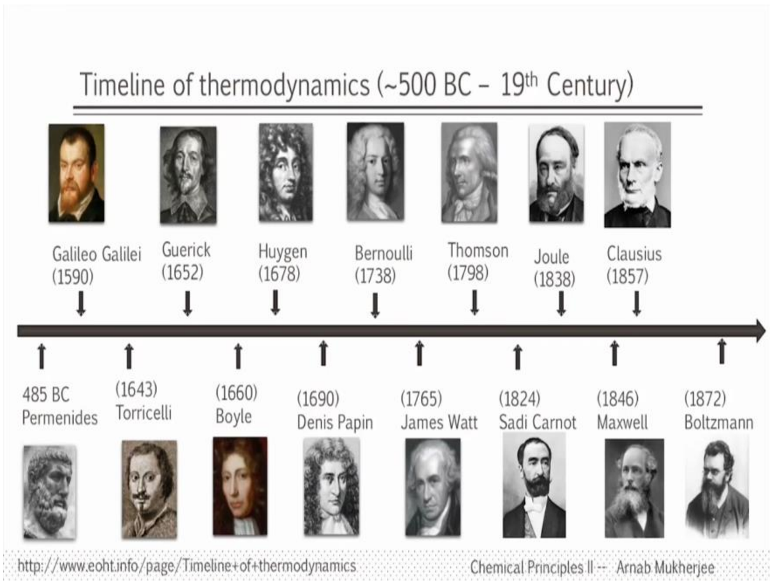

So this is a summary of the progress with time again as I said that there are a lot of other scientists contribution which are not mentioned here. We tried to give as many important contribution of people here as possible.