Introduction to Chemical Thermodynamics and Kinetics

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Lecture – 01
Introduction to Chemical Thermodynamics and Kinetics

Welcome to the first lecture of our course which is titled as Introduction to Chemical Thermodynamics and Kinetics. We will first give you a brief history of classical thermodynamic to begin with. Now when we start touching a thermodynamics or talking about thermodynamics or chemical kinetics, let us first discuss what physics is all about any physics or any physical science or physical chemistry deals with constant interaction between energy and matter because matter and energy are constantly interacting between themselves.

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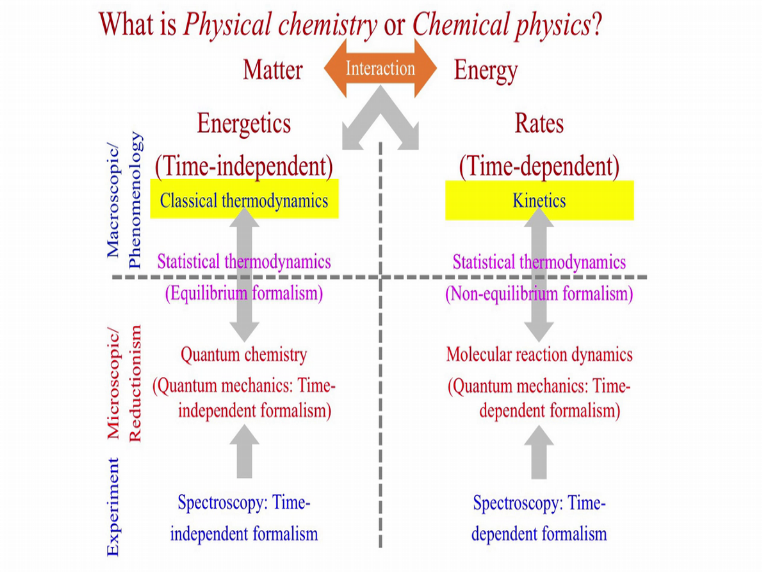

What is *Physical chemistry* or *Chemical physics*?

Matter ⟷ Interaction ⟷ Energy

Energetics (Time-independent)

Rates (Time-dependent)

Macroscopic/ Phenomenology

Classical thermodynamics

Kinetics

Statistical thermodynamics (Equilibrium formalism)

Statistical thermodynamics (Non-equilibrium formalism)

Microscopic/ Reductionism

Quantum chemistry (Quantum mechanics: Time-independent formalism)

Molecular reaction dynamics (Quantum mechanics: Time-dependent formalism)

Experiment

Spectroscopy: Time-independent formalism

Spectroscopy: Time-dependent formalism

Now, the question is at what level you want to understand or study this interaction now you can think of energetics which is a time independent process and you can also talk about kinetics or how this exchange of interactions is happening with respect to time where we talk about the rate which is at inherently time dependent process. Now the question is how will you propose a model that will satisfactorily explain the phenomena which we observe.

Now interestingly or chemical kinetics or the classical thermodynamics was developed in the same way where people tried to explain some something which is phenomena and they tried to develop an approach which is known as phenomena logical approach, where you observe a particular phenomena and you try to explain based on some logical footing. The same way chemical kinetics was also developed and, but here the important thing here is the they do not need any fundamental understanding or any understanding of how the microscopic world looks like meaning you can actually describe the entire thermodynamics and chemical kinetics in a macroscopic way, where they it is not necessary to build a model of microscopic understanding.

For example how a material or a how a matter is made up of we know that matter is made up f atoms and molecules, but that concept is not absolutely necessary as long as we are dealing with some explaining some experiments which are macroscopic in nature. Now similar concept also applies to reaction kinetics so or understanding of the microscopic world is has been started with a development of quantum mechanics and there we talk about again time independent processors, where we talk about the energetics or the energy levels of atoms and molecules.

Similarly you could also ask how the these molecules interact with themselves when they say for example, collide if they themselves among themselves, how one molecule transforms into an another molecule and that is the basis of chemical reactions and you can ask this question what is the time dependent process and how a particular molecule evolves into another molecule then you talk about dynamics of the process that is also inherently dynamics.

So, what I have seen now what I have shown on this slide you can you can see here that you have 4 quadrants on your top left quadrant we are talking about the energetics, which is the content of this course or the major part of this course, which is classical thermodynamics and on your right end top side you see the position of chemical kinetics where we will be discussing with kinetics again from a microscopic phenomena logical point of view. And the horizontal line actually differentiates between this macroscopic approach and the microscopic approach whereas, the vertical line differentiates between the 2 other approaches like whether you are talking about a time independent process or a time in dependent process.

Now, our fundamental understanding of microscopic world is dependent very much on the studies of spectroscopy by spectroscopy it can be optical spectroscopy it can be other forms of spectroscopy when we shine some light on the molecules and we know that molecules are particular energy levels. So, then you will actually see not a continuous absorption from this molecules, but a discrete lines of in the absorption or the emission spectre and that is how quantum mechanics was emerged. And there we again talk about time independent formalism of quantum mechanics where we talk only about the energy levels of the atoms and molecules, we could also talk about time dependent formalism of spectroscopy when it want to study something like reaction dynamics.

Now, the bridge between this macroscopic realisation and this macroscopic observation is statistical mechanics and similarly just like we discussed the time independent process. So, we can have an equilibrium formalism of statistical mechanics, where you talk about the energy levels of atom atoms and molecules and then you ask can we actually build up from this fundamental principle of the in AB Intitio way all these macroscopic variables or observables are all these thermodynamics properties.

And that connection is equilibrium statistical mechanics or equilibrium sometimes we call it as equilibrium thermodynamics. Similarly you could have a non-equilibrium formalism of thermodynamic, where you start with a molecular reaction dynamics starting with a time dependent quantum mechanics and then you can actually explain the rates of macroscopic processes which you had already described phenomena logically.

So, this slide describes the overall picture of how one can actually taken an macroscopic approach processes or macro microscopic approach to describe either a time independent processes or time dependent processes. Now we will restrict our self to this section which I have highlighted here. So, we will only discuss about classical thermodynamics where the understanding of the microscopic world of the understanding of the very much working of how the microscopic is not absolutely necessary; however, we will give you some examples just to clarify few concepts.

So, are we will use very brief idea or very preliminary ideas of quantum mechanics and then we will explain some of these phenomena. Similar things also happens for kinetics we will be only discussing with the classical kinetics or the phenomena logical rate equations and try to describe the reactions or chemical reactions in terms of a macroscopic view point.

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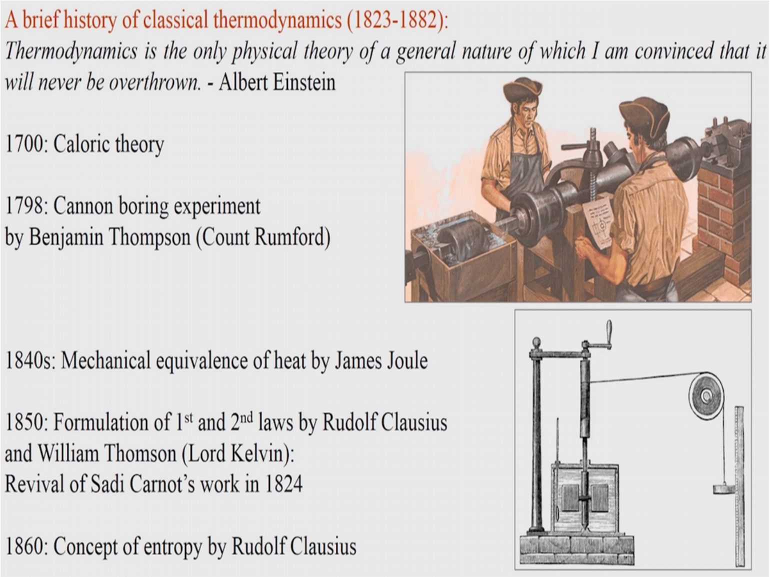

A brief history of classical thermodynamics (1823-1882):

Thermodynamics is the only physical theory of a general nature of which I am convinced that it will never be overthrown. - Albert Einstein

1700: Caloric theory

1798: Cannon boring experiment
by Benjamin Thompson (Count Rumford)

1840s: Mechanical equivalence of heat by James Joule

1850: Formulation of 1st and 2nd laws by Rudolf Clausius
and William Thomson (Lord Kelvin):
Revival of Sadi Carnot's work in 1824

1860: Concept of entropy by Rudolf Clausius

Now, to talk about the classical thermodynamics or the development of the classical thermodynamics we will mostly the describe the core years meaning 1823 to 1882 where major developments in thermodynamics happened.

Now, the concept of heat and work was already established and then I mean by 1600 or so, but we are choosing this particular period because the reason is during this period lot of great minds appeared in the history of science and they contributed a lot in the development of thermodynamics. Now thermodynamics is one of the very classic subjects.

So, in the sense that it is it is foundations are very strong and it is very much experimental in driven science people are did some experiments and they observed something and then they formulated all this observation by a set of very simple laws which we will discussing throughout this course. Now we to begin with start with a quote by albert Einstein and he once said thermodynamics is the only physical theory of a general nature of which I am convinced that it will never be over thrown.

Now, this statement shows the how rigorous or how the strong thermodynamics or it is logic are built are in. Now as I said that by 1600 already the concept of heat and work was established, but around 1700 or so there was a theory called caloric theory, which is to say that heat is a form of fluid that transforms from one body, to another body and the presence or absence of the caloric actually dictates the temperature of the body.

Now, although there are some experiments which refuted the caloric theory most of the people were are scientist or actually accepting that theory that point and then finally, 1798 or so Benjamin Thompson who is also known as count Rumford did a fantastic experiment, what he did is that count Rumford observed that when we boring the cannon or the making barrels of canon by making a holes making holes inside that piece of metal, he found that lot of heat is generated and he connected he Deviced an experimental arrangement where we connected this bore of the cannon to bucket of water and he found that actually water boils from that he concluded that there is a mechanical equivalence of heat.

Now, this tried to realise is very important concept because earlier people used to think that boiling of water is possible only in the presence of fire and count Rumford showed that no actually do not need 5 even if a mechanical work which is just a boring of a cannon can actually produce enough heat that can boil the water.

And this was the very important concept, but which actually reputed caloric theory, but the final disposal of the caloric theory came with a experiments by James Joule and who again made a very nice experiments we will discuss this experiment in detail when we will be discussing the first law of thermodynamics and joule actually made an arrangement, where he was making a lifting or actually falling some weights in a in the surrounding and that ha weight was connected through a well to a paddle system and the if the weight actually falls from a higher latitude to a lower altitude.

Then the paddle will rotate and that will increase the temperature of water which within which the paddle was emerged and from this experiment Joule very convincingly proved that there is a mechanical equivalence of a between heat and work. Which means that if id o some machine work which can be a pressure volume or which can be a displacement work which are all connected that can also produce heat and that can actually warm up water, it is similar to what count Rumford did, but here actually by from this experiment Joule also quantified the pressure volume work with work with a amount of heat produced and which lead to the formulation of first law of thermodynamics.

Now, by 1840 it was very well known from joules experiment that this caloric theory is wrong, but around 1950s then to great figures in thermodynamics appeared Rudolf Clausius and William Thomson who is also ha known as lord kelvin.

So, they theoretically or basically formally derived all these or formulated all these laws into 2 basic laws which are known as first law and second law of thermodynamics, based on the experiments of joule and count Rumford. And the second law they actually I mean it they the second law actually stemmed from the experiments from French engineer named Sadi Carnot which will be will be discussing about these experiments. When we discuss about the second law now Carnot experiment was done long time back in 1824, but nobody actually realised that time that the importance of his work and later on Clausius and Kelvin they revived Carnots work and they said that this is the foundation of second law of thermodynamics.

So, Clausius and Kelvin had a several statements of the on the laws of thermodynamics which are of course, equivalent statement and will be discussing about those statements of the first law and second law. There is also a law called the Zeroth law of thermodynamics which was actually realised later that the more fundamental thing other than the first law or the second law is the concept of temperature, that if 2 bodies are of same temperature or there may not be any heat flow between them or 2 bodies are in thermal equilibrium they will have the same temperature. So, that was realised much later and that is why by that by that time already Clausius and Kelvin talked about first law and second law and people realised that this concept of this temperature is more fundamental.

So, let us call it as a Zeroth law because already people have chosen the names first law and second law and there is also another law of thermodynamics which is third which we will not be discussing in this course that talks about the irreversibility of a this process or the spontaneity of the process that was developed by (Refer Time: 13:49).

And then interestingly around 1860 Clausius gave the fantastic concept of has state function which he called as entropy and he showed that for any irreversible process, which are any spontaneous processes by the irreversible in nature he showed that you can think of that the entire system and entire process will have them if the entropy of the uni phase is ever increasing and that is known as Clausius inequality which also will be discussing detail how we can actually derive Clausius inequality from Carnot cycle.

Now, Parallelic to the thermodynamics also can the kinetic theory of gases which was very very important because in many cases we will be giving the examples based on very simple system or very simple idealised system like a ideal gas confined in a container and for that development.

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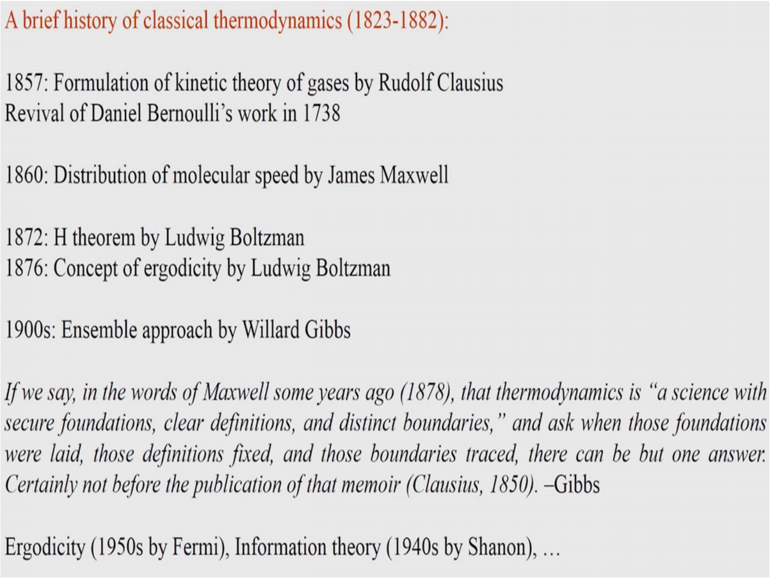

A brief history of classical thermodynamics (1823-1882):

1857: Formulation of kinetic theory of gases by Rudolf Clausius
Revival of Daniel Bernoulli's work in 1738

1860: Distribution of molecular speed by James Maxwell

1872: H theorem by Ludwig Boltzman
1876: Concept of ergodicity by Ludwig Boltzman

1900s: Ensemble approach by Willard Gibbs

If we say, in the words of Maxwell some years ago (1878), that thermodynamics is "a science with secure foundations, clear definitions, and distinct boundaries," and ask when those foundations were laid, those definitions fixed, and those boundaries traced, there can be but one answer. Certainly not before the publication of that memoir (Clausius, 1850). –Gibbs

Ergodicity (1950s by Fermi), Information theory (1940s by Shanon), …

The first formalism again was given by Rudolf Clausius around 1857, but he basically revived the very early work by Daniel Bernoulli another French scientist, who did all this important work on kinetic theory of gases around 1738 or so and there are also parallel development if you remember from you high school studies like Boyles law and Charles law and also the combination of this Boyles and Charles law to get the these universal gas law which was applicable for ideal gases only. And then people also realised the deviations from ideal behaviour and where people proposed many models that also will be discussing in this course.

Now, for around 1860 or so, in stemming from this kinetic theory of gases Maxwell gave a idea how one can calculate the distribution of molecular speed, because Kinetic theory says that a gas molecule a gas actually microscopic system is composed of molecules which are of in random chaotic motion and that how will you describe the motion of this molecules. And how will you get a formula to describe what is the average speed of these molecules for particular temperature.

That actually you can derive using the prescription by Maxwell and later on 2 important theories were put forward by Ludwig Boltzman and he found that you can actually start from Maxwell's distribution of molecular speed and you can show that the entropy some quantity which is equivalent to entropy can actually increase with respect to time for any equilibrium or non-equilibrium system. And that was the catch in Boltzman's theory and that is usually known as H theorem, but there was an inconsistency initially because Boltzmans theory fundamentally assumes the reversible nature of collisions.

Then it predicts or then it predicted that actually spontaneous process can also be can also run in reversed direction, which is contradictory with Clausius statement that any spontaneous process entropy increase entropy of the universe.

So, to survive his moral Boltzman later on put forward another important concept in statistical thermodynamics, which is known as concept of Ergodicity we will not discuss this theories in detail because we will be only confining ourselves to the macroscopic description of matter and energy and then this is just to let you know that along the same line along 1900 or so Willard Gibbs put forward his very monumental work on classical statistical thermodynamics.

Where he introduced the concept of ensemble and what is said the essence is that if you look at a macroscopic system and if you think of there are many microscopic system are composing this entire macroscopic system. Then every microscopic state if you watch particular microscopic state or realisation of the system over time that will actually you can actually think of that is time averaging over sufficiently long time of any microscopic realisation of the system essentially equivalent to saying that we are doing all these microscopic measurement.

So, this will only happen for if the Ergodicity concept is correct and gives correctly showed that there is no alternative approach to statistical thermodynamics, which is known as ensemble approach. And later on so Gibbs formulated in his own way and, but he gave the full credit to Clausius and there are many controversies on this particular aspect or who is the father of thermodynamics, because some people say that that the work actually is inherent in count Runfords work and some people say as no actual the work was actually done main work was done by Sadi Carnot, but what let us see what Willard Gibbs said he said; if we say in the words of Maxwell some words some years ago around 1878 or so the thermodynamics is and he quotes Maxwell a science with a secure foundation clear definitions and distinct boundaries and ask those formalism of were laid. These definitions fixed those boundaries traced there can be, but one answer and that one answer he said a certainly not before the publication of the memoir and this memoir was published by Rudolf Clausius in 1850, where we revived Bernoulli's work where he revived Sadi Carnots work and he basically formulated the entire thermodynamics or classical thermodynamics the way we look at thermodynamics in today.

Now, this particular work of this Gibbs and others laid to foundations of many other branches ins science for example, this Ergodicity was later on rediscovered or reformulated by Enrique Fermi, who was working on some coupled spring problem and he was trying to see how the if the Ergodicity is valid how the energy S, if I dump energy in a particular spring which is connected to many springs how the energy flows.

And he accidentally discovered that actually the energy does not flow in a uni directional fashion the energy actually comes back and forth and then eventually flows, and what he basically discovered is a recurrence phenomena and which in today's modern language we call as the formation of solid items. And parallel to this there were lot of interesting discoveries in information theory, which are particular important for computation and development of the computer science as a whole and then around 1940s Shannon gave a very brilliant idea how we can actually connect the Boltzman entropy with a information content and this is known as information theoretic approach of entropy.

Now we will not discuss all these things this is just to let you know that the classical idea which was developed by Clausius kelvin extended by Boltzmann and then by Willard Gibbs how it also shaped the future of many other areas in modern science and technology.

Now, we will give a very brief outline of chemical kinetics or the classical chemical kinetics, now compared with chemical thermodynamics classical thermodynamics kinetics is more or less a newer field.

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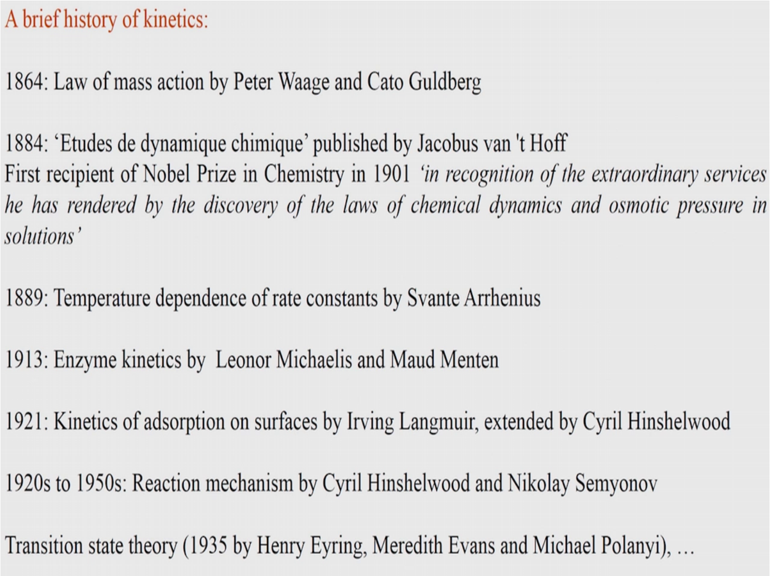

A brief history of kinetics:

1864: Law of mass action by Peter Waage and Cato Guldberg

1884: ‘Etudes de dynamique chimique’ published by Jacobus van 't Hoff
First recipient of Nobel Prize in Chemistry in 1901 *‘in recognition of the extraordinary services he has rendered by the discovery of the laws of chemical dynamics and osmotic pressure in solutions’*

1889: Temperature dependence of rate constants by Svante Arrhenius

1913: Enzyme kinetics by Leonor Michaelis and Maud Menten

1921: Kinetics of adsorption on surfaces by Irving Langmuir, extended by Cyril Hinshelwood

1920s to 1950s: Reaction mechanism by Cyril Hinshelwood and Nikolay Semyonov

Transition state theory (1935 by Henry Eyring, Meredith Evans and Michael Polanyi), …

In the sense that although the concept that, If you want to study the process or the rate of some processes we know that at any instance the rate will be proportional to the activity or the concentration of the substances which is known as the law of mass action, which was put forward by Waage and Guldberg way back in 1864 that it was not very much realised that time.

The first realisation or the first logical formulation of the foundations was put forward by Jacobus Vant Hoff and who published a book on his monumental work on thermodynamics and chemical kinetics in 1884 and that is kind of the beginning of modern research on chemical kinetics Vant Hoff by the way was the first recipient of Nobel Prize in physics in 1900 and 1 and the citation said in the recognition of the extra ordinary services he has rendered by the discovery of the laws of chemical dynamics and the osmotic pressure in solutions.

Now, we will be discussing some of Vants Vants Hoffs particularly his fantastic work on the how chemical equilibrium can be modified or the equilibrium composition can be modified by application of temperature which is known as Vant Hoff equation. Now later on 1889 or so Arrhenius gave a very important concept he started experimentally many reactions and he was trying to find out how the rate constant of reaction whereas, with temperature and he came up with a phenomena logical equation where he tried explain everything or the variation of the rate constant with temperature by introducing a concept, which is known as energy of activation now this was a very very important concept because he said if you have reactants say a and b that will not readily give the product until and unless they cross some react energetic barrier and this barrier exists we know and today we call it as activation energy and this actually stemmed from Arrheniuss; I mean experiments and that expedition for artificial energy or how one can actually include that very cleverly in a model of rate reaction dynamics came much later though.

Now, along the same time the people are also interested in devising some mechanism of the reactions by mechanism, again it is not the microscopic it is again a macroscopic approach where you say that a particular reaction is actually a composite, which can be decomposed into many elementary reactions which cannot be further decomposed and all these elementary reaction together constitute the macroscopic or the composite refraction that we observed in reality.

Now the first such approach was actually applied in a real life example on Enzymes by Michaelis and Menten in 1913 although the concept of chemical reaction mechanism was not very popular by that time, but Michaelis Menten what actually prided the in that sense the chemical reaction mechanism and they showed that how one can conceive a very simple mechanism to understand the initial rates of enzymes how it varies with initial subset concentration.

So, in when you will be discussing the kinetics part we will be discussing this Michaelis menten model in to some much more detail and around 1920es or so Irving Langmuir first came up with a idea how during the reaction between a gas and the in presence of a solid surface one can consider the idea of adsorption. Now it is different from absorption in the sense in absorption molecules actually penetrate the surface and go inside the bulk layer, but what Langmuir gave a concept is the molecules are only stuck on the surface and that laid to a the new field which is known as surface science, which is later extended by the American physicists Cyril Hinshelwood and that is a many people think that this is not only the birth of the chemical the surface science it is also the birth of the chemical kinetics in general.

And later on 2 scientists namely Cyril Hinshelwood and the Russian scientist Nikolay Semyonov they extended they did a monumental work on his reaction mechanism, how one can actually formulate composite reaction and then get all these elementary reactions very logically and try to explain the entire reaction mechanism by adding all these elementary reactions.

Hence Hinshelwood and Semyonov got a Nobel Prize in chemistry for this particular work where they mostly studied what known as chain reactions and then I have written here few historical things which were followed, but this list is really endless particularly when it talk about chemical reaction dynamics. The first conclusive or convincing theory came around 1935 when Henry Eyring Michael Polanyi and Meredith Evans came up with this concept of transition state theory, we will not be discussing the transition state theory in this lecture, because it need it requires some knowledge of statistical thermodynamics, but we will be discussing an alternate approach where you can actually Maxwell Boltzmann distribution and just consider the collision among the gas molecules, and thereby you can say that this how this you can actually formulate or device the rate of reaction and we will also I mean we just conclude our historical or the chronological development here.

So, in the next lecture or the which will be the first lecture of this of this course we will start from the gas we will start from some basic concepts, but before that of thermodynamics, but before that we will first start with a review of the kinetic theory of gases, how you can not kinetic theory how you can actually formulate the gas laws the ideal gas law and also the deviation from the ideal behaviour and how one can actually formulate the equation of state for real gas. Those things will be first discussing and then we will discuss the first law and then the applications of the first law and then second law and in that we will approach.

So, to summarise in this lecture we gave you a brief over view of classical thermodynamics and classical kinetics. Again the we will end what we were we started with remember, we said we just started this discussion with a beautiful has statement by Einstein and who said that thermodynamics is perhaps the only general theory that will never be over thrown.

So, you should always keep that in mind that there has been lot of theories which has been invented like quantum mechanics and many other things which has changed our concept or regarding the perception of this nature of the nature of the universe. However, thermodynamics is still the laws of thermodynamics still holds and they are just Unrefutable they through the work of Clausius Gibbs and many others. So, we will see how this formulism got developed and we will be discussing throughout this course about this thermodynamics and classical kinetics, but we will considering mostly the applications in chemistry.

Thank you