Nanotechnology Science and Applications
Prof. Prathap Haridoss
Department of Metallurgy and Material Science
Indian Institute of Technology, Madras
Lecture - 05
Impact of the nanoscale on thermodynamics considerations

Hello in this class and in the classes that we will look at going forward, we will first begin by looking at the Impact of the nanoscale on thermodynamic considerations. This is important for us to look at in this course because when you look at material science in general and also in any other related field, the starting point is usually thermodynamics.

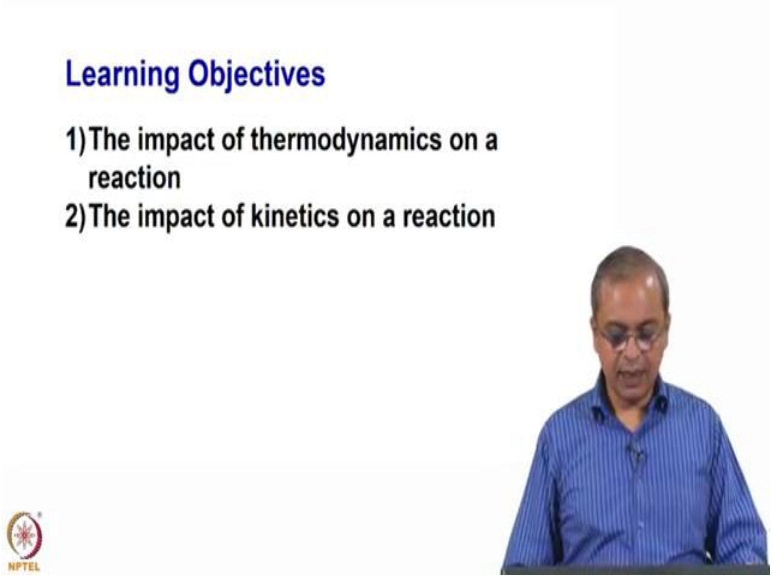
And so, we need to understand what is the impact of nanoscale on thermodynamics. At some fundamental level thermodynamics is the same, we are not really changing anything, but what you will see is that when you learn about thermodynamics in your thermodynamics course. Usually, the equations are written, but they are typically return under some consideration. In other words, it is already addressing a certain type of system maybe you are addressing ideal gases or you are addressing some phase change that is happening and so on.

So, when you write that equation typically focus on the terms that are relevant to that particular system, what is often maybe not immediately apparent is that in that same format you can actually have some more terms which we are not typically writing there. And the reason we are not writing there is that those terms are essentially 0 or are or evaluate to 0 or near 0 in the case of that particular system. And therefore, there is no meaning in writing those terms there and therefore, we do not write that and many of the books put it that way.

So, sometimes when you see that equation you do not realize there is a more detail in that equation which can be added and when you look at systems which are dramatically different from the system that is being discussed in your book, then those kinds of terms may become relevant. And that is the meaning in saying that we need to understand the impact of nanoscale on thermodynamic considerations. It is not that suddenly there is different thermodynamics because you are going to the nanoscale.

Thermodynamics is a much more fundamental science and I mean everything we have learnt about the nature around us, strongly suggest that this is like sort of unifying aspect of across all systems and it does not fundamentally change. So, it is thermodynamics it is just that there are terms that you start paying more attention to.

(Refer Slide Time: 02:50)



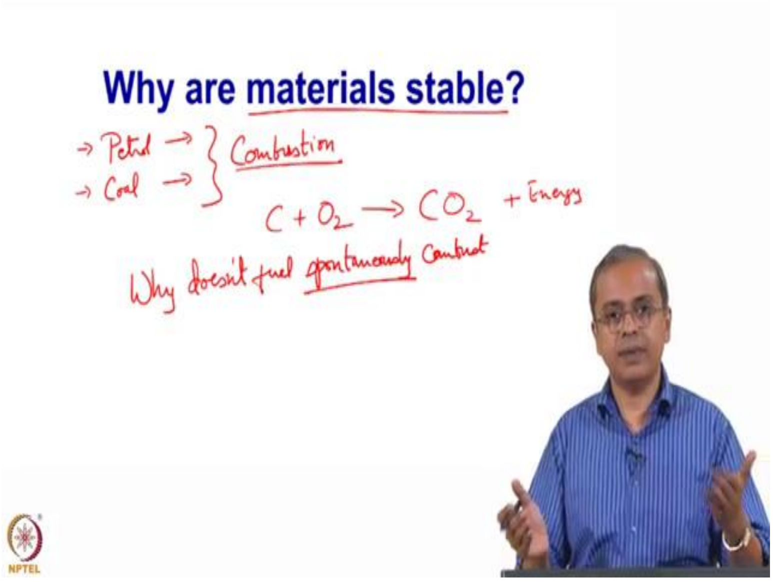
Learning Objectives

1) The impact of thermodynamics on a reaction
2) The impact of kinetics on a reaction

So, in this class we will look at; we will start by looking at the impact of thermodynamics on a reaction and that in a more general sense what is happening when you talk of the thermodynamics with respect to reaction and we will also look at the impact of kinetics on a reaction. These are two very interesting points that you have to understand and we will see why it is of interest to understand both. In fact, one of the other aspects that we have to keep in mind is that just like I mentioned in that in thermodynamic equations sometimes some terms are not indicated because they are not relevant for that particular system under that condition.

It is also true that we sometimes learn about thermodynamics separately in a course and then you will learn about kinetics separately in a different course. And sometimes you do not understand that they are both, I mean that you have to keep both of them in mind when you are looking at a system, and that is sometimes is not immediately apparent. Because they tend to get taught independently and unless you make the connection in your mind you will miss making that connection. So, we will see that through this class.

(Refer Slide Time: 04:08)



Why are materials stable?

→ Petrol →
→ Coal →
} Combustion

$C + O_2 \rightarrow CO_2$ + Energy

Why doesn't fuel spontaneously combust

So, let us begin by asking ourselves this first question, why are materials stable? So, that may seem like a very a simple question why are material stable, but if you think about it there is a lot of interesting detail there. So, for example, let us take any source of energy that we are using today. So, let me just put something. So, we are using petrol.

So, petrol is being converted to energy in our cars and with or in any kind of automobile that we are using petrol, we may be using coal. I mean these days we do not use coal in our houses that time frame is gone, but even today for example, in India significant fraction of the electricity we get is because of thermal power plants which are running of coal. So, coal is actually being used and we are sort of indirectly using coal I mean you think you have come to the modern era. But actually, you are using coal, the power that you are receiving is directly from coal and or significant fraction is from coal.

So, we have not really gone away from that source of energy, so that we are using there. So, how are we getting this energy? So, we are doing combustion. So, we are doing the combustion of petrol in the engine that is there in your vehicle two-wheeler or four-wheeler or any other vehicle that you are travelling in.

So, there is combustion that is going on petrol or diesel or natural gas whatever some combustion is going on and similarly, you are able to extract energy from coal by again burning the coal which is basically combustion you are burning the coal in a thermal power plant. So, when you do this combustion what is typically happening is that you have oxygen you have this fuel petrol or coal or diesel or something and they react. And in the process of that reaction energy is released and the reaction results in the formation typically of carbon dioxide, typically we are getting.

So, like in general if it is a carbon-based fuel. So, you are simply having $C + O_2 \rightarrow CO_2$. So, we are simply typically having $C + O_2 \rightarrow CO_2$ that is the general reaction for any carbon-based fuel which is releasing some energy for us. so, we get some energy. So, ΔH is no negative so, it is just releasing energy for us.

So, now clearly this is a favorable reaction, that is why it is able to happen and that is how we are able to get energy. So, it is a very favorable reaction there is a very strong to use that term there is a very strong driving force to make it happen and it happens and therefore, we end up getting the energy. So, we have to ask ourselves the fundamental question, why are these materials stable? why do you even find coal, why do you find petrol, how is it the petrol even sitting in your petrol tank, how is it even sitting in the petrol bunk, why does not it just burn?

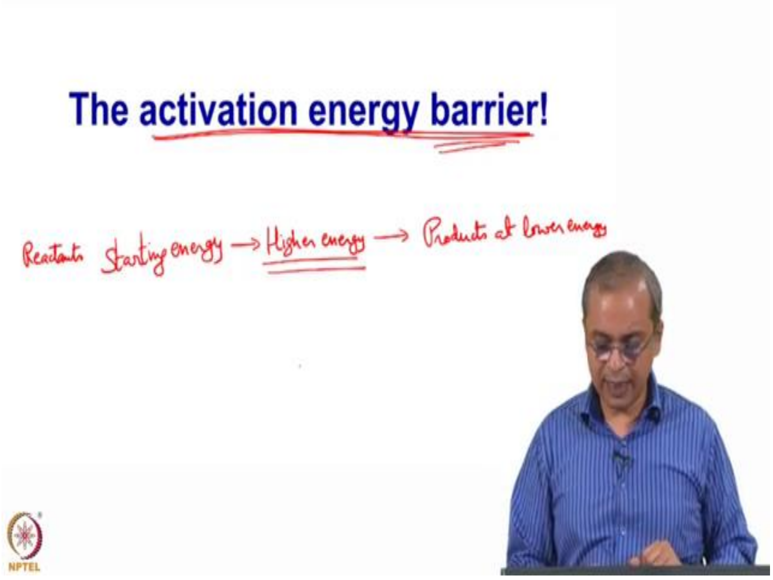
So, why does not fuel which could be petrol or whatever, why does not fuel spontaneously combust; why does not it spontaneously combust there is seems to be a strong driving force and it should be burning. I mean it is its seems to ready to burn it should burn the reaction is very much in favor of occurring and so we have to ask ourselves why does not it burn.

And that is a very fundamental question why does it not spontaneously burn? Spontaneously burn is the important thing, why does it not spontaneously burn by of its own occur should be just burning; stuff should just burn. And that is true for anything you look at wood that can also burn I mean any fabric we use anything any organic material all of that can burn.

But in reality, you look around your doors are there, your tables are there everything seems stable your table is stable, your door is stable we ourselves we are organic material we are stable. And so, a similarly, petrol setting in a petrol tank is stable you can hold a piece of coal in your hand it is not going to burn. So, all those things are sitting stable, despite a strong clear understanding that you can actually burn it those items and it will burn they will burn very well, they will burn rapidly and they will release a lot of energy.

So, we need to understand why are material stable; ok, so that is a very fundamental question. So, we need to understand that.

(Refer Slide Time: 09:13)



The activation energy barrier!

Reactants Starting energy → Higher energy → Products at lower energy

So, the reason that they are stable is because there is a barrier; there is an activation energy barrier, there is an activation energy barrier which prevents that reaction from occurring spontaneously. Any of that reaction petrol getting burned or coal getting burnt could have accurse spontaneously, but because of this barrier, that reaction does not occur spontaneously.

So, what do we necessarily have? We have the materials that we are dealing with have some starting energy. So, they are sitting at some starting energy and then as the reaction proceeds, they need to go to higher energy; higher energy intermediate; intermediate stage through that reaction they go to certain higher energy. So, the reactants have some starting energy, then they go up in energy, they go they increase in energy temporarily as they go through this process of completing a certain reaction and then they go to certain lower energy.

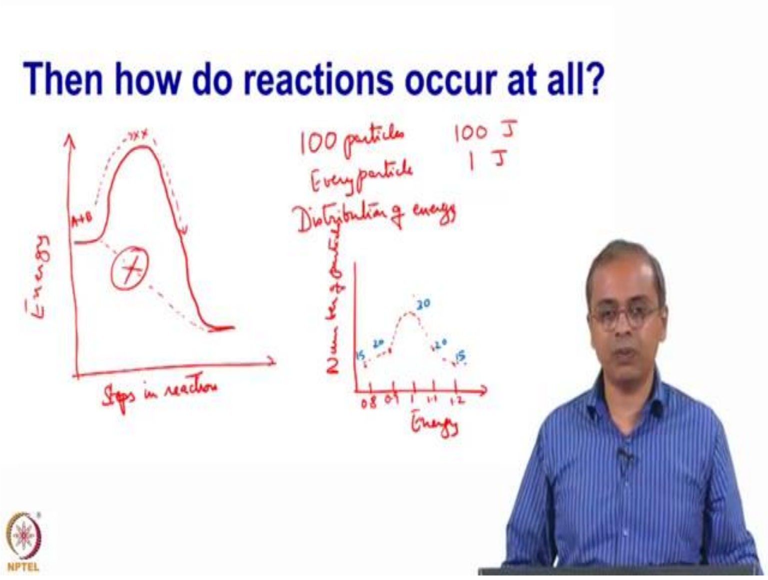
So, this is the typical process that seems to be happening in nature and this intermediate higher energy is the barrier is called the activation energy barrier and you have to push the reactance above this barrier for the reaction to complete. So, that is the idea of the activation energy barrier that exists and that is the reason why things are stable.

So, you should look at it sort of reverse way, I mean it is nature has set it up this way this is many of this thing you have to understand we are trying to see why nature is performing the way it is performing or how is nature performing the way it is performing. So, we have understood that in general in nature things move from higher energy to lower energy this is what happens naturally. So, left to thing; left to itself nature will move from anything in nature will move from higher energy to lower energy, it is always trying to move towards the lower energy.

So, now we understand that when you do a combustion reaction and release energy etcetera that is exactly the process that is happening. So, therefore, we ask ourselves then why is this not happening spontaneously. So, you leave things in nature they should all just automatically end up in lower energy, you should never find carbon you should only find carbon dioxide.

So, therefore, we ask ourselves why that is not happened, then when we examine the system, we find that actually for that to happen in between. It has to actually go above it has to rise in energy to something to a higher energy level and only after that if you drop a lower energy level. And it is that process of going up to higher energy level that forces fair bit of carbon to remain as carbon, and you have to do something to push it over that barrier and then the reaction proceeds. So, this is the idea.

(Refer Slide Time: 12:35)



Then how do reactions occur at all?

So, how do the reactions occur at all? So, now let us just see here. So, let us put some energy here on our y-axis. So, we will say energy and then some reaction process that is happening here. So, steps in reaction. So, now, we have some starting location. So, our starting materials are sitting at that location. So, that is where they are and as I said natural will move towards lower energy considerations; so, a lower energy location.

So, when you are done with the reaction as you proceed in the steps in the reaction and you move towards the completion of the reaction. So, you will have the final state of the products at much lower energy that is the only reason there reaction is happening it is gone from the set of reactants where at higher energy level they have now moved to a lower energy level. So, this is how it is supposed to happen.

So, in principle if I put a dotted line here essentially this is what has happened, it has gone from higher energy to lower energy, but if the process happens the way it is drawn now with that dotted line then indeed it will happen spontaneously. You leave it there it is just like keeping a ball at the edge of a slope, it will slide down; it will just slide down and there is nothing that prevents it from sliding down. So, if you have reactant sitting down; sitting on top of a slope that I just headed down they will simply slide down and you will have spontaneous reaction happen.

So, in reality, what is happening is that it is not happening that way it is starting here and actually going up in energy and then coming down. So, this is the process that is actually happen. So, that is how this is process is happening. So, whatever reactants you have here. So, if you put A plus B, they have to all actually go up this hill first, they cannot take this route this is not possible they have to go up that hill and then they will start sliding down.

So, now you can ask yourself this more is another fundamental question, why do they at all go up the hill; why should they at all go up the hill I mean it is, after all, going up in energy. So, why should it even consider going up the barrier? So, in fact, if you look at this consideration if you look at the picture this way the process of reaction occurring with this diagram in mind in principle reaction should never occur. Now, we go to the other extreme even though energy is finally, low it should never climb up the barrier, it should never go over the hill and therefore, the reaction should never occur.

The reality is that the reactions occur. So, why do the reactions occur? So, the reactions occur because you have a system of say 100 particles having and the overall system is now sitting a 100 Joules; 100 Joules of energy this is the system that you have hundred particles having 100 Joules. So, one way to look at this system is to think of it as a system where every particle has exactly 1 Joule. So, you can think of it is as a system where every particle has exactly 1 Joule. The reality is this is not how a typical system behaves, what we see again in nature is that there is a distribution of energy.

So, if even if you take a system like this you have 100 particles with the total overall energy of 100 Joules, if you look inside those particles you will find that there is a distribution. You will find some particles at 1 Joule, you will find some number of particles at 1.1 Joule, some number of particles at 1.2 Joule, similarly you will find some number of particles at 0.9 Joule, 0.8 Joule etcetera.

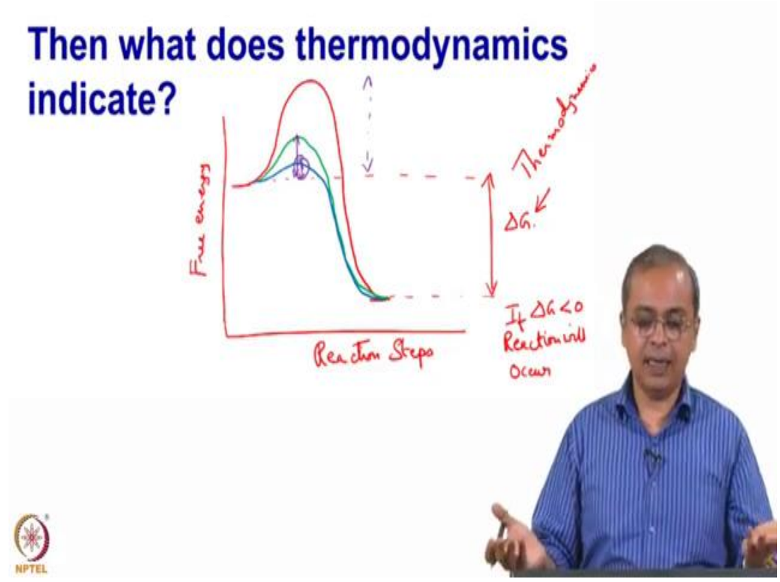
So, normally if you look at the distribution of particles, so if I put here a number of particles and if I put energy here and I put say a number of particles. And it is just for simplicity sake, there are only 4 energy that it there 4 or 5 energies they could have this is 1; so, this is 1, this is 0.9 and this is 0.8 and this is. So, 1.1, 1.2 this is all that we have available to us as possible energy states that it could have, then we will have some number of particles. this is 30 particles, 30 particles are sitting at 1 Joule, then you will have and so, then you will have 70 particles remaining.

So, let me put 20 particles are both sitting at 1.1 Joule and 0.9 Joule. So, that is you have 30 plus 20 plus 20. So, that is already 70 done and you have 15 particles sitting at 0.9, 15 particles sitting at 1.2. So, this is typically how the system would be. So, would actually have this kind of a distribution I have just given you some numbers, but point is that is how the distribution is. So, the number of particles are distributed across energy like this.

So, therefore, at any given instant you will have some number of particles which are actually having higher than the average amount of energy and some number of particles lower than the average amount of energy. So, with this kind of distribution you have a situation that you will actually even though the reactants are actually on average sitting at some level of energy amongst the reactors there will be some particles which are now in a position to which together have the energy which is equal or above that barrier and that is how the reaction starts.

So, then you put them; so, some number of particles are actually sitting at this level of energy and then they start sliding down they can react when they slide down. And as the react they release some energy they push more particles up the hill and this they all start sliding down. So, this is how the process happens and if you see here if you basically look at this possibility here you see that this it climbs up the hill and climes down. So, if you take a particular reaction and you look at the different possibilities that are there for it thermodynamically this is what is happening.

(Refer Slide Time: 20:10)



Then what does thermodynamics indicate?

So, if you look at what does the thermodynamics indicate? Thermodynamics indicates basically this it may indicates exactly what we just put down here. So, it basically says there is a starting point. So, if I write this as free energy and I write this as reaction steps thermodynamics says that is there is a starting point there is an endpoint and it marks this difference as your ΔG, this difference is ΔG the change in free energy. And as long as ΔG is negative and this case it is negative because the products are at a lower energy state is then the reactants.

So, if ΔG is negative or is less than 0 reactions will occur spontaneously; spontaneously these will occur, so this is the idea. What we are also understanding is that the reaction does not just like that occur there is a barrier. Now, this barrier is what tells you how fast or how slow this reaction will occur so in fact, for the exact same reaction, you can have a barrier like this you can also have some other barrier let us just put this in some other color here.

So, in green, I will put another barrier. So, another barrier different barrier and then let us think of a third barrier here. So, we have three different barriers, but please remember ΔG is exactly the same; ΔG is exactly the same so, therefore, the height of the barrier does not change the ΔG of the reaction, the ΔG remains the same. Now, but the height of the barrier makes a very important impact in the sense that you can see here if the height of the barrier is such that it is 1.2 Joules.

So, supposing you have to put 20% extra energy to cross that barrier you will find that only a small number only 15%; only 15 out of these particles. So, I just put some numbers here I put this as if I remember this is 30 particles here and then we had 20, 20, 15 and 15 particles, just to give you some ideas its distribution would have to be done differently, but I am just taking some discrete points on this distribution. So, we had these particles.

So, if you said that the barrier was 1.2 Joules, then only 15 particles at any given instant of time are actually at that are having that energy to be able to do this jump. On the other hand, if the barrier has been lowered to 1.1 Joules, then 15 plus 20 you have 35 particles now in a position to do the reaction. So, you suddenly see 35% of the reaction starts moving quickly.

So, that is the situation the closer to you get to that 1 Joule per thing then the moment starts happening faster and faster. So, therefore, the height of the barrier tells you how easy it is to do the reaction. So, the height of the barrier tells you how easy it is to do the reaction and that is how you can speed up a reaction or slow down a reaction. So, many times the reaction is set.

So, for example, when you look at say corrosion processes the natural tendency is for the reaction to happen, but we want to slow the reaction down. So, that is what we are trying to do with corrosion. On the other hand, some other reaction the release of energy from in a battery, for example, you are trying to speed up that reaction you want maximum current from the battery as quickly as possible; so, you want speed up the reaction.

So, always in nature, there are some reactions which are going to occur spontaneously sometimes we want to speed up those reactions, sometimes we want to slow down the reactions. What are we doing; what are we doing that helps speed up a reaction or what are we doing that help slow down a reaction? We are basically dealing with the barrier that is basically what we doing, we are affecting the kinetics of the reaction this speed at which the reaction occurs is called the kinetics of the reaction. The possibility that the reaction will occur at all is the thermodynamics of the reaction.

So, this ΔG is the kinetics is the thermodynamics of the reaction; so, this is thermodynamics. So, that is thermodynamics ΔG, so that remains exactly the same the barrier which you see here that is the kinetics of the reaction. So, this barrier whether you have this higher barrier or you have this higher barrier or you have this higher barrier that is the kinetics of the reaction that decides how quickly or more difficult or slowly the reaction will occur and this simply represents different reaction pathways; so that is all it means.

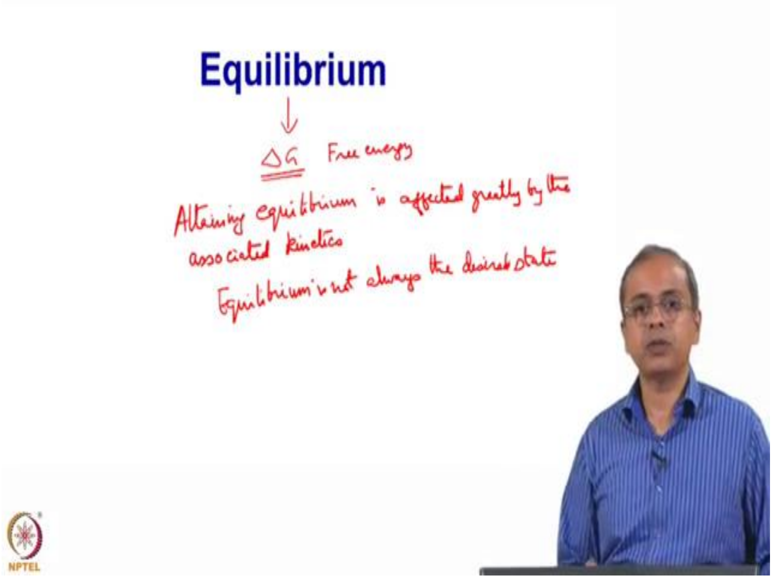
So, when you talk of catalysis when you say you used a catalyst to speed up the reaction that is exactly what you do. By using a catalyst, you are lowering the barrier to this barrier where you are saying that on the surface of the catalyst particle it is much easier for those reactants to react with each other and therefore, the barrier for the reaction is lowered.

So, if you simply put the two reactants in a chamber, they would take their own time to react, it might take an hour to react. On the other hand, you put these catalyst particles which have high surface energy available to them and these two reactants are able to come in stick to that surface easily, then they are finding energy available at the surface plus there are also very close to each other they react very fast.

So, that is how a catalyst helps speed up the reaction and that is how the catalyst helps the kinetics of the reaction. So, thermodynamics tells you whether or not the reaction will occur, kinetics tells you how fast the reaction will occur. And I mean you want to use some mundane example there may be something interesting that you wish to buy.

And so, there is a strong driving force to buy it, but depending on which route you take I mean you can use a vehicle to go, I mean you can use some the traffic is slow. And you have a car, you can go very quickly to the shop and buy it or you can use a circuitous road you can walk and take a long distance to reach the same shop and buy. So, you can take much longer time to go and buy. So, the overall purchase process is the same which is the ΔG, but the route you take a determines the kinetics. So, that is basically what you are seeing here.

(Refer Slide Time: 27:03)



Equilibrium

$\downarrow$

$\underline{\underline{\Delta G}}$ Free energy

Attaining equilibrium is affected greatly by the associated kinetics

Equilibrium is not always the desirable state

So, equilibrium is a concept that is basically defined by ΔG. So, that is the idea that you have to keep in mind. So, the equilibrium process is what ΔG is all about is defined by the free energy, and free energy changes associated with the reaction help you determine what is equilibrium, but the important thing and so, that is a very defining parameter. So, the equilibrium is what nature moves towards. Equilibrium means if you leave the system like that indefinitely you come back technically you come back after a thousand years it will sit an exactly the same position.

So, that is an equilibrium that is the ability of the system to just sit because that is the lowest energy state it can attain. That is why, it is sitting like that there is no other greater sanctity to it the idea is that, it has to hit a low energy state it has found the low energy state and therefore, it is there indefinitely that is the idea of equilibrium. And that is captured very well, but changes in the free energy and you hit the lowest free energy available for the system it will just stay that; so that is equilibrium.

But what we also have to understand is that attaining equilibrium is affected greatly by the associated kinetics. So, attaining equilibrium is affected greatly by the associated kinetics. So, therefore, many of the systems that we actually see in real life; in real life many of the materials that you deal with that you use routinely use in your household, routinely use in your at work, routinely use as part of transportation etcetera. Many of those systems have actually not completely attained an equilibrium, because the final step in the equilibrium may take under room temperature conditions, it may take several years may be several hundreds of years before it attains that equilibrium.

So, for many times even though when we say in thermodynamically the equilibrium will be attained and so on in real life many times we are actually not attaining equilibrium and even more importantly many times it is desirable not to attain equilibrium. If the reason being sometimes the product that is there, the final product that you get as a result of equilibrium is perhaps the product that does not have the properties that you desire. The properties that you are interested in which will be of interest for the end-use that you are putting it to.

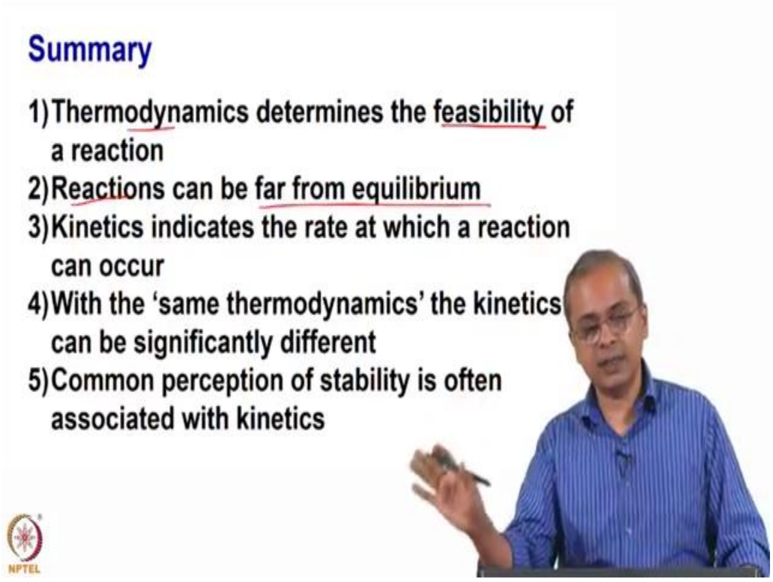
So, therefore, the final equilibrium product may not be interesting to you. On the other hand, some non-equilibrium product which has not completely attained equilibrium, but is creeping its way crawling its way towards equilibrium and may take 100 years to reach that equilibrium, that product is having much better properties and you are going to put it to use for say 5 years.

Let us say you are vehicle is going to run for 5 years or your part in that vehicle is going to be changed in 5 years time or 10 years time. And therefore, since the reaction is going to take 100 years to complete in 10 years by enlarged it is going to be unchanged you are going to see the part perform just perfectly fine for the 5, 10 years you use it like that.

So, many times the products that we use are actually non-equilibrium products not that there is anything wrong with the idea of equilibrium nature is moving towards equilibrium, it is just that the properties that we desire may be there in some non-equilibrium products. So, we just freeze the system in the non-equilibrium state and ensure that the kinetics has been slow down dramatically and we use it in that process.

So, equilibrium is not necessarily desired; is not always the desired. So, equilibrium is not always the desired state it is the state that many times the system will head towards, but it is not the desired state.

(Refer Slide Time: 31:27)



Summary

1) Thermodynamics determines the feasibility of a reaction
2) Reactions can be far from equilibrium
3) Kinetics indicates the rate at which a reaction can occur
4) With the ‘same thermodynamics’ the kinetics can be significantly different
5) Common perception of stability is often associated with kinetics

To summarize what we just discussed thermodynamics determines the feasibility of a reaction. So, if something says if ΔG is negative then we know that naturally there is a spontaneous push towards that reaction happening. So, the thermodynamics is what tell us whether or not a reaction will happen.

Many times, in reality reactions, can be far from equilibrium that is the point I made just now made, many times, in reality, the system that you deal with can be far from equilibrium the whereas, thermodynamics is pushing it towards equilibrium. Thermodynamics which tells you the feasibility of the reaction is basically pushing the reaction towards equilibrium. But these typical systems that we deal with can be situations where the reaction is only partially done it is far from completed, it is far from reaching equilibrium. Kinetics is the idea that captures this concept or captures the reality that there is a rate at which a reaction is occurring, that concept is being captured by kinetics.

And the kinetics is primarily defined by that barrier that activation energy barrier that is required to be overcome for the reaction to occur. So, that is the barrier that decides how fast or slow the reaction will occur and that is being captured by this whole idea of kinetics. And since that barrier can be changed with the same thermodynamics ok, same thermodynamics meaning for the same system; for the same system where you doing the calculation of ΔG naturally that ΔG calculation is going to remain unchanged.

So, thermodynamic that is what I am referring to the same thermodynamics with the same thermodynamics; the kinetics can be significantly different because you can have totally different routes for getting the reaction done, you could use a catalyst which will speed up the reaction you could put something else there which actually prevents the reaction from occurring.

So, you can either accelerate a reaction or decelerate a reaction, if it is the desired reaction you accelerated, if it is undesired reaction you slow it down. In our body also in our biological systems many of those things are happening, there are reactions that are in biologically the system is pushing it forward and the other reactions that are being deliberately slowed down. So, with the same thermodynamics, the kinetics can be significantly different.

And often our common perception of stability when we look at something and say that this is stable, this is stable at room temperature. I have I am carrying something with me and it is in the same condition for the last 5 years, that idea of stability that we have in our mind of materials being stable or systems being stable is actually associated with the kinetics. It is not necessarily associated with the thermodynamics, thermodynamically it may be an unstable system, but kinetically it may be a stable system because it is going to take forever for the thermodynamics to happen.

So, therefore, many times real life is actually dealing with the kinetics of reactions is actually working with the kinetics of the reaction rather than completely with the thermodynamics of the reaction. So, these are some concepts that we have to keep in mind as we go forward as I said these ideas were going to implement with respect to the nanoscale. And therefore, having a clear picture of this will help us understand what is it that we need to additionally consider when we look at the nanoscale and so that we will do as we go forward.

Thank you.