Carbon Materials and Manufacturing
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Lecture - 10
Carbon Allotrope Conversion

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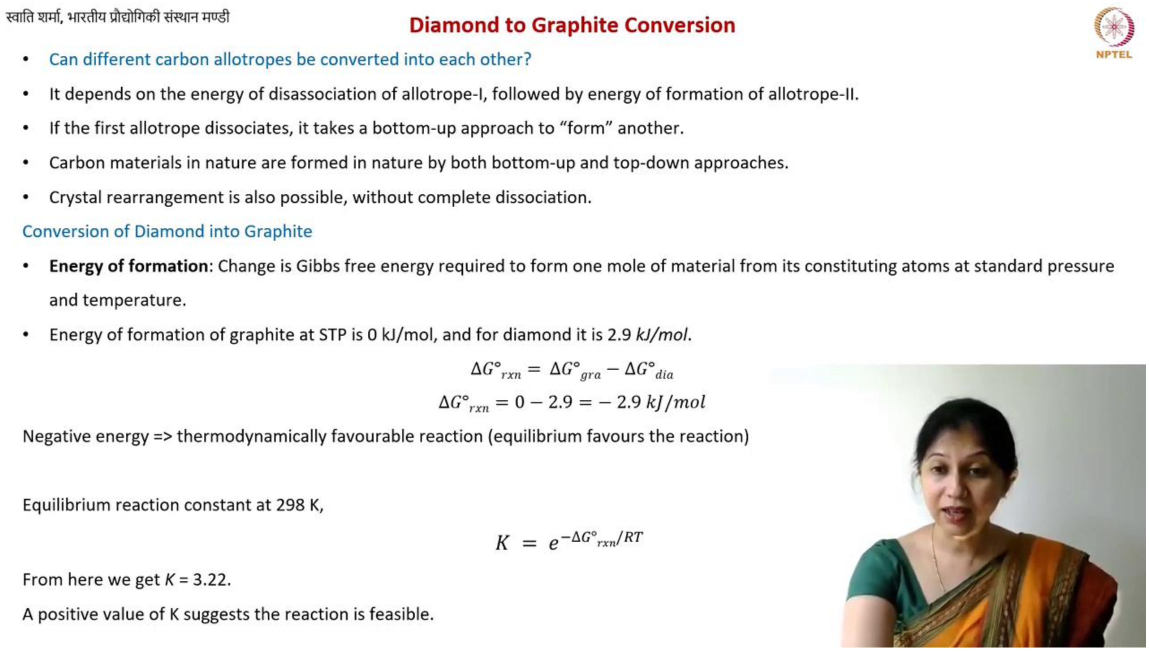

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Diamond to Graphite Conversion

- Can different carbon allotropes be converted into each other?
- It depends on the energy of disassociation of allotrope-I, followed by energy of formation of allotrope-II.
- If the first allotrope dissociates, it takes a bottom-up approach to “form” another.
- Carbon materials in nature are formed in nature by both bottom-up and top-down approaches.
- Crystal rearrangement is also possible, without complete dissociation.

Conversion of Diamond into Graphite

- **Energy of formation**: Change is Gibbs free energy required to form one mole of material from its constituting atoms at standard pressure and temperature.
- Energy of formation of graphite at STP is 0 kJ/mol, and for diamond it is 2.9 *kJ/mol*.

$$\Delta G°_{rxn} = \Delta G°_{gra} - \Delta G°_{dia}$$

$$\Delta G°_{rxn} = 0 - 2.9 = -2.9\ kJ/mol$$

Negative energy => thermodynamically favourable reaction (equilibrium favours the reaction)

Equilibrium reaction constant at 298 K,

$$K = e^{-\Delta G°_{rxn}/RT}$$

From here we get $K = 3.22$.

A positive value of K suggests the reaction is feasible.

Hello everyone. In today’s lecture we are going to learn how one carbon allotrope can convert into another. In the previous lecture, what did you learn? You learnt what are carbon allotropes and how do we classify them based on their hybridization states. We also learnt that we can you can make a chart of carbon allotropes like a periodic table and you can always find things that are hybrid between two hybridization states, simply hybrids of hybrids.

You can find many carbons, many arrangements are possible with carbon atoms and that is how you can have a wide range of carbon allotropes. Now, how do we make these carbon allotropes? Some of them are available in nature but also in nature how are they formed? Are they always formed starting from an atom?

You know that we were talking about these red giant stars and we know that there you have fusion of helium and after that you have carbon atoms being formed. So, there you have actually a lot of carbon atoms available and those atoms then assemble and come together and then they form molecules such as fullerenes or they can also form any other type of carbon. So, that is the bottom-up approach of the formation, starting from the atom.

But if you just have one allotrope either you may have it in nature, let us say you have some diamond in nature. Is it possible that it will over time convert into graphite or convert into any other form of carbon? Similarly, is the other way around possible? Can you convert graphite into diamond?

So, this is what we are going to learn in today’s lecture. We are also going to do some basic thermodynamic calculations especially for this diamond to graphite conversion. The reason is also that this is something which has been studied a lot of diamond to graphite and also graphite to diamond conversion. Because these were the two very well-known forms of carbon and also these forms are available in bulk they are available in nature.

In the next lecture, we are going to learn about the phase diagram of carbon and which also mainly talks about diamond and graphite phases and of course certain liquid and its non-solid phases as well. But these are the two allotropes that have been studied very extensively.

Now forget about starting from the atoms. If you want to convert one allotrope into another what are the two types of energies required? You need to provide some energy for sure, as you have learned in one of these previous lectures that diamond is a metastable form of carbon. Metastable means it is not the most natural stable form, at some point it should convert into graphite.

However, there is an energy barrier. So basically you need to provide activation energy and once that is provided then it will cross that barrier and then it will naturally occur and then it will convert into graphite. But we need to provide some external energy activation energy.

So, there are two types of energies required. Now, we need to understand why are these energies required at all. First of all, you need to pull the atoms of diamond away from each other. This is also a very stable crystal structure by the way. You also know diamond is the hardest technological material so it has very strong bonding. It’s not like diamond is very weakly attached to each other.

First of all you need to provide certain energy to the diamond crystal to dissociate it, to make sure that you have atoms away from each other only then they will form something else. So, that is energy number one. Energy number two would be then the energy of formation of graphite.

So, you do know that energy formation system is a thermodynamic property. And you take atoms that are at infinite distance from each other and you form one mole of a certain material then that is the energy of formation of that material. So, you need the energy of dissociation of allotrope I and energy of formation of allotrope II.

Now, once this first allotrope dissociates, let us assume that we have diamond dissociated into tiny little atoms which are at infinite distances from each other. And then you need to form now graphite. So, what will be that approach? That will be a bottom-up approach right. Anything when you start from the atom scale or when you have smaller units and you make or assemble them and make something bigger, that is going to be a bottom-up approach. However, when you have carbon in nature, do you always have materials formed by the bottom-up approach? Not necessarily, sometimes you also have top-down approach. Top down approach means you take something bigger and remove the material from it.

So, what would be a good example of that? Coal or the graphite that you mine. Why? Because these things are formed from the organic materials? So, when you had a lot of organic materials whether they were trees or animals or whatever, when they were buried under the earth then all the non-carbon atoms were dissociated and whatever you had left was your carbon. Now of course in this carbon material, at some point, the carbon atoms would have come together and formed the bond and you can say that is the bottom up approach. But you can say it’s a combination of both top-down and bottom-up because you are also removing some material. So, you have both types of approaches when it comes to naturally found carbon allotropes.

Do we always need to start from these single atom individual atoms? Not necessarily, again if we are talking about converting one allotrope into another maybe you do not need to completely break it apart, maybe there is a certain distance between the atoms after which if you provide the energy then a crystal rearrangement takes place.

So you do not completely break things apart for example lego blocks or any of these little blocks that children play with you assemble these blocks and make something. Now, if you make a house using these little blocks and now you want to make a completely different house. There are two options either you can you know protect some parts of this house and you can just remove few things and then rearrange them. Or if the other house is completely different, in that case you may have to completely break every single lego block apart and then reorganize it. So, both of these things are possible.

Similarly in some cases for some allotropic conversion of carbon, you may have to completely break the crystal apart. And in most cases, you can just do rearrangement of crystal. But for all of this you need to provide energy and that energy is the activation energy.

Activation energy is also a very interesting and very general term. Why do you need this activation? Activation energy can be used to activate anything that is actually happening inside the material. Think about what is that activation energy or whatever energy we are providing, what is that energy actually doing?

So, in the case of allotropic conversion what is it doing? It is the energy that is used for breaking crystal number 1 and forming crystal number 2. That is our activation energy in this particular case. Now, we will do both thermodynamic and kinetic calculations. You know that for any chemical reaction to take place there are two things. There are thermodynamic and kinetic aspects of it. Kinetic aspects will tell you what is the rate of the reaction? How fast is it? How slow is it? if it is possible or not? Thermodynamic calculations will tell you the initial state and the final state and you calculate the energy. You do not really care about the paths or the rate of the reaction, how it happens, slower or faster all these things you do not factor into thermodynamic calculations right. That is why we are talking about state functions in most cases. Now, you can probably recall what is Gibbs free energy? You know there is something also known as the energy of formation of this material when a material is formed. Energy of formation is defined as the change in the Gibbs free energy which is required to form one mole of material under standard pressure and temperature conditions because otherwise, the things will change.

When you are considering the energy formation then you assume that the atoms were at infinite distances from each other. Because you do not start with any predefined arrangement already. If you start from 0 and you form one mole of graphite that will be the energy of formation of graphite. Because graphite is the most stable form of carbon that is what carbon should naturally be and all carbon should in principle be graphite unless some other energy is provided. So, in that case the energy of formation of graphite at standard room temperature and pressure is 0kJ/mol. But in the case of diamonds that is not 0. It is a finite number, this energy is 2.9 kJ/mol.

When you want to calculate the energy or Gibbs free energy of a certain reaction how do you do that? You take the products minus the reactants.

So, the energy of formation of the product minus the energy of formation of the reactant this is very simple calculation.

$$\Delta G^{\circ}_{rxn} = \Delta G^{\circ}_{gra} - \Delta G^{\circ}_{dia}$$
$$\Delta G^{\circ}_{rxn} = 0 - 2.9 = -2.9\text{kJ/mol}$$

When you have the ΔG^{o} of a certain reaction is negative. That actually means it’s a favourable reaction.

When you have some negative energy of a certain reaction that means equilibrium actually favours this reaction which is also obvious to us if graphite is more stable then it should be possible to form it if we consider only the initial and final state.

We only consider diamond and graphite, then graphite is more stable. This is also clear from the negative energy of reaction ok. Now we will calculate the equilibrium constant again at STP. We are calculating the reaction constant for this reaction this is the formula for it:

$$K = e^{-\frac{\Delta G^{\circ}_{rxn}}{RT}}$$

Now, if you will do the calculations, I have not written all the steps here, but you will find some value of approximately 3.22.

Now there is another conclusion that you derived from this calculation is if your K is positive and the value of K is positive higher than 1 then you will see that then the reaction is thermodynamically feasible.

In fact, if K is much much higher than 1 then the reaction is faster. And if it is a positive number anyway then it is a thermodynamically feasible reaction. So we know that this conversion is thermodynamically feasible and as I mentioned again if you just look at the initial and final steps, this is very much possible. Now, we will look at the kinetic aspects of this reaction.

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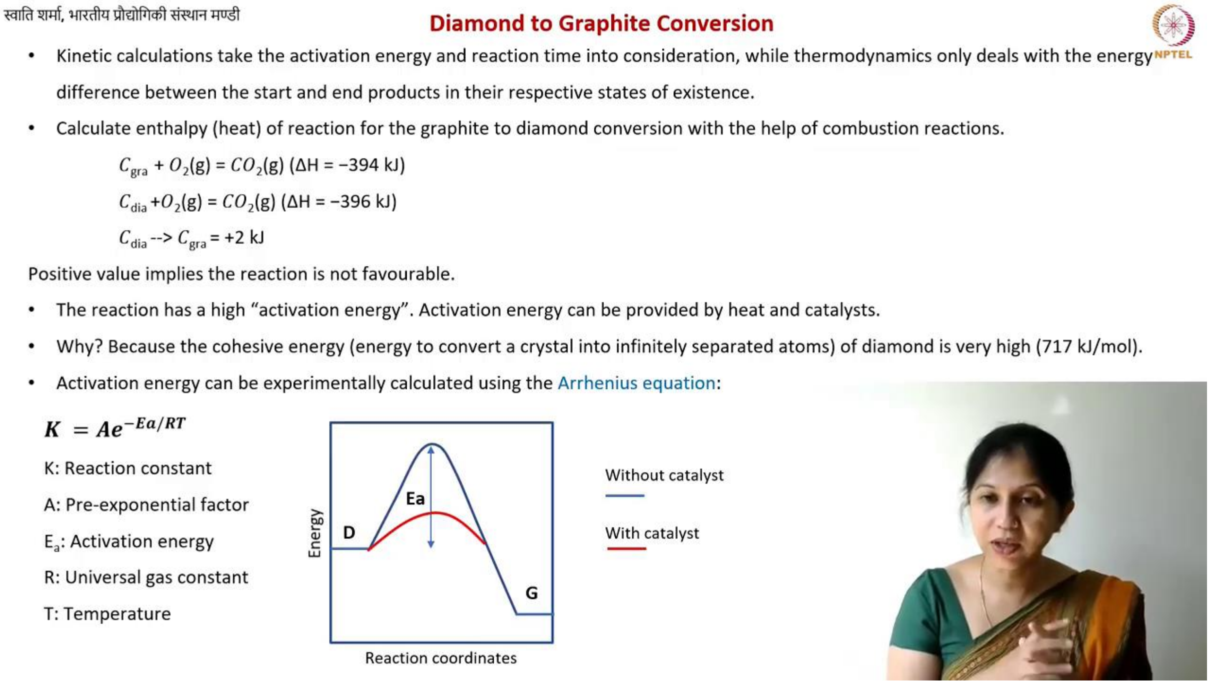

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Diamond to Graphite Conversion

- Kinetic calculations take the activation energy and reaction time into consideration, while thermodynamics only deals with the energy difference between the start and end products in their respective states of existence.
- Calculate enthalpy (heat) of reaction for the graphite to diamond conversion with the help of combustion reactions.

$C_{gra} + O_2(g) = CO_2(g)$ ($\Delta H = -394$ kJ)

$C_{dia} + O_2(g) = CO_2(g)$ ($\Delta H = -396$ kJ)

$C_{dia} \dashrightarrow C_{gra} = +2$ kJ

Positive value implies the reaction is not favourable.

- The reaction has a high "activation energy". Activation energy can be provided by heat and catalysts.
- Why? Because the cohesive energy (energy to convert a crystal into infinitely separated atoms) of diamond is very high (717 kJ/mol).
- Activation energy can be experimentally calculated using the Arrhenius equation:

$\boldsymbol{K = Ae^{-Ea/RT}}$

K: Reaction constant

A: Pre-exponential factor

E_a: Activation energy

R: Universal gas constant

T: Temperature

If we consider the kinetic aspects of the reaction, we need to now factor in the activation energy which we have ignored. Till now we were just thinking about the final and initial stages. Now, what do we do? We can calculate the enthalpy of the reaction itself. So, we are taking the full reaction into consideration. How do you do this calculation? This is very simple, you take the reaction of diamond with oxygen and reaction of graphite with oxygen. And these are some of the very well-known reactions. We know a lot of experimental details of these reactions and we can subtract them and then we can find the enthalpy of the diamond to graphite conversion reaction.

So, let us quickly do that you have carbon in the form of graphite. And when it reacts with oxygen it forms carbon dioxide and the enthalpy for this reaction is -394 kJ. Similarly when you have carbon in the form of diamond and it forms carbon dioxide then you again know the value of the enthalpy of this reaction. Subtracting the two you will get the conversion of diamond to graphite and the energy of this reaction plus 2 kJ. Now, you know that if this is a positive value that means this is an endothermic reaction. Endothermic means if this reaction naturally takes place then it will take heat from the atmosphere. So, this reaction then is naturally not feasible.

Now, why is that? Again we know very well that there is certain activation energy. Now how can we do this? If we really want to convert diamond into graphite what can we do? We can provide this activation energy. Activation energy can typically be provided by either heat or by catalysis and what do catalysts do? They lower the value of the activation energy. And in that case, you have the reactions taking place either naturally or with a very little bit of external energy requirements.

So, again as I mentioned before that this activation energy is required because you need to separate the diamond atoms and you need to bring atoms back to form graphite. And this seperation energy by the way for diamonds is pretty high. This energy is known as the cohesive energy in terms of crystal structure. For any crystal, the cohesive energy is the energy that is required to again take the atoms apart to an infinite distance and that energy for diamond is pretty high. It is 717 kJ/mol. So, what this actually physically means that taking atoms apart from diamond is not easy. That requires a lot of cohesive energy. So, that is the energy that you need to provide?

That is what we now call activation energy? Can we calculate this energy experimentally? You probably recall there is something called an Arrhenius equation. The Arrhenius equation looks like this:

$$K = Ae^{-\frac{\mathrm{Ea}}{RT}}$$

This reaction is very similar to what you also previously saw in a lot of yeah thermodynamic and kinetic calculations when chemical reactions are taking place. They are pretty much in this form e^{-x} form. So this function e^{-x} is an exponential decay function. what is decaying exponentially? In some cases, you will say the concentration of the reactants is decaying exponentially. Here in this particular case, K is the reaction constant. So, it is the K that is exponentially decaying or the value of K. What does it mean that? When a certain reaction takes place initially there is a certain time when the rate of reaction will be very high and that rate of reaction will then slowly decay it will never go to 0, that is the exponential decay.

So, we will never say that it goes to 0 but it becomes close to 0. So that is how you can actually understand many reactions and most of the reactions are exponential decay reactions. And for that we have this Arrhenius equation.

I have also mentioned A pre-exponential factor which is a constant, Ea in this particular expression is the activation energy. So, definitely this is where you actually now factor in the activation energy for any reaction.

If you increase the temperature of any reaction the atoms and molecules will move faster. So, that increases the kinetic energy. So, RT is actually the term that takes care of the kinetic energy of the constituting atoms or molecules.

And R is the universal gas constant, when you are doing this kind of calculation you need to make sure that you are converting the units properly. You need to have energy in joule if you are using gas constant also in Joule.

Ea/RT is a dimensionless property and that is why you have e^{-x} kind of function. So, K is also dimensionless in that case. So, this is the Arrhenius equation from here you can experimentally calculate the activation energy, I have not shown those calculations here.

So you can keep on changing the temperature for example and then you can calculate the value of K. These are the two things you can find out experimentally. So it would be the constant anyway for its characteristic of a certain reaction. Now, if you keep on changing the value of T and you can experimentally note down the value of K, you can observe then the only thing that is left is Ea which is your variable. That is the value you can calculate for any particular reaction, here we have the diamond to graphite reaction.

In this diagram, you can see that you have diamond slightly at higher energy and you have graphite slightly lower energy. However, there is this energy barrier. And this energy between the diamond’s natural state and the state where the diamond atoms will be far enough from each other. That energy is known as the activation energy. And as I mentioned before what does a catalyst do? It lowers the value of the activation energy. So here with the red curve I have shown the lowered activation energy value and the blue one is for the standard value of activation energy.

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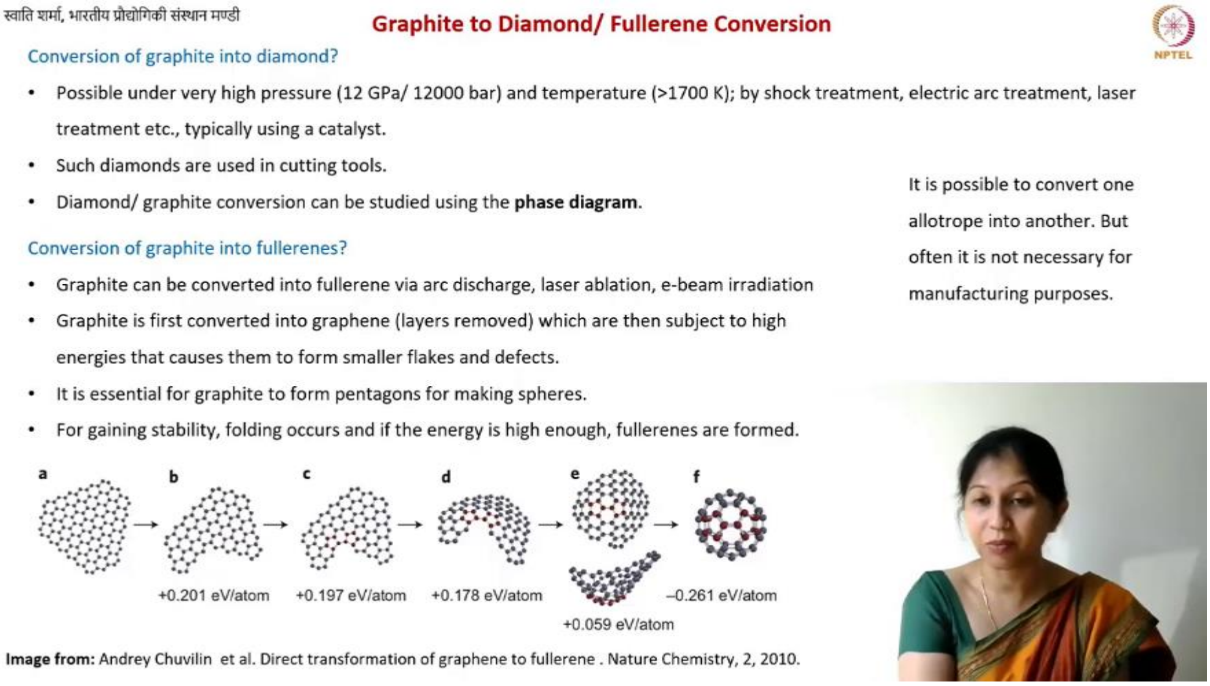

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Graphite to Diamond/ Fullerene Conversion

Conversion of graphite into diamond?

- Possible under very high pressure (12 GPa/ 12000 bar) and temperature (>1700 K); by shock treatment, electric arc treatment, laser treatment etc., typically using a catalyst.
- Such diamonds are used in cutting tools.
- Diamond/ graphite conversion can be studied using the **phase diagram**.

Conversion of graphite into fullerenes?

- Graphite can be converted into fullerene via arc discharge, laser ablation, e-beam irradiation
- Graphite is first converted into graphene (layers removed) which are then subject to high energies that causes them to form smaller flakes and defects.
- It is essential for graphite to form pentagons for making spheres.
- For gaining stability, folding occurs and if the energy is high enough, fullerenes are formed.

It is possible to convert one allotrope into another. But often it is not necessary for manufacturing purposes.

Image from: Andrey Chuvilin et al. Direct transformation of graphene to fullerene . Nature Chemistry, 2, 2010.

I said that diamond can be converted into graphite. Is it also possible to do it the other way around? Can we convert graphite into diamond? Then you can convert all pencils you have at home into diamond jewellery. It’s not that people have not tried; you are not the first one to think about it. In fact in the 1980s there was a lot of research that went on in making artificial diamonds.

And we have been successful in making artificial diamonds. The only thing is that those diamonds are not really of high quality. What is the quality in case of diamond? One is the purity, you can still obtain because it is not that difficult. In fact, sometimes people want to induce impurities to give different shades and colors to the diamond. So, purity part is still possible and even crystal defects can be controlled to some extent. But the point is that you cannot grow really big crystals, you can only grow sort of micro-scale crystals and we have not been able to synthetically grow very large diamond crystals and this work is still going on.

The second thing is also that you require such high energies for this particular reaction and its not worth it, it’s too expensive to get those tiny little time crystals. Scientifically it is possible to convert graphite into diamond but the idea remains the same. Of course, you will now require much higher activation energy because you are going from a lower energy state to a higher energy state. However if you can cross the activation energy barrier in principle it should be possible and then you can somehow induce another type of crystal formation in this particular case if you induce the formation of diamond.

So, it is possible to convert not just graphite but also certain other forms of carbon. There are many different types of carbons curved carbon like these non graphitizing carbons contain a lot of curved carbon in them and these kinds of carbon structures can also be converted into diamonds.

As I mentioned, I have not shown detailed thermodynamic calculations but you can actually do using the same values that you used for doing for graphite to diamond, you can also do from for diamond to graphite in the other way around. Because the numbers remain the same, the enthalpy of reactions of oxidation and all other values that I have shown before. The only thing is that the calculations will reverse. So, you will see that its not feasible to convert graphite into diamond thermodynamically but there is a certain activation energy that you can provide then you can do so. However, as I mentioned this activation energy requires really extreme conditions you need 12 GPa or higher pressure. And you also need temperatures above 1700 K, if you can increase the temperature little bit you can reduce the pressure. But in this case you always typically always require high pressure, just only temperature will not do. In the case of the diamond to graphite conversion, you could do it just by using very high temperatures.

In this graphite to diamond require very high pressure because you need to provide a certain type of crystal structure and that crystal structure is not the natural form of carbon. So to induce sp3 hybridization in the carbon atoms you also require a lot of pressure. Then there are also some other methods called for example, shock treatment, electric arc treatment. What is an electric arc? You probably remember arc welding, so you create an electric arc. That also provides sudden energy. Electric arc or even laser treatment and all of these things will actually provide very sudden high energy which forces the atoms to reorganize. And all of these methods that I mentioned, have to be done in a very controlled fashion. Even you cannot perform arc welding of your graphite pencil and it will convert into diamond, it does not work that way.

All of these things need to be also typically in the presence of a catalyst you need to perform this reaction. So, you can imagine that it’s not easy to do it; however, it is possible to do it ok. Now, this kind of artificial diamond are typically used in cutting tools. They are not really used for jewellery applications as I mentioned that you have tiny crystals. However, their hardness is pretty good because they are artificially synthesized even if you have certain impurity but you do not much care about that.

You can get these kinds of diamonds very inexpensive, these diamond cutting tools. Even I have such a diamond tool and I could show it to you. There is something called a diamond scriber that looks like a pen but the tip of that scriber is a tiny diamond. And that is used for cutting silicon wafers in the cleanroom when you are doing microfabrication.

So, these kinds of cutting tools are nowadays available for a reasonable price. Of course, you cannot have them using natural diamonds otherwise they would be much much more expensive. So we are using these artificial diamonds.

In the next lecture as I mentioned we are going to study something called the phase diagram. The phase diagram is something where you will learn about different crystalline and amorphous phases of carbon. And we’ll also look into liquid and vapour phases and how they are possible at different phases.

I think you must have learned about phase diagram in your other courses. You will always learn about the iron-carbon phase diagram. That is not even iron-carbon phase diagram because you never go to a hundred percent of the carbon in that diagram. You will start pure iron and you stop at the cementite phase. Never mind that is a very important diagram for engineering applications, but there you have two elements. And there is something different when you have two elements and then composition of these two elements how much carbon? How much iron do you have?

The composition becomes an axis of your phase diagram it becomes an important parameter. In fact, based on the composition you study the rest of the properties. But if you have only an element you are always talking about 100 percent carbon there is nothing else mixed in there. Then the phase diagram definitely looks slightly different and this is what we are going to learn in the next lecture.

Now if diamond to graphite and graphite to diamond is possible then it should also be possible to convert graphite into fullerenes or into curved carbons. Here I am talking about fullerenes and I am talking about the spheres. The answer is yes, that is also possible. Again graphite being the most stable form of carbon and whenever you want to convert graphite into something you will need to provide a lot of energy. So, it can be converted into fullerenes by again things like laser ablation or arc discharge and something similar that you do for diamond and you can do electron beam irradiation as well.

Electron beam irradiation means if you heat it with a beam of electrons at high voltages. So, all of these things can facilitate the conversion of graphite into fullerenes and how does this actually happen? When you want to convert graphite into fullerene, you will first convert graphite into graphene what does that mean, you will remove one layer. So, removing layers is possible and there are many methods, we will we talk about them in detail like even you can just take scotch tape and place it on top of graphite and just peel it off even then you can get single sheets which then you would call graphene.

So, you first remove the graphene sheets from graphite typically. And then you subject those graphene sheets to very high energies. So, here we are not doing what we were doing from when we were doing this graphite to diamond conversion. We were taking graphite crystal but here we are taking single graphite sheets and then we are converting it when we provide them high energies because they are 2D and flat structures and when you suddenly provide them a lot of energy in any form then they will typically tend to minimize their surface area. This means that the flat sheets would typically want to convert into circular objects or spherical objects or curved objects.

If you want to make fullerenes you need to ensure that there are pentagons otherwise this thing will not happen. The curvature will not be the right curvature. So, in that case here it is important that this graphene sheet should break apart into smaller pieces and then the hexagons should either convert it to pentagons or somehow you should induce them as defects. So, once you have a sufficient number of pentagons then depending on the number of these pentagons you will have either curved carbon or you will have a complete fullerene.

There is a publication, I have given this reference here and I have also taken the image from there. So, you can see how it works and there are also energies written here. This was done by electron beam irradiation as I mentioned.

You see there are some pentagons being created at some point by certain energy that you provide. And these pentagons then lead to the curvature and then this curvature at some point forms a stable structure which is the fullerene structure. So, the point is that allotropic conversion here also is possible.

So, in conclusion allotropic conversion is possible, but it depends if it’s necessary or not. If you are doing manufacturing then typically you will just start with one material or one type of allotrope and you will see how to process them. And you will figure out how to manufacture something out of it.

Typically it is not necessary to do the allotropic conversion. However, in certain cases even if you don’t want to, it happens for example, the conversion of the disordered conversion carbon into graphite or the other way around. Sometimes you want something which is very graphitic, but you cannot get it. Sometimes you have some amorphous regions and you provide a little bit of heat and it converts into graphite. So, these kinds of things happen and this is something that you need to understand in principle. You will not get complete allotropic conversions when you are making something.