Carbon Materials and Manufacturing

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Lecture - 11
Phase Diagram of Carbon

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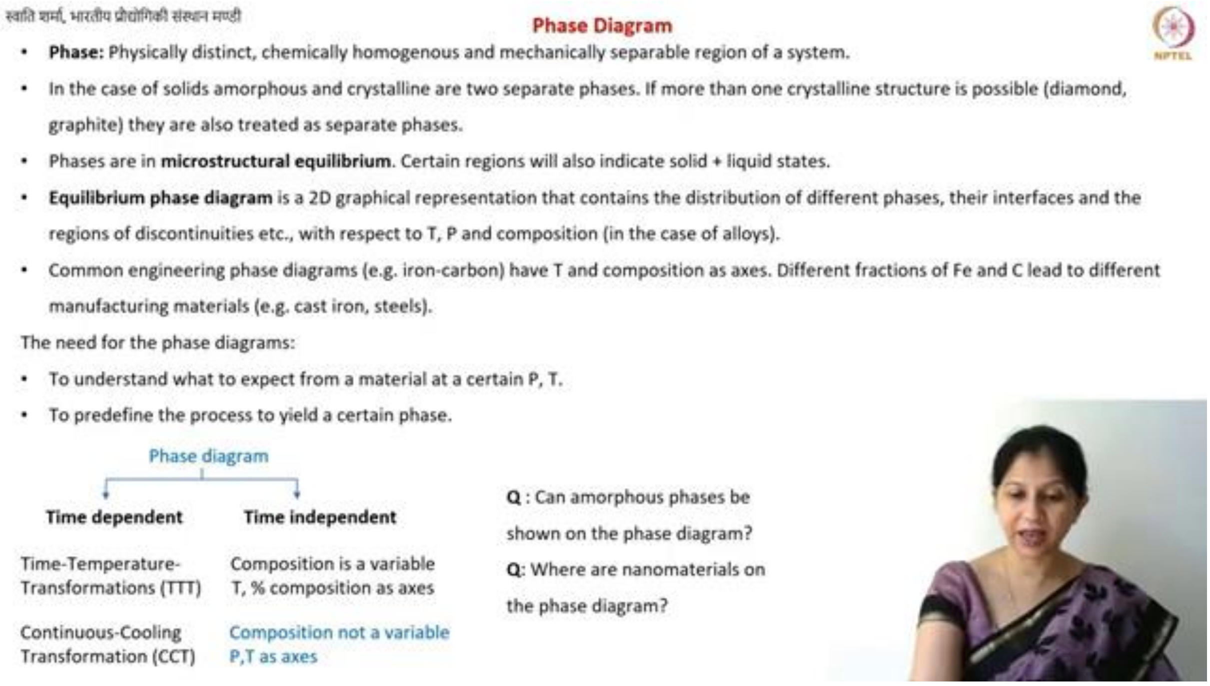

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Phase Diagram

- **Phase:** Physically distinct, chemically homogenous and mechanically separable region of a system.
- In the case of solids amorphous and crystalline are two separate phases. If more than one crystalline structure is possible (diamond, graphite) they are also treated as separate phases.
- Phases are in **microstructural equilibrium**. Certain regions will also indicate solid + liquid states.
- **Equilibrium phase diagram** is a 2D graphical representation that contains the distribution of different phases, their interfaces and the regions of discontinuities etc., with respect to T, P and composition (in the case of alloys).
- Common engineering phase diagrams (e.g. iron-carbon) have T and composition as axes. Different fractions of Fe and C lead to different manufacturing materials (e.g. cast iron, steels).

The need for the phase diagrams:

- To understand what to expect from a material at a certain P, T.
- To predefine the process to yield a certain phase.

Phase diagram

Time dependent	**Time independent**
Time-Temperature-Transformations (TTT)	Composition is a variable T, % composition as axes
Continuous-Cooling Transformation (CCT)	Composition not a variable P,T as axes

Q : Can amorphous phases be shown on the phase diagram?

Q: Where are nanomaterials on the phase diagram?

Hello everyone, in this lecture we are going to learn about the phase diagram of carbon, but I will also tell you some basic things about the phases and the phase diagram. In the previous lecture, you learnt that we can convert one type of carbon into another or one carbon allotrope into another like diamond and graphite in particular.

Diamond and graphite are also considered two different phases of carbon. When you think of the phase diagram you typically think of iron-carbon phase diagram or for other alloys because you know these are important for engineering applications. And there you have the composition of iron and carbon and how much carbon you mix in iron and that is what leads to different phases of the material for example, there are different types of steel and cast iron. These phases will also have sometimes different crystal structures and in this particular case we also have different compositions. But when we have only a single element or single component for that matter for example water then what are the phases?

One option is that you have solid, liquid and gas forms of the same element or the same compound. So, these are three distinct phases, and in addition to that if you do have different crystal types of the same material then those are also considered different phases.

So, by definition what is the phase? Phase is something that is physically distinct, but within itself it is chemically homogeneous. So, what does it mean? It means that you can separate the two phases in principle like diamond and graphite they are physically distinct, you can differentiate between them even if you have tiny little diamonds mixed inside a graphite matrix or little crystals of graphite mixed inside a diamond matrix. Even in that case, you can physically differentiate between them. So, these are physically distinct phases however, the tiny diamond crystal should be homogeneous that you see in the graphite matrix. You should not have some other hybridized carbon or other types of carbon or even graphite inside that diamond crystal. You should be able to physically separate them.

In the phase diagram, you will also see that you have solid plus liquid region. In fact, this happens all the time where solid and liquid are sort of in an equilibrium state. Now we are talking about some sort of microstructural equilibrium at that point.

In the case of bulk solids which is important for all engineering applications bulk solids. So, here if you do not think about the liquid regions then you have amorphous and crystalline as two separate phases. However, typically on a phase diagram you will not show amorphous regions and there is a reason for it because we believe that at every given temperature and pressure combination, there exists a certain crystalline phase that would basically dominate that region which is the least energy state minimum energy state at that particular temperature and pressure combination. So, we typically do not show amorphous regions in a phase diagram. However, amorphous and disordered regions also have been shown on the phase diagram here and there in the particular case of carbon.

There can be several non-graphitizing carbons and we will come to it later. They are physically amorphous but microstructurally they are crystalline. They may not look like diamond or graphite crystal but something else maybe it has a lot of curved carbon structures.

But, even they make a bulk solid which has crystallinity, but it shatters on breaking. So, in the case of carbon you will also see some phase diagrams where you see these kinds of disordered carbons also on the phase diagram, but here what we will talk about we will mainly have diamond and graphite phases. And of course other than liquid and vapor phases of carbon, if at all they are possible and we will see at what temperature and pressure they are possible. In fact, the reason why we have phase diagrams is that this is kind of an easy chart that we have this temperature and this pressure then this is the carbon allotrope that should exist.

Or if I go to go on to another planet or on a certain star where I have the daily temperatures like 6000 Kelvin, at that time which type of carbon I am going to find there? What should I expect? For studying all of these and of course for the manufacturing applications, we have phase diagrams.

As I mentioned already phases are in microstructural equilibrium so it should be possible to separate them using simple physical method. In the case of disordered carbon if you have both amorphous and crystalline regions then it is very difficult to separate them. They are mixed so well, they are not just mixed they are almost homogeneous at a larger scale. So, these are very difficult to separate. So, we will not have those kinds of disordered carbons in the phase diagram for sure. Now, the phase diagram is also known as the equilibrium phase diagram that is because we believe that the phases are in an equilibrium state. At that particular temperature and pressure, this is what will exist. If there are two phases then they are in microstructural equilibrium with each other. And this phase diagram is your 2D representation. It is like a map you can read where is what if you have these conditions then this is the material you are expecting.

Now, as I mentioned that when you have alloys for example, iron-carbon alloys, steel and cast iron and, in that case, the composition of the material becomes very important. How much carbon you have in your iron? That becomes very important. So, the composition is then always one of the axis of the phase diagram.

And typically you will only have two-axis but you can also have three on the right-hand side like you can also mention pressure. But typically you will mention temperature and composition in the case of a two-component phase diagram.

Now, phase diagrams can also be of different types, because we want to study the materials and we can have different conditions not just change in temperature and pressure but we can also change the time.

How do you change the time? For example, if I keep a certain carbon materials material at 900°, I keep it at 900° for 5 minutes or I keep it for 1 hour, that will make a lot of difference also to the composition of that or the crystallinity of that carbon material.

So, these will be your time-dependent phase diagrams, but the easier ones or the ones that we typically study are time-independent because we do not want to have too many variables. First, we want to understand the structure of the material or the composition or the behavior of the material simply without considering the process of time.

So, we typically would study time-independent phase diagrams. However, depending upon your requirements you can also have these time-temperature transformations. As I mentioned when it comes to cooling also for how long did you cool something, obviously it will make a difference. So, these are the kind of time-dependent phase diagrams.

What about the time-independent ones? As I mentioned the first type is composition where the composition is a variable, this is the one where you have two components. And then another type is that where the composition is not a variable, we are always talking about one certain type of element or compound as in the case of water or carbon.

So, the blue one composition where the composition is not a variable is what we are going to learn. This is going to be time-independent and our axes are going to be pressure and temperature. In principle, you can have temperature on y-axis and pressure on x-axis or the other way around.

Note that we will always be talking about 100 percent carbon. We are not considering any impurities or anything we are always talking about 100 percent carbon hence no change in the composition of the material.

As I mentioned, you can find different types of phase diagrams, some of them can actually get very complicated because they may have the different phases alpha, beta, gamma. But that will probably not happen in the case of carbon because you always have a single component. So, it is relatively easy.

So, why do we need the phase diagram? As I said we want to learn what to expect from a material, if I have a certain temperature and pressure combination what should I expect from my carbon. And sometimes when we want to make a certain type of carbon then this helps us in predefining the process parameters if we know what to inspect. So, these are some common uses of phase diagrams.

Now, as I already mentioned, amorphous phase is typically not shown on the phase diagram and the reason for this is that we believe that there is a certain crystalline phase at every temperature pressure combination that exists and dominates that temperature pressure combination that is why we do not consider any amorphous regions. Because amorphous is not the most stable phase for any material. So, the material always wants to get into a crystalline phase. So, there should exist a crystalline phase at every point in the phase diagram and that is why we typically do not show the amorphous phases.

Now, one more interesting question, are nanomaterials shown on the phase diagram? The answer is no because nanomaterials is a completely different game altogether. We have nanocrystals in bulk they are powders. And the materials that we talk about on the phase diagram are bulk solids or bulk liquids. They are bulk engineering materials. Nanomaterials can also be used for engineering purposes not directly but you have to bind them into something because each one of them is a distinct nanocrystal.

So, somehow you have to bring them together before you do any manufacturing with them and let us say I make a composite out of nanocrystals I put inside a resin then that particular material can be considered a bulk solid but not the nanomaterial itself. So, we do not show them on the phase diagram. As I mentioned that the material needs to be in the microstructural equilibrium. Now, we do not really go down to the nanoscale. We should be able to physically separate out a certain phase from the material. But nanoscales as on date we do not show on the standard phase diagrams.

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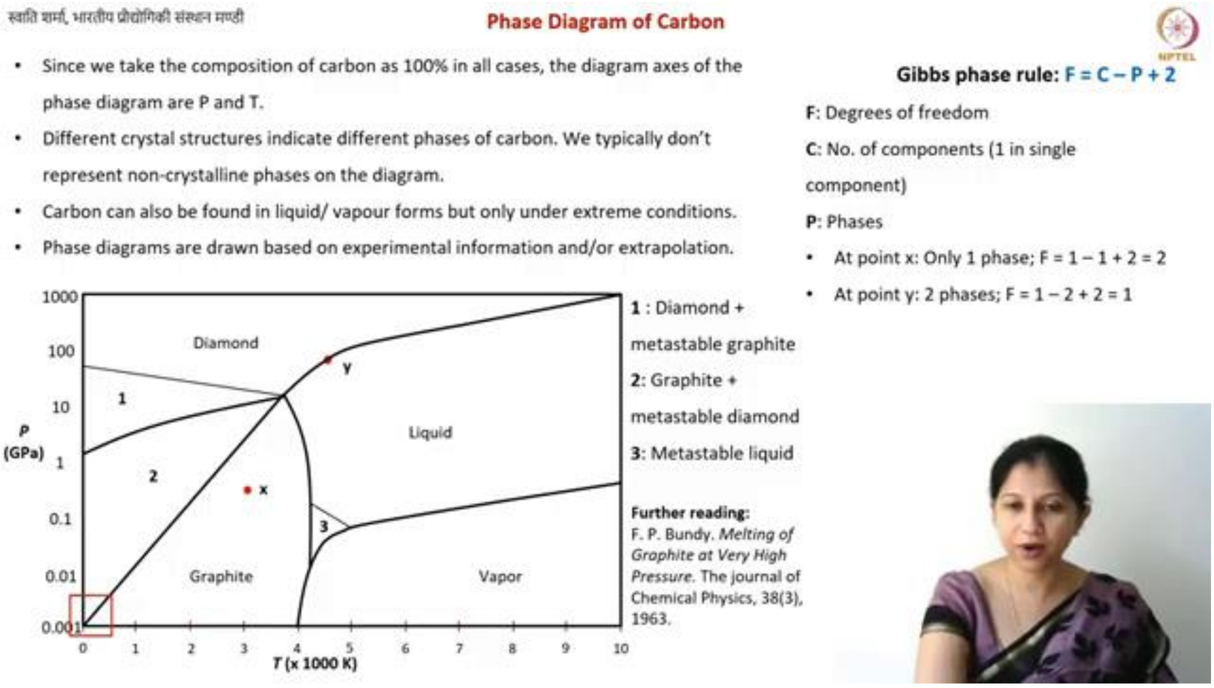

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Phase Diagram of Carbon

- Since we take the composition of carbon as 100% in all cases, the diagram axes of the phase diagram are P and T.
- Different crystal structures indicate different phases of carbon. We typically don't represent non-crystalline phases on the diagram.
- Carbon can also be found in liquid/ vapour forms but only under extreme conditions.
- Phase diagrams are drawn based on experimental information and/or extrapolation.

Gibbs phase rule: F = C − P + 2

F: Degrees of freedom

C: No. of components (1 in single component)

P: Phases

- At point x: Only 1 phase; F = 1 − 1 + 2 = 2
- At point y: 2 phases; F = 1 − 2 + 2 = 1

1 : Diamond + metastable graphite

2: Graphite + metastable diamond

3: Metastable liquid

Further reading:
F. P. Bundy. *Melting of Graphite at Very High Pressure*. The journal of Chemical Physics, 38(3), 1963.

Now we come to the phase diagram of carbon. As I mentioned we have 100 percent composition in all cases. So, without talking any further I will show you the image. This is our phase diagram of carbon now. I have pre-drawn all the lines here. You see what are the different phases, you see the diamond, graphite, liquid carbon and vapor carbon. Now, you did not know about liquid carbon and vapor carbon before right, this is the first time you are hearing about them and the reason you can see already in this diagram. If you see the x-axis you have temperature*1000 Kelvin. Upto 4000 K, there are no liquid carbons and no vapor carbons so in your daily life you will not see any liquid-vapor carbon. You see that you have graphite which directly goes into the vapor phase at 4000 K as long as the pressure is not too high.

If you keep on heating graphite at the standard pressure, at a certain point which is approximately 4000 Kelvin that will directly convert into vapor. What does that mean? It will sublimate, it will never convert into a liquid. This is at standard pressure when we just increase the temperature.

See this phase diagram makes it so easy for you to understand the processes. I will explain the regions 1 2 3, but you will say that I do not have any diamond at standard room temperature and pressure in the graph but we do see diamonds in standard room temperature pressure right. The point is that here the y axis is in Giga Pascal, and why did I take it in Giga Pascal? Because we have to go up to 1000 Giga Pascal. We have to go to really high pressure. So, we need to choose the axis in such a way that we can fit in you know this entire range of pressure onto it.

That is why I have started from 0.001 Giga Pascal and the standard atmospheric pressure is actually is 0.0001 Giga Pascal. So, that is kind of not shown here. So, that little square box now you see, if you zoom it then that is the region where you have your standard pressure and temperature conditions and that is where you actually see only diamond graphite has two phases. You do not see liquid carbon, you do not see vapor carbon and this number 2 region has diamond in but that diamond is metastable.

Now, what happens if you keep on increasing the pressure and temperature as well and at very high pressures, the more stable phase would then be diamond. Those are really high pressures, you see that 100 Giga Pascal and above then you do not have graphite there. Then you rather have a diamond. You also need to be at a slightly higher temperature size, but even if you have room temperature but very high pressure in that case diamond becomes the more stable phase. And in region number 1 that is shown in this diagram, there you actually have diamond that is more stable and graphite that becomes now metastable.

You may also find some graphite at that pressure but that we will try to convert into diamond. So, that is your metastable graphite. In the case of region 2, where have room temperature and pressure that we have in our daily life, there you have graphite as a more stable form and diamond here is the metastable form?

Of course, you can not naturally convert graphite into diamond and diamond into graphite because of this activation energy barrier and so on. This is the distribution of carbon allotropes.

Now, what is the liquid carbon and what is the vapor carbon? You can see that these phases do not exist under standard room temperature or pressure either way. However, it is possible to have liquid carbon and vapor forms of carbon. And these are the forms that are not very well known because those experiments are very difficult.

In the case of iron-carbon diagram or other alloys the temperatures are not so high, you can still perform the experiment. But in the case of carbon, the temperature-pressure conditions are so high that it is extremely difficult to do experiments. These are not the forms that we would encounter every day and there is not so much known about liquid and vapor phases of carbon and they will only exist at very high temperature and pressure.

I have already shown the vapor and liquid forms will only exist under extreme conditions. So, you do not need to worry about the liquid carbon in your daily life and no matter what you are not going to convert carbon into a liquid for manufacturing applications. You are not going to use those high pressure-temperatures in any way.

you don’t need to worry about them unless you are scientifically interested in liquid and vapor carbons. A lot of this data has actually been placed in the diagram by extrapolation or simulations.

In fact, a lot of simulation studies are being conducted in the last 20-30 years. People were mostly relying on the experimental data before that. Now, simulations make it easy to extrapolate the data on the phase diagrams to some extent. And there when you are performing the simulations you can go up to whatever 1000 or 100 Giga Pascal and you can also simulate it at very high temperatures.

Of course, this will also depend on how you simulate and what kind of effects you are considering for example, when you have such high temperatures then what kind of radiation will take place? What kind of cooling will take place? Are you going to consider this material is in space where there is no cooling taking place and there are no external factors?

So, these are the inputs that you need to give in to your model. Several different types of modeling simulation studies have been carried out based on all of this inputs. The region number 3 here is the metastable liquid form of carbon. Again you can understand the same way you have understood metastable diamond or metastable graphite. Now, you see this region 3 falls between liquid, solid, and vapor phases of graphite. You may have all 3 phases in that region that is why the liquid phase at least would be metastable and it can convert into both solid and vapor.

This is the first phase diagram of carbon and the experimental data on the first phase diagram of carbon was provided by Bundy. This is this paper that I have shown here. This is one of the first papers on the elemental carbon phase diagram.

So, if you are further interested you can read this paper and it will give you some interesting insight on how you can conduct experiments at such you know high pressure and temperatures. And the author actually observed the possibility of melting of graphite at very high temperatures and pressures. If you are further interested you can read.

Now, one thing I would like to tell you, the standard rules apply whether it is a single component or many components in the phase diagram for example, the Gibbs phase rule. I am sure you all remember when you count the degrees of freedom;

$F=C-P+2$

So, let us say we take one point here x in the graphite region. Now, the number of components will always remain 1 that is the only thing you need to remember because it is a single component phase diagram. So, the number of components C will always remain 1 the phases will change. So, in this particular case at point x you have only 1 phase so you will have 2 degrees of freedom.

2 degrees of freedom what does that mean? In the context of the phase diagram, if you increase or decrease pressure or temperature or both basically you can go in any direction from that point x still you will have the same phase. You will maintain the same physical phase or composition of your material. So, that is what you mean by the degrees of freedom.

You take another point y which is on the line between diamond and the liquid phase of carbon. You can also take the diamond graphite line or any line. Now components still remain 1 so now the degrees of freedom will be 1 for that case.

Degrees of freedom 1 means you can either change the temperature or change the pressure the other value will remain fixed. This means if you only have 1 degree of freedom and if you change both temperature and pressure then you will lose the phase. So these standard kinds of rules would apply to a double component or binary phase diagram. And these rules will also apply to this kind of carbons phase diagram.

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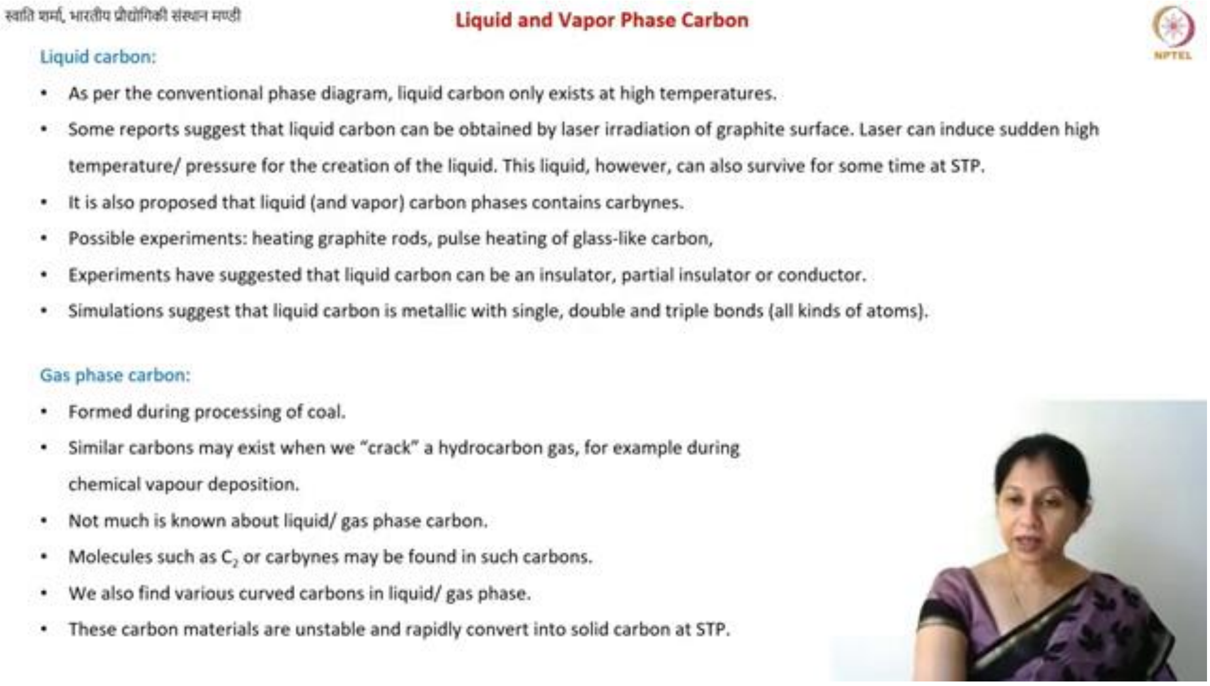

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Liquid and Vapor Phase Carbon

Liquid carbon:

- As per the conventional phase diagram, liquid carbon only exists at high temperatures.
- Some reports suggest that liquid carbon can be obtained by laser irradiation of graphite surface. Laser can induce sudden high temperature/ pressure for the creation of the liquid. This liquid, however, can also survive for some time at STP.
- It is also proposed that liquid (and vapor) carbon phases contains carbynes.
- Possible experiments: heating graphite rods, pulse heating of glass-like carbon,
- Experiments have suggested that liquid carbon can be an insulator, partial insulator or conductor.
- Simulations suggest that liquid carbon is metallic with single, double and triple bonds (all kinds of atoms).

Gas phase carbon:

- Formed during processing of coal.
- Similar carbons may exist when we "crack" a hydrocarbon gas, for example during chemical vapour deposition.
- Not much is known about liquid/ gas phase carbon.
- Molecules such as C_2 or carbynes may be found in such carbons.
- We also find various curved carbons in liquid/ gas phase.
- These carbon materials are unstable and rapidly convert into solid carbon at STP.

As I mentioned we do not know very much about the liquid and vapor phases of carbon. This is very interesting in the case of carbon. I think half of the time I tell you that we do not know much about this carbon material. It is one of the oldest materials that people have known and studied. Even 1000's of years ago people were using coal and carbon inks. Some of the first carbon inks were made in India a long time back which were being also exported and even being sent to China. And you know Kajal and all kinds of carbon-related cave paintings and writing tools were made of carbon.

Even if we do not go that far in history, if you think about the 18th 19th century some of the discoveries for example when Thomas Edison made the light bulb. The fiber which was used was also a carbon fiber which was derived from cellulose. So, during that time all kinds of batteries and all kinds of adsorbents were made using carbon. Carbon was the most important material at that time and even today it is the most important technological material and yet we know so little about this material we know so much about the material, but still so little.

The same thing about the liquid and vapor phases of carbon. So, we know that in the phase diagram it should exist. It has been experimentally validated but there have been only a few experiments performed under very high energy conditions like the surface of graphite was melted.

Some of them suggest that liquid carbon could be a conductor. Some of them suggest that this might be not a semiconductor but a mixture of conductor and insulator so semi insulator sort of material. And some also suggest that it might be completely insulating. So, experimental work has been done.

We do know one thing that at standard pressure and temperature it is extremely difficult to have liquid or vapor carbon. You can have vapors of hydrocarbons that will deposit carbon onto something but should we call them carbon vapors? That is also questionable.

We talked about carbynes. We talked about these linear elemental carbon molecules and it turns out that people have observed carbynes also in liquid and vapor phases of carbon. So, already these are very difficult experiments to conduct however these things have been observed.

Actually, I forgot to tell you one thing about carbynes that they are also found when some object like a meteorite hits the surface of the earth. So, one such case because the meteorite hitting the surface of the earth is a very high energy event, that has a lot of impacts if there was some carbon let us say there was a tree so that can convert a tree or charcoal into some sort of a silver-white carbon. And that white carbon when it was analyzed it was said that it contains carbynes. So carbynes are solidified then it is quite possible that they will have a silver-white colour.

Again these things are just out of interest. If you want to read about these things, you can read about white carbon that also contains carbynes. It has been suggested that both vapor and liquid phases may contain carbyne. And then there have been a lot of the experiments for example, heating of graphite rods, pulse heating of glassy carbon and there are many other examples which I have not mentioned here. Basically, any very high-energy experiment can convert your carbon into carbyne. And as I mentioned it could be an insulator, a partial insulator or also in some cases some experiments suggest that it could be metallic conductor.

However, most of the information that we have about liquid carbon is based on the simulations and not the experiments. Now, similarly for gas-phase carbon, you can obtain when you are processing the coal when you are doing petrochemical refinery So, you can find some gaseous carbon in the case of gasifying coal under a very controlled environment.

And similarly, when we crack the hydrocarbons and there is some process known as chemical vapor deposition which is a film deposition technique that we will learn later in the course. These films are deposited from the vapor phase. In fact, these films are also interesting from the phase diagram point of view because just before converting into solid the vapors may contain some vapor phase carbon.

So, remember that vapor phase carbon does not mean hydrocarbon. We are still talking about elemental carbon. Hydrocarbons are vapors in most cases and they are in the gaseous form. So, it is very easy to have hydrocarbon vapors but it is not that easy to have carbon vapors. But these hydrocarbon vapors may contain some carbon vapors, at least right before their conversion into solid particles.

So, we do not know too much about liquid gaseous carbon phases. It is also suggested that there is a molecule known as C_2 similar to H_2, O_2 and N_2. We can also have C2 molecules which may be found in gas or vapor phase carbons We do not know too much about the composition of liquid-gas phase carbons we can actually find various different new carbon allotrope. So, these are interesting materials to study because these materials can potentially show us the new carbon allotropes. But right now we do not know too much about liquid carbon and vapor. They are unstable and they convert into solid carbon at standard pressure and temperature. When they convert into solid carbon for example, using this chemical vapor deposition technique then they have diamond-like carbon, and sometimes they have graphite like carbon. And that is something very interesting for us to study, maybe in the next lectures, we will talk a little bit about that.