Materials Science
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Lecture 16
Crystal Imperfections

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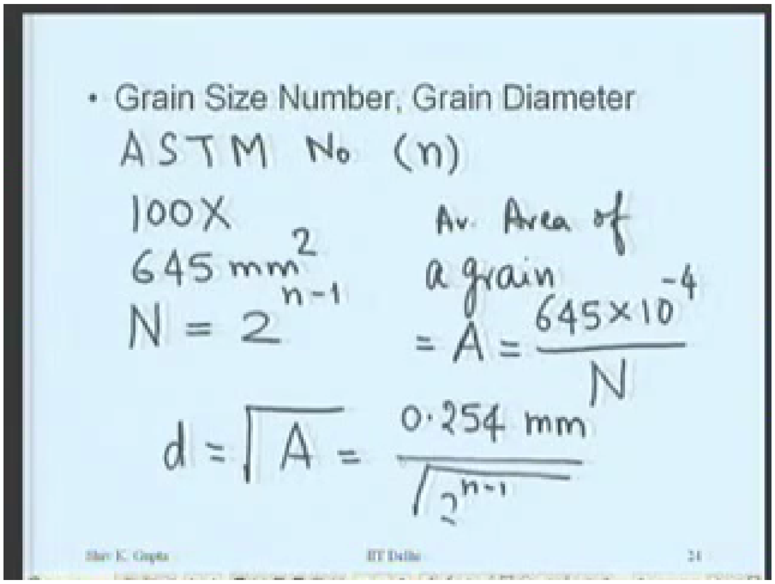

- Grain Size Number, Grain Diameter

ASTM No (n)

100X

645 mm^2

$N = 2^{n-1}$

Av. Area of a grain $= A = \frac{645 \times 10^{-4}}{N}$

$d = \sqrt{A} = \frac{0.254 \text{ mm}}{\sqrt{2^{n-1}}}$

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Right, we were talking about the surface imperfections in the last class and we talked about the grain boundaries, talked about the stacking faults, we talked about the twin boundaries, the kind of internal surfaces which we have in material. However properties are dependent upon the sizes of the each crystallite which is present in the material. Therefore we define the size of each crystallite, what we call the grain, is also called the grain size, grain diameter or grain size number.

We shall define this. There is an international standard for this and we use that international standard which is used even in communist countries. This standard is called ASTM number which we give by let us say n. A stands for American, S for society, T for testing, M for materials. So it is American Society for Testing and Materials, it is not testing of materials, it is testing and materials. Right?

And this standard is what we use. For this we have to look at the structure of the grains. We prepare the specimen sheet under the microscope. Usually metals and alloys are opaque and to see these crystallites we have to prepare the specimen hatchet so that grain boundaries are delineated and we then measure the number of grains in a given area and that we use for this a magnification of, linear magnification of 100.

Linear magnification we write as 100X. So aerial magnification would be square of this, 10 to the power 4. And unit area when the standard was made was one square inch. Today we call it 645 millimeter square which is a square of 25.4, the 25.4 millimeters in an inch and we just square this, it becomes 645 millimeter square. So at 100 linear magnification when we view the microstructure, we take 645 millimeter square area and in that area we count the number of grains. Let us say that number of grains turns out to be N. Then we express this N as 2 raised to power n minus 1, n is then the ASTM number.

"Professor-student conversation starts."

Student: What is N?

Professor: N is the number of grains which we have measured in the area 645 millimeter square, measured at 100 linear magnification. It would mean then the area and average area of a grain because no grains are looking alike, they are space filling polyhedra basically. Some are smaller, some are bigger. So average area of a grain would be, let us say A, it is 645 millimeter square multiplied by 10 to the power minus 4 divided by N.

Because these many grains in this much area, so average area is area divided by number of grains. And the grain diameter is then defined as under root of A. If I do that, under root of this shall become 0.254 and since that is in millimeter square, so it becomes millimeter. And N is 2 to the power n minus 1, so it becomes under root of 2 to the power n minus 1. That is the average grain diameter and n is the ASTM number.

We can define the grain size either by d or by n, they are related. And you have noticed that as the grain size number increases, the grain diameter decreases. Is that clear? We will be measuring this in the next laboratory class, we will be doing that.

Student: What are the grains in particular?

Professor: What I have written here, you tell me. It is for you to tell me now.

Student: Intermediate size?

Professor: I have defined that I am measuring in a 645 millimeter square the number of grains, in that area and that is at linear magnification of 100.

Student: Sir, why do you magnify at that point of phase initially?

Professor: So this is a magnification of 100 linear, I told the aerial magnification would be square of this. So I have multiplied by 10 to the power minus 4 to make it actual millimeters square, right? So this is the actual millimeter square, is the number n because you cannot see at that (magni) actual size, it is too small. So you magnify it 100 times. 1 millimeter length becomes 100 millimeter but 1 millimeter square would become 10 to the power 4 millimeter square. Is that clear? That is what it is. Is this clear now? All right.

“Professor-student conversation ends.”

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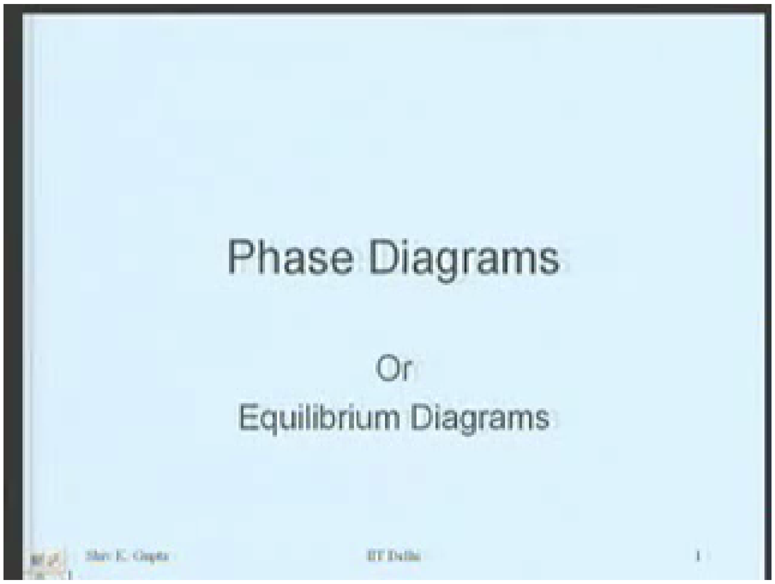

Phase Diagrams

Or

Equilibrium Diagrams

So we finish with the crystal imperfections and then we can now move onto, all right, now we shall talk about phase diagrams or equilibrium diagrams. Equilibrium you have already seen in the initial classes when we talked about bit of kinetics and equilibrium. It is defined by the minimum of the free energy whether it is a metastable equilibrium or the stable equilibrium which we call the more stable equilibrium, free energy is at its minimum.

Minimum what is defined in mathematics, you have seen that. The slope there is going to be 0 and second derivative is going to be positive. So that is what the minimum is, minimum of free energy. This we are referring to the equilibrium, equilibrium as I said earlier can be metastable equilibrium or the stable equilibrium. That is what we are using the materials. In their state most of them are in the metastable state.

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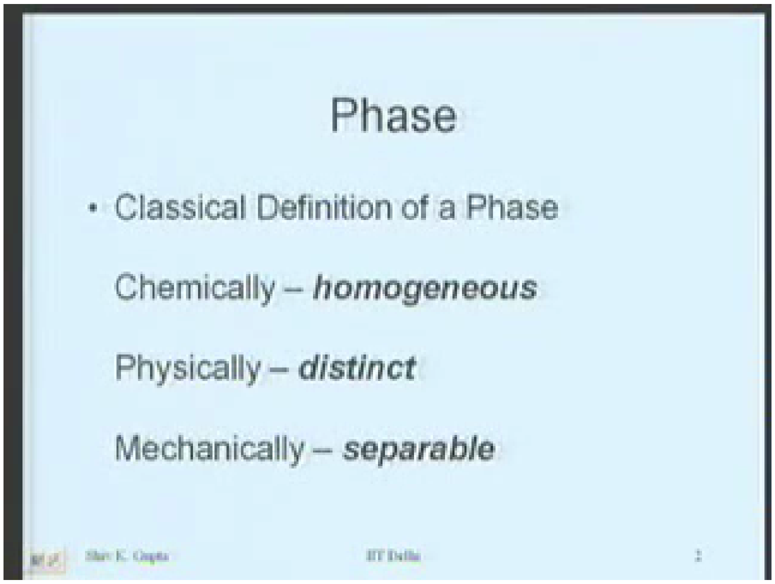

Phase

- Classical Definition of a Phase

Chemically – ***homogeneous***

Physically – ***distinct***

Mechanically – ***separable***

In the phase diagram, the word first is a phase and yesterday also I said that we shall define what is the phase in the next class. First of all, let me talk about classically what is a phase. Classical definition of a phase is it is something which is chemically homogenous, it is physically distinct, and mechanically separable. Let us first understand the meaning of these one by one.

Something what is chemically homogenous, if you take water which is not polluted, pure water whether you are in Himalayas or you are in Delhi or you are in South Chennai, you analyze this water, anywhere it is H2O. Chemical analysis is H2O. And whatever you have bicker, from the bicker you can pour it into a small test tube or you take bigger bucket, same H2O. Any part of the water you take from the bicker from any corner, it is H2O, no difference.

It is chemically homogenous everywhere. That is what I mean by chemically homogenous. What is not chemically homogenous, let us see that. If I add some oil in water, shake it well, try to make it as much (pos) homogenous as possible, leave it for a while, well, oil will come floating top. You take from the bottom corner, you take with it small quantity droplet or something analyzed, it will be H2O or take from the top, it will be oil. But there will be an interface where you can take water molecules as well as in the interface you can take the oil molecules.

This is something not homogenous, it is heterogeneous. They are two different things. In the same container I have two different things. This is not homogenous. All right. If I go on, let us say talk about water, I add some sugar to it, dissolve sugar in it, add more sugar, keep dissolving, it will keep dissolving for some time. Then after that, if you add sugar, how severe stir, it will not dissolve, it stays in the bottom.

If you leave it, do not stir it, it will stay in the bottom. Now there is something dissolved in water. If you take any droplet from anywhere, analyze this, you will have certain part of sugar, certain part of water. If you take some quantity from other corner, it will be same amount of sugar, same amount of water. But when you take out the sugar crystals which are still settled in the bottom, it will be 100 percent sugar, now water there.

So therefore this is not (hetero) homogenous, it is a heterogeneous thing. I have sugar crystals as well as syrup, the solution of sugar in water. But sugar in, dissolved in water, the syrup is homogenous. Anywhere I take…….

“Professor-student conversation starts.”

Student: In saturation, it will be homogenous.

Professor: Yes, that is what I am trying to arrive at, what is the difference between something homogenous, something not homogenous. When I have the salt crystals in the syrup not dissolved, it is heterogeneous. When everything is dissolved, only the syrup, it is homogenous. Okay.

Physically distinct, I have already said that. Syrup, distinct from the crystals of the sugar. So you can say the syrup is one phase and sugar crystals are another phase. In that heterogeneous system, they are two different things. So physically distinct means looks a different. Say for example, I give an example of oil and water, you shake it and leave it. After some time all the oil is on top, all the water is in the bottom. You can distinctly see, because the colors which you see, oil will be different from that what you see in water.

Oils are usually less transparent as compared to water, right. You will be able to see that. And they are mechanically separable. If I give you syrup and ask you to separate the water, sugar and water from this syrup, you can do it. How?

Student: They are products.

Professor: You will boil off, the water will be evaporated and these vapors can be collected, condensed, you get water and sugar is left behind. Okay. This is not the mechanical means of separation. This is not the mechanical means of (sep), what is mechanical means of separation? You pick something like this and keep it here. Pick another thing here and keep it there. That is mechanical means of separation.

But when I have syrup and sugar crystals, you can take a tea set, put it in a syrup, take out the crystal, crystals have been separated from the syrup because sugar crystal which is settled in the bottom is not dissolved. Similarly when you have water and oil, you can just make a small hole in the bottom of the test tube, all the water will first flow out and then when comes interface, you seal it back, oil will be left behind. Okay. This is mechanical means of separation. Mechanical, not any chemical or physical means of separation. It is mechanical means of separation.

“Professor-student conversation ends.”

So anything which can be separated from another by mechanical means is a different phase. It looks different from the others. They are different phases. And each one by itself chemically homogenous, right? If you look at the definition of syrup which you looked at or you give another solution of let us say alcohol and water, they also dissolve in each other in proportion. It is mixed, you cannot say alcohol can be seen different from the water. They are, once they are mixed, they are mixed. Looks at one single phase, right.

So I can say now like we have a solution is a phase. Solution where the crystals or the molecules of sugar are mixed with the water molecules at the molecular level, that is the syrup. That is why I am not able to separate them physically. I have to evaporate all the water to get the sugar back. So like that in solid state, because we are going to talk about materials which are solids, solid solutions are there, I talked about the substitutional solid solutions and interstitial solid solutions. So solid solutions are going to be freezed. Right?

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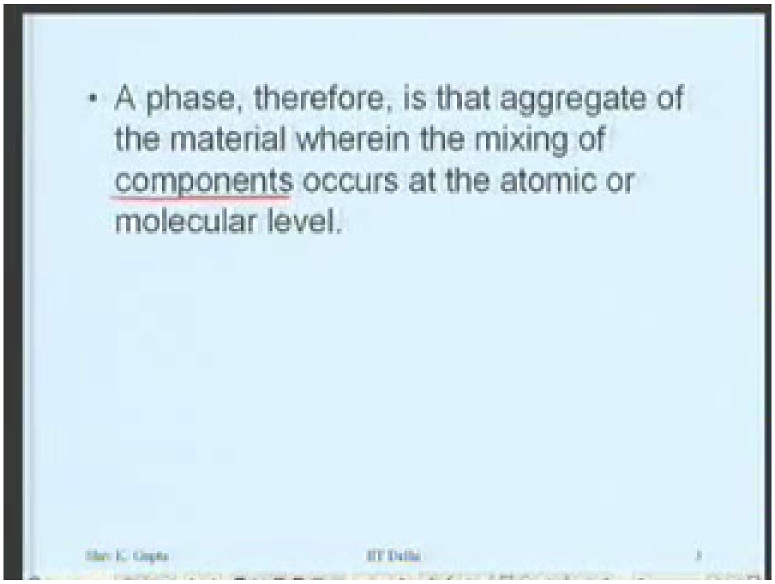

- A phase, therefore, is that aggregate of the material wherein the mixing of components occurs at the atomic or molecular level.

So therefore classical definition of a phase is a phase therefore is that aggregate of the material wherein the mixing of components occurs at the atomic or molecular level. Now here I have introduced another term which is called component. We have to understand this word component. Various components are mixed with the atomic or the molecular level, the example I gave is sugar syrup. Molecules of H_2O form one component and molecules of sugar, $C_{12}H_{22}O_{11}$, that forms another component. Okay. If you look at the elements, there is hydrogen, there is oxygen and there is carbon. These are three elements. But I have only two components. So I must define now what is a component.

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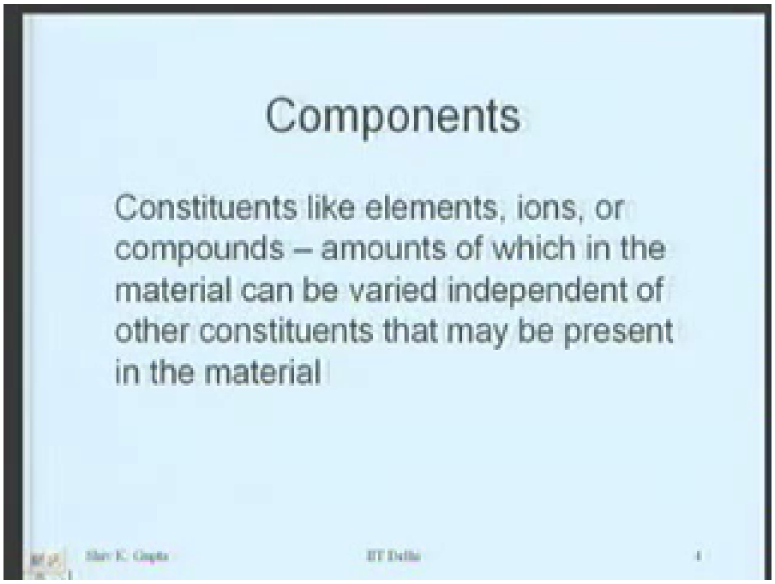

Components

Constituents like elements, ions, or compounds – amounts of which in the material can be varied independent of other constituents that may be present in the material

Components are the constituents like elements, ions, or compounds in the system, whatever solid state system I am talking about. The amounts of these material can be varied independent of other constituents in the system, the ones which are present in material. So in the syrup I have sugar, I have water, I have, otherwise elements if you look at, I have hydrogen, carbon and oxygen. Let us talk of water alone, H2O. Can I change the amount of hydrogen independent of the amount of oxygen in H2O? No.

So what I can change is the amount of H2O, so H2O becomes one component. Let us look at the sugar, C12H22O11, can I change the amount of carbon irrespective of the other elements, hydrogen and oxygen? No. So therefore sugar and water are the two components, not carbon, hydrogen and oxygen. The amount of which I can change independent of the others which are present in the system, is that clear? So components are these. Now having defined a phase where I introduced the word component and having defined components, I have to look at the equilibrium.

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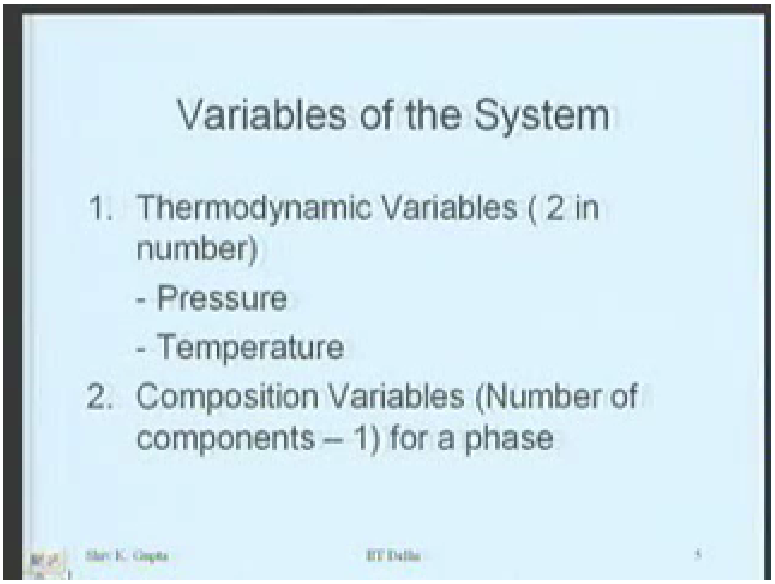

Variables of the System

1. Thermodynamic Variables (2 in number)
   - Pressure
   - Temperature
2. Composition Variables (Number of components – 1) for a phase

To look at the equilibrium, first of all let us try to understand what are the variables in the system. My system has two variables which are called thermodynamic variables: temperature and pressure and these are two. Pressure can be varied from perfect vacuum to very high pressures to whatever interested you can reach, could be a few gigapascals. It can be, it is possible probably to reach.

And then we have other than these thermodynamic variables, the pressure and temperature, of course temperature is also absolute value is 0 kelvin and it can go up to high temperatures, maybe in laboratory you can develop up to 3,000 kelvin easily. Then we have talked about the components, the constituents of the system. So composition of the system, those are called the composition variables.

And if there are more than one phase, I have to define the composition of each one of them. That is what is called, I mean that is what I mean, composition variable for a phase, right. So number of components is what you have to define. That is what I have to define is let us I have a system, which contains sugar and water, example I gave the syrup. I say it contains 30 percent sugar, so 70 percent would be water. I need to define only one composition, 30 percent sugar.

If I give you an gold ornament, I say it contains 20 percent copper. So the remaining 80 percent is gold. So I have to define only one but if I have three things like in steel, I have iron, I have carbon, let us say I have manganese. Steels can have more than three. Just take an example of three, iron, carbon and manganese. I say it contains 0.2 percent carbon and it contains 1.8 percent manganese, right? Then the amount of iron is defined, 98 percent. So I have to define one component less in number of variables. That is what I have given, number of components what are there in the system minus 1. This is minus 1.

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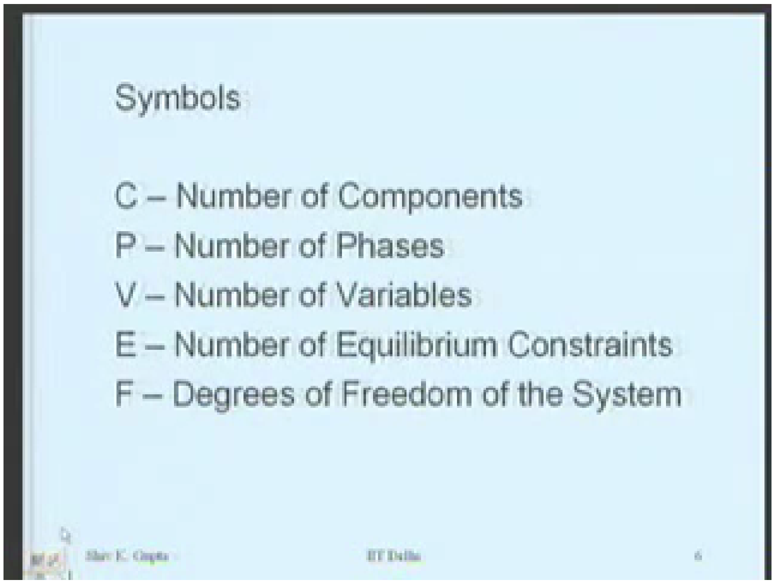

Symbols

C – Number of Components
P – Number of Phases
V – Number of Variables
E – Number of Equilibrium Constraints
F – Degrees of Freedom of the System

Then now we start writing these things in terms of variables unknowns and I define the symbols for them. C I use for number of components like I have gold copper alloy, number of components are two, gold and copper. C is equal to 2. Sugar syrup I have sugar and water, two components, sugar and water. Number of phases in a system, it can be one, it can be two, it can be three, it depends how many phases are there, that is P, I represent by P the number of phases.

Number of variables in the system I define as V. We shall work it out how much it should be because I already stated what thermodynamic variables plus the composition variables, that we can work out depending on how many phases are present in the system. And E is the number of equilibrium constraints, what is defined by the equilibrium. If two phases are present in equilibrium, meaning thereby is equilibrium was defined as if you give infinitesimally small perturbation to the system, free energy should not change, it should remain the same, infinitesimally small.

There is limit delta extending to 0 is what? Infinitesimally small. And smallest delta x. But once I say delta x tending to 0, means the infinitesimally small disturbance to the system and it does not change its free energy, it is in equilibrium. Okay. That is number of equilibrium conditions or constraints we have to work out. Then we shall see how much degrees of freedom the system has. Means what are the variables which can be changed maintaining the system in equilibrium. Degrees of freedom meaning I can change these variables of the system, still the system is in equilibrium. Okay, that is what we shall see. All right.

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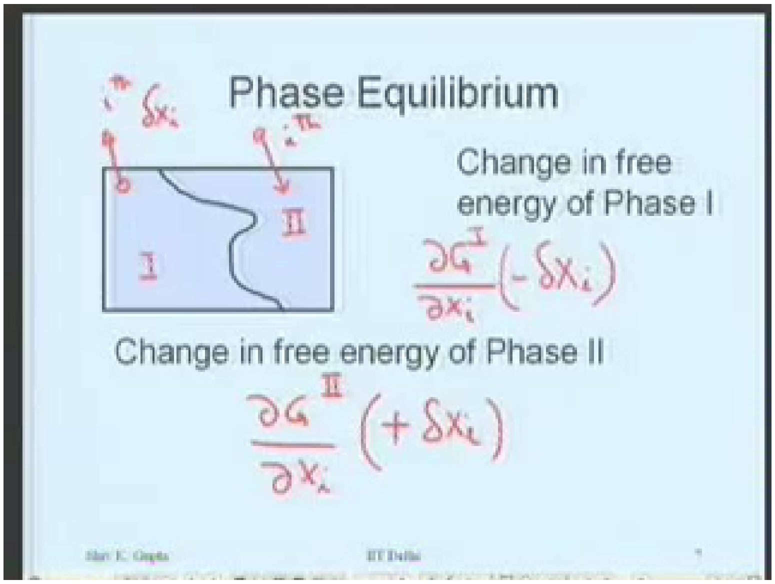

Phase Equilibrium

Change in free energy of Phase I

$$\frac{\partial G^{I}}{\partial x_i}(-\delta x_i)$$

Change in free energy of Phase II

$$\frac{\partial G^{II}}{\partial x_i}(+\delta x_i)$$

Let us first of all talk about the equilibrium. Let us say I have the phase I here in the system and this is the phase II in the system. And there are certain components in this, C components in the system. So those C components are present in I, they are also present in II. But relative amounts in I are going to be different from the relative amounts in II of all the components. That means composition of the phase I is not the same as the composition of phase II, they are different.

But once I have the system, I have certain mass of the system, that shall remain the same. But it is distributed between phase I and phase II. All right. Infinitesimally small disturbance will not change my equilibrium. Let us say I have a few components in here like I have copper, I have nickel, I have silver, I have zinc, I have tin. Number of components are present in this system. The smallest disturbance I can give to the system without changing the pressure and temperature let us say is I can add or remove one atom of one of the components. Let us say I remove from here one atom out of the ith component.

“Professor-student conversation starts.”

Student: There are same components.

Professor: Components will be same, their relative amounts will be different. The whole system is one, there are no two systems. There is one system but it has two phases. Like oil and water it contain as one system or sugar syrup and sugar crystals is one system.

Student: So then 30 percent sugar should be given, during sugar whole region will be different ratio?

Professor: There are different phases if they are not dissolving in each other. If they dissolve, make it 40 percent or 45 percent, then is one phase. If they separate out, they do not mix, yes, it is one single and there are two different phases. That is true. Is that clear? Right. It is possible in solid states, things will happen like that too.

"Professor-student conversation ends."

So I have changed the free energy of the phase I. Let us say this amount of one atom corresponds to the amount equal to delta xi because ith is the component. I call this one atom as amount equal to delta xi. If the free energy of the phase I changes with the ith component with a certain rate, let us say that rate is free energy of the phase I with respect to ith component, and keeping the other component same without changing them, let us say is this.

And the amount which I have removed from this is the delta xi, this is the rate at which it is changing and then the total amount which is removed is, so this is a change which I made to the free energy of the phase I. Now I have removed one atom from the system. Mass of the system has changed. When I have given a system, mass cannot change. So let us put this atom back in phase II. The same atom is put back, so I changed the free energy of phase II also.

What is the change I caused the free energy of phase II? The rate at which it changes, let us say that rate is this for the ith component. And the amount is added to it. This is the amount which is added, this is the change in the free energy of phase II. This is infinitesimally small perturbation we have given to the system. You cannot make smaller than that. One atom, simply one atom you have removed and put it back into the phase II, mass is not changed. So net change in free energy at this state must be 0 if it is an equilibrium. Okay. Let us see what does it give us.

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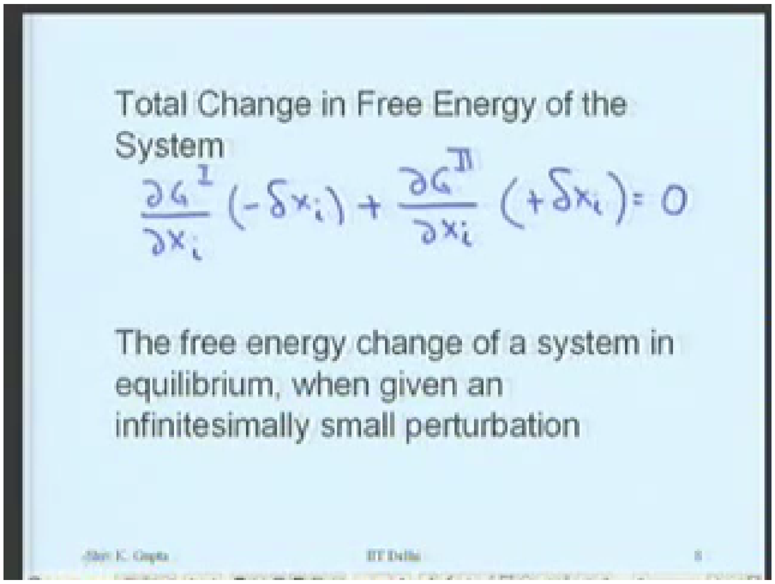

Total Change in Free Energy of the System

$$\frac{\partial G^{I}}{\partial x_i}(-\delta x_i) + \frac{\partial G^{II}}{\partial x_i}(+\delta x_i) = 0$$

The free energy change of a system in equilibrium, when given an infinitesimally small perturbation

The total change in free energy of the system now is therefore, that is what it is, it is 0. The free energy change of a system which is in equilibrium with small perturbation must be 0.

“Professor-student conversation starts.”

Professor: And what does it give us then?

Student: We have to change G1.

Professor: Yeah, it give us the rate of change of free energy of the phase I with respect to the ith component, is the same as the rate of change of free energy of the phase II with reference to the same component. This derivative must be equal to this derivative.

“Professor-student conversation ends.”

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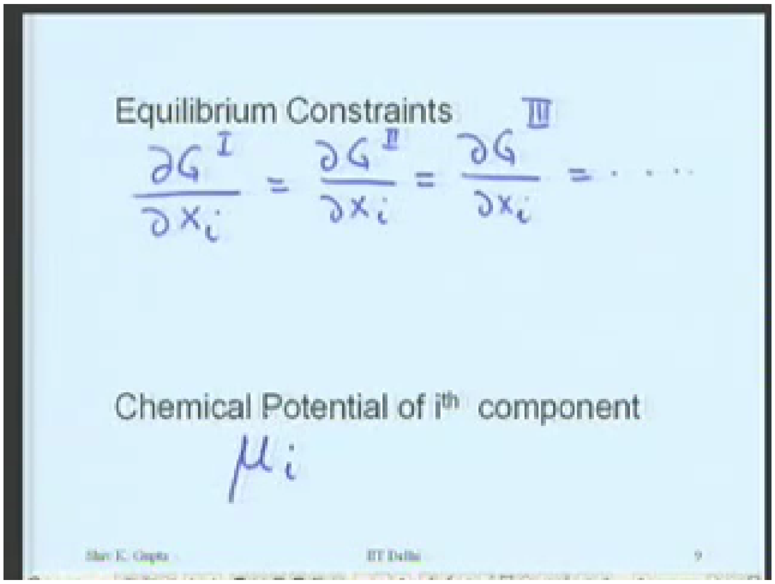

Equilibrium Constraints

$$\frac{\partial G^{I}}{\partial x_i} = \frac{\partial G^{II}}{\partial x_i} = \frac{\partial G^{III}}{\partial x_i} = \cdots$$

Chemical Potential of i^{th} component

μ_i

So I get the equilibrium constraints from this. And if there are more than two phases, it shall go on.

“Professor-student conversation starts.”

Student: Sir, while there is a net free energy change of a system is 0, net overall……

Professor: Because small, I have given infinitesimally small perturbation because I am at the minimum of the free energy. At a small disturbance, it should remain, free energy remain the same, that is the slope is 0 there. Right.

“Professor-student conversation ends.”

This derivative is called the chemical potential of ith component in the system and we write it as, so chemical potential of the ith component in phase I is the same as in phase II, is the same in phase III, same in phase IV, same in phase V and so on and so forth. That is the equilibrium. I have done it for one component. If there are C components, this will be valid for all the C components.

So like that, let us say you talk about some component which is Gth component, delta G1, delta xj is equal to delta G2, delta xj equal to delta G3, delta, so on and so forth. Chemical potential of jth component in all the phases will be same. That is the meaning of equilibrium in a system. All right.

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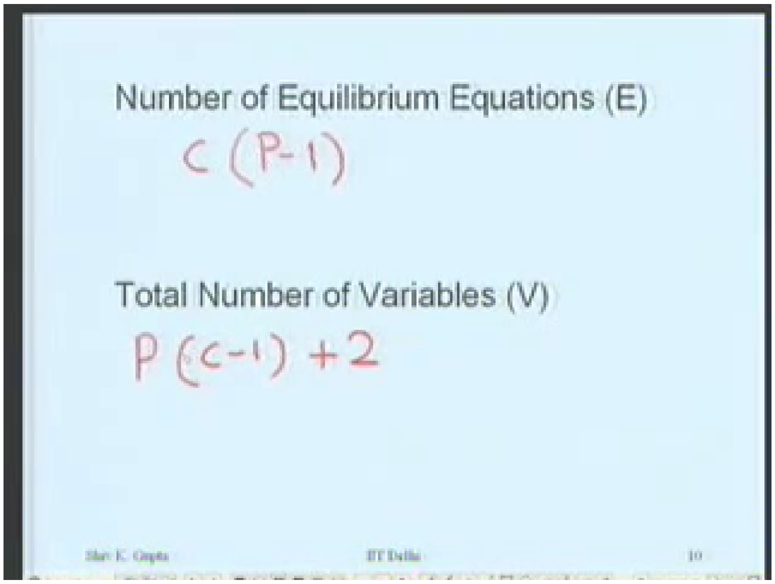

Number of Equilibrium Equations (E)

$C(P-1)$

Total Number of Variables (V)

$P(C-1)+2$

Now we shall take care of how many variables do we have and how many equations do we have.

“Professor-student conversation starts.”

Professor: So how many number of equilibrium equations do I have?

Student: Number of equations…..

Professor: Number of phases for each……

Student: Probably minus 1.

Professor: Number of phases minus 1 for each component. All right. I defined already the components. Let us say I have C components and for each component I should have P minus 1 equations where P is the number of phases. Is this clear? mu i in phase I is equal to mu i in phase II is equal to mu i in phase III is equal to mu i in phase IV and so on and so forth. Is that clear? If there are two phases only, let us say mu i in phase I is equal to mu i in phase II, how many equation do you have?

Student: One.

Professor: One. If there are three phases, mu i in I is equal to mu i in II, mu i in I is equal to mu i in III. mu i in II is equal to mu i in III, how many equations?

Student: 2.

Professor: Only 2. There are only 2 independent equations, third one is not independent, third one is relationship, right? So when I say mu i I equal to mu i II, equal to mu i III, that means there are only two equal to signs and two equations only. That is why I put P minus 1, multiply it by C, it becomes number of equilibrium equations we have. Then total number of variables what we have in the system, each phase shall have how many components? C, how many composition variables do I need? For the one phase I am talking about. How many composition variables would I need? C minus 1.

Student: C minus 1.

Professor: If there are gold and nickel, I need to define only nickel, gold is already defined.

Student: C minus 1.

Professor: C minus 1, Right. So composition variables would be C minus 1 for each phase and there are P phases. Plus, two thermodynamic variables, pressure and temperature. This is the total number of variables. Now I have a situation. This is the kind of situation you have come across in the school, you have done it in your first year also. If you have set of equations in certain number of variables, you can, you had solved them. There are three equations and three variables, you have solved all the three uniquely and you get one solution.

“Professor-student conversation ends.”

There is no degrees of freedom for the system, is uniquely defined. We call it a system with 0 degrees of freedom if number of variables is equal to number of equations. However if you have a system where you have less equations and more variables, say for example, I give you three equations and five variables. In five variables, three equations are independent equations. You can solve this system, you will get large number of solutions.

Provided you can choose arbitrarily two variables, let us say one and two, two variables you have chosen. Let us say x1 and x2 you have chosen. x3, x4, x5, you will be able to determine from the set of equations. We have fixed the values of x1 and x2. If you fix the value of x1 and x5, you can find out x2, x3, x4 from the equations. So two variables which you choose, the choice is yours, it is arbitrarily.

We say the system has 2 degrees of freedom. Okay. And you will get large number of solutions. Such a situation physically in a material is also possible. That water remains water at 1 atmosphere and water remains water at 1.2 atmosphere pressure also, does not change. So this is possible. What is the next situation is when I have five equations and three variables only. This situation is not a real situation, it could not be the real variables.

This situation exists for complex systems but it cannot exist for real systems. My material systems are physically present, they are real systems, they cannot be imaginary. Water is here, water is not there. Beaker is full of water and there is no water there, is not situation possible. Such imaginary situations are not possible. Therefore I have to have systems which are real and this will not be possible. What it will be possible is to have more variables and less equations or at the most number of equations equal to number of variables.

“Professor-student conversation starts.”

Student: How then it will be possible that we have three equation and five variables, for example, how physical conditions can happen?

Professor: We will come to that. We will see the diagram, we will show you the variables and we shall show you the existence of a system and we will be changing the variables and all that we will talk about. Then physical examples I will give. So it is possible for me to have more variables and less equations or variables equal to the equations. But I cannot have number of equations more than the variables, it is not possible. And then we define the degrees of freedom as number of variables minus the number of equations.

“Professor-student conversation ends.”

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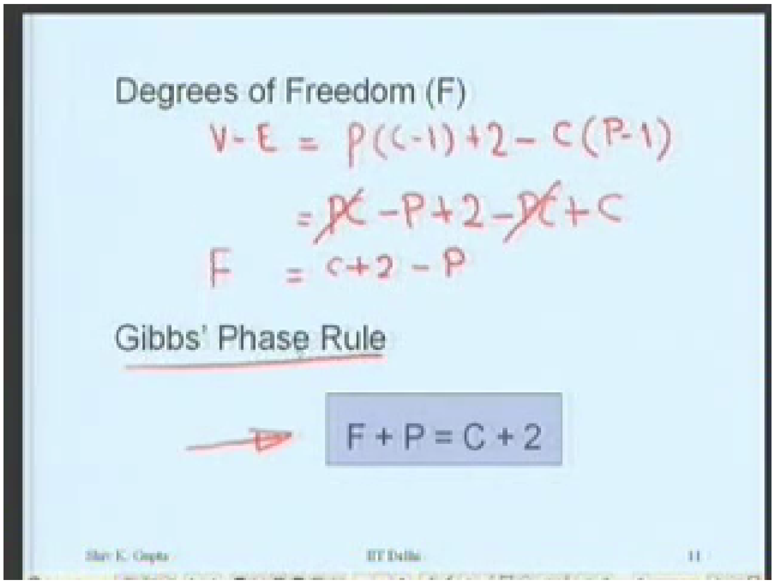

Degrees of Freedom (F)

$$V - E = P(C-1) + 2 - C(P-1)$$

$$= \cancel{PC} - P + 2 - \cancel{PC} + C$$

$$F = C + 2 - P$$

Gibbs' Phase Rule

$$\boxed{F + P = C + 2}$$

Right, so let us define the degrees of freedom now. Degrees of freedom as I said is number of variables minus the number of equations. Variables I wrote down is P into C minus 1 plus 2 minus the equations I wrote down were for each component I have P minus 1 equations. You can simplify this. It becomes P into C, minus P plus 2, minus P into C again plus C. This P into C cancels with this P into C, I am left with this C plus 2 minus P. And this is what degrees of freedom F is, we call it the Gibbs' Phase Rule and we write it like this, easy to remember.

A well-planned family will give you two children. So you will not forget it, you will remember it. Okay. So that is how you shall write, normally you can write it like that but this is the way to remember it. This is Gibbs' Phase Rule, that gives us the degrees of freedom in a system with P phases present and system has C components and two of course are pressure and temperature variables which are there.

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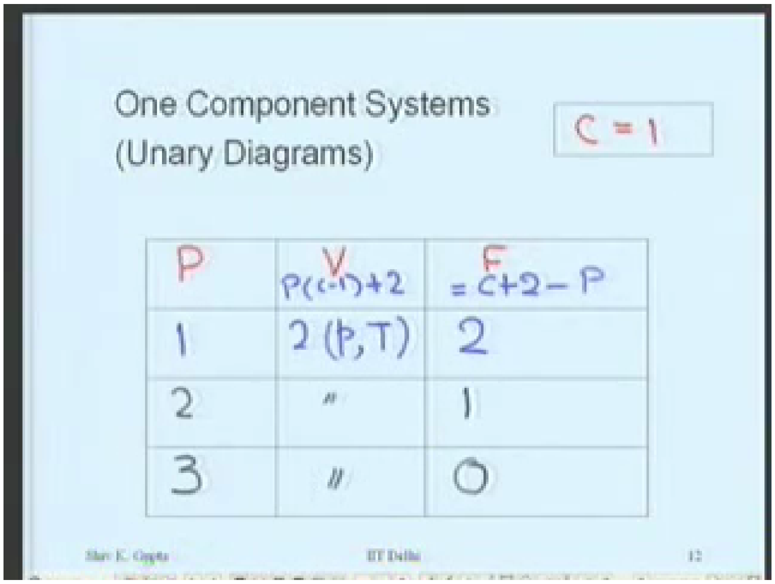

One Component Systems
(Unary Diagrams)

C = 1

P	V P(C-1)+2	F = C+2 - P
1	2 (P,T)	2
2	"	1
3	"	0

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All right. Now let us, you ask me some question, we shall start with single component system today. Let us we talk about C is equal to 1. All right. Let me write number of phases in the system. Let me write what are the number of variables in the system and let us write what is the degrees of freedom in the system. I start with one phase, I cannot have a zero phase, at least one phase would be there in the system.

"Professor-student conversation starts."

Professor: One component system having one phase and recall your variables, what will be the variables? Variables we have already stated, is how many?

Student: Greater than 2.

Professor: Since there is one component, C minus 1 become 0. So it will be no composition variable, only one component, pure gold is pure gold. Okay. The only two variables are there and two variables are pressure and temperature. Pressure is one variable, temperature is another variable. How many degrees of freedom do I have in the system? F is equal to C plus 2 minus P. C is 1, 1 plus 2 is 3, is 3 minus P. 3 minus P is 2.

I have two variables, pressure and temperature, I can change both. That is the degrees of freedom, water will remain water. Between 0 degrees and 100 degrees, I change the temperature, water remains water. Below 0 degrees, I can go up to 0 kelvin to 273 kelvin, it is all ice. From

100 degree centigrade I go to 1,000 degree centigrade, all steam. I am changing temperature, I can also change the pressure. Of course, there is going to be limit of changing the pressure and temperature beyond which it will not be possible to see that equilibrium is to be seen. And therefore I am able to get this. Right?

Student: Can we simultaneously change pressure and temperature?

Professor: Yes, we can. I will show you the diagrams. We will come to that. Let us first complete this table, then we shall go to the diagrams. Let us have two phases present in the system. Variables I shall still have two because P becomes 2, C minus 1 is 0, so that number remains 0, so it remains still 2. It is the same as this. And the degrees of freedom I have in the system now are 3 minus 2, that is 1.

To see the two phases in equilibrium, I have one degree of freedom. Means I can change pressure, I can change temperature, I cannot change both. So I want to see the equilibrium between ice and water, I fix at 1 atmosphere and it happens only at 0 degree centigrade, nowhere else. At a temperature higher than 0 degree centigrade, lower than 0 degree centigrade, at 1 atmosphere which I fix as 1 degree of freedom, it is not, two of them are not present. They are present only at 0 degree centigrade. Is this meaning of degree of freedom become clear? All right.

Student: Fixing the pressure we cannot now change temperature independently?

Professor: Yes, we cannot, 0 degree centigrade when I want to see the two of them together. All right. Let us go to the next one, the 3 degrees, 3 phases present in the system. Variables will still be 2, pressure and temperature and degrees of freedom would become now 0. Both pressure and temperature are fixed when you want to see the three phases in equilibrium. In this case ice, water and vapors and that is slightly different from 1 atmosphere and temperature is slightly greater than 0 centigrade. And we get the three of them present in the system.

All right. So that is the phase rule and how these variables are worked and how these phases give rise to that. I cannot have more than three phases in such a system because degrees of freedom cannot be negative. Maximum it can be, minimum it can be 0, right, so therefore I do not have the four phases present in equilibrium.

“Professor-student conversation ends.”

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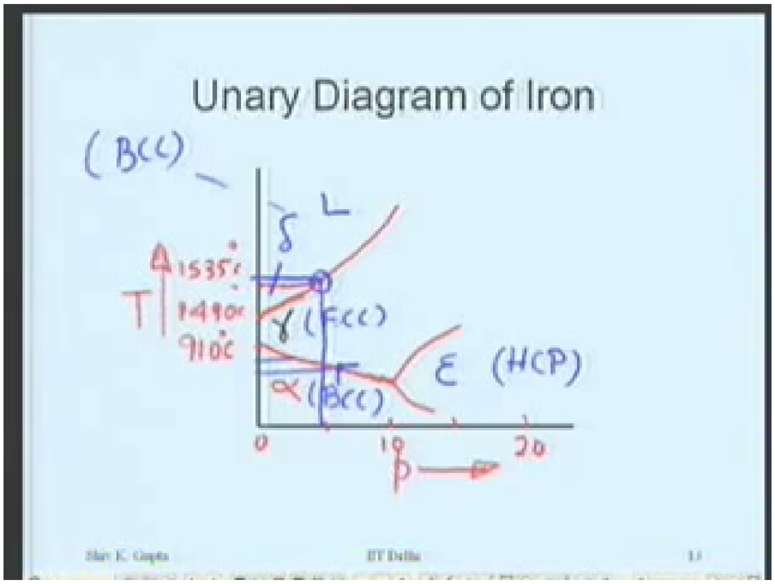

Unary Diagram of Iron

I will show you the unary diagram of iron. Usually in chemistry you have studied the y axis they take as the pressure and x axis as temperature are taken that we know. x axis I shall take pressure, sorry, and y axis we shall take temperature. Why I am doing this? All the diagrams which I am going to talk, they all will have the y axis as the temperature. So the unary diagram, or unary means one component system, I am going to see the temperature in this.

Well, the pressure values will be varying from let us say 0 pressure here, in terms of gigapascal say 10 or 20 here. Temperature, this one let us say 910 degree centigrade and here is 1,490 degree centigrade and then its melting point is very close by. It may not be to the scale 15-35 degree centigrade. Here we have from, starting from the absolute 0 around 1 atmosphere, we have the BCC form iron what we call alpha.

Then from 910 degree centigrade where the transformation occurs, it becomes FCC iron which we call gamma iron, it remains up to 1,490 degree centigrade or so. Okay. And then at that temperature it becomes BCC iron which we call again the delta iron. So up to the melting point it remains delta iron, let us call this delta iron. At a melting point after that, it is all liquid. And at very high pressures which is beyond 10 gigapascals and at some temperature below 9 and 10 degree centigrade it becomes HCP iron, what we call epsilon.

Epsilon iron is HCP. Alpha iron is BCC, gamma iron is FCC and delta is also BCC. Now let us look at the your table which you have seen earlier. One phase in equilibrium, okay. Alpha is in equilibrium, it is an area bounded by the boundaries. Epsilon is an area bounded by the boundaries, delta is an area, gamma is an area and liquid is an area. Two variables, both pressure and temperature can be changed in the area, will remain in equilibrium. And you can also see that there are two phase equilibrium exist along these lines. Along this line exist equilibrium between gamma and alpha. Along this line exist the equilibrium between gamma and epsilon.

“Professor-student conversation starts.”

Student: These are two phase equilibrium.

Professor: Yeah, along, two-phase equilibrium along the line only between alpha and epsilon. So if I am here, I have alpha and gamma in equilibrium. If I change the pressure, increase the pressure let us say, where do I go? Gamma phase field. It is no more two-phase equilibrium. If I decrease the temperature from here, I reach into alpha region. So I cannot change any one of the variables.

And this was fixed here, once I have chosen this temperature or this pressure, at this point I have chosen that, I cannot change the other one. I have exercised my one degree of freedom. Now come to the triple point, I have no degrees of freedom. Pressure and temperature, both are fixed, I have no choice. It is just a point in the whole diagram. This is the line, I could have chosen the temperature here, I could have chosen the temperature there. I have one degree of freedom when two phases are in equilibrium.

But here all three are fixed, all two are fixed in the three phases. Temperature is fixed and the pressure is also fixed. I cannot change anyone of them. Degrees of freedom is 0. Right? I think it answers your question. Okay, we shall start from here in the next class.

“Professor-student conversation ends.”