Basics of Materials Engineering
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Lecture – 55
Phase Diagrams
(Language of Phase Diagrams, Types of Binary Phase Alloys)

Before we actually study phase diagrams, we need to make ourselves familiarized with language of phase diagrams. We should understand different terminologies that one would use when dealing with phase diagrams; that is what we will do in the following module.

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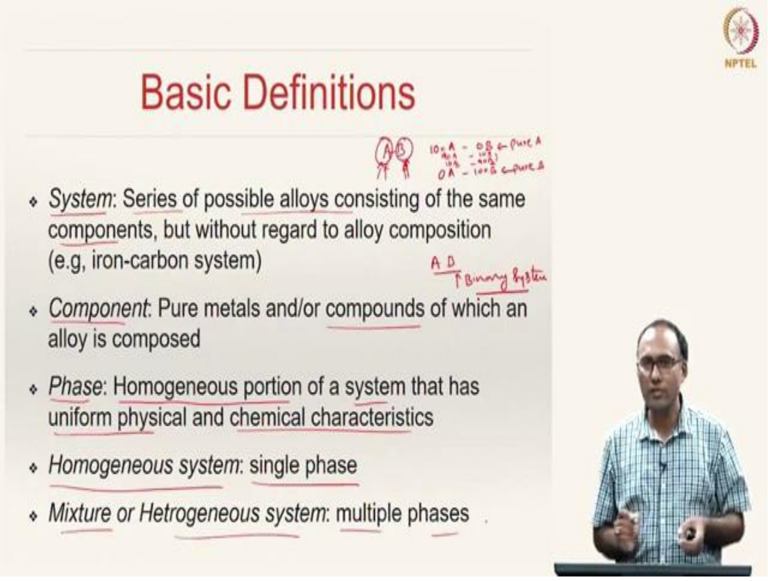

Basic Definitions

- *System*: Series of possible alloys consisting of the same components, but without regard to alloy composition (e.g, iron-carbon system)
- *Component*: Pure metals and/or compounds of which an alloy is composed
- *Phase*: Homogeneous portion of a system that has uniform physical and chemical characteristics
- *Homogeneous system*: single phase
- *Mixture or Hetrogeneous system*: multiple phases

Let us look at some of the basic definitions. What do we mean by a system? A system is a series of possible alloys consisting of the same components. In an alloy, let’s say made of A and B, there are different kinds of possible combinations with respect to the weight fraction of A and the weight fraction of B. For example, you can have 100 A, 0 B - which is pure A; that means 100% A, and 0% B.

You may have 0% A, 100% B - which is pure B. And in between, you can have all combinations, right? For instance, 90% A, 10% B; 10% A, 90% B and so on. In principle, you can have infinite such combinations. A series of all such possible alloys consisting of the same components A and B, but having different compositions, can be considered as one system.

For instance, if you take iron and carbon, all combinations of different weight fractions of carbon and iron is called iron-carbon system. In the system, what do we mean by component? A component is basically the pure metal. If we are making an alloy system out of pure metal A and pure metal B, then A and B can be treated as the components.

A component refers to the pure metals or compounds which constitute an alloy. A component need not be only pure metal, it can also be a compound. So, one of them can be a compound, another can be a pure metal and so on. If there are only two components in an alloy, such a system is called binary system. In this class, we will only be dealing with binary systems.

What do we mean by phase? Phase is defined as the homogeneous portion of a system that has uniform physical and chemical characteristics.

Suppose if you take a solution of A and B, it has uniform physical and chemical characteristics in the liquid state, and hence it is called liquid phase. If in the solid phase, it has uniform physical and chemical properties, then that is called another phase. Multiple phases in a liquid state or a solid state are possible. When we say multiple phases, each phase has a specific kind of physical and chemical properties. What do we mean by a homogeneous system? A homogeneous system has only a single phase. A mixture or heterogeneous system is the one which has multiple phases.

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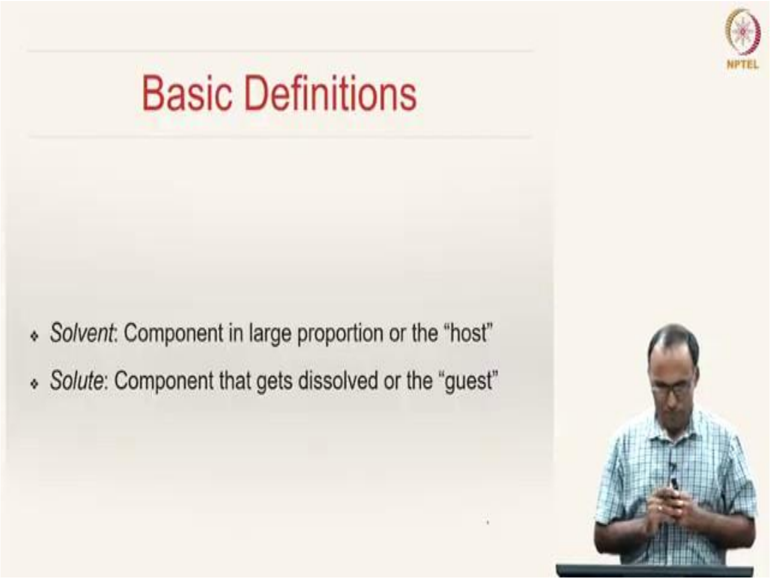

Basic Definitions

- *Solvent*: Component in large proportion or the "host"
- *Solute*: Component that gets dissolved or the "guest"

We already know the definition of solvent and solute - we have already looked at it in the previous classes. Solvent or the host is the component in larger portion, and solute is the component that gets dissolved in the solvent. Solute can be thought of as guest which is coming and sitting amongst the solvent cloud or host cloud.

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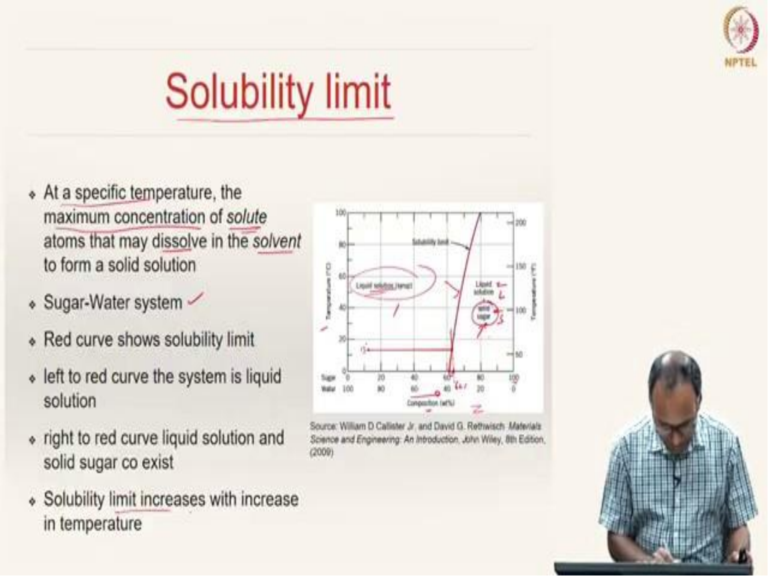

Solubility limit

- At a specific temperature, the maximum concentration of *solute* atoms that may dissolve in the *solvent* to form a solid solution
- Sugar-Water system ✓
- Red curve shows solubility limit
- left to red curve the system is liquid solution
- right to red curve liquid solution and solid sugar co exist
- Solubility limit increases with increase in temperature

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

Next, we will try to understand an important concept called solubility limit. As we have discussed, there is a limit to which you can add a material A to material B and vice versa, and that is what we call the solubility limit.

At a specific temperature, the maximum concentration of solute atoms that can be dissolved in the solvent to form a solid solution is called solid solubility limit. For instance, we can take the example of sugar-water system; here in this graph, the red curve here -- this curve, shows the solubility limit of sugar-water system.

Here, temperature is on the y-axis and composition is on the x-axis. To the left of this red curve, the sugar-water system is in liquid solution and to the right, liquid solution and solid sugar are present. So, this is liquid solution and here you will have still some solid sugar.

Left to that it is a single-phase region, and right to that you have two-phase region - one liquid and one solid phase - and the components are water and sugar. So, left to that only liquid solution exists; right to that both liquid solution and solid sugar coexist. As you can see, for instance, if you take let us say this composition -- at this composition you can clearly see that, at 0° C, we are in two-phase region.

That means there is liquid solution and some sugar. Why there is solid sugar? Because the solubility limit is this. The weight percentage of sugar as shown here range from $0 - 100$. At this temperature, the maximum solubility of sugar in water is about 61. But we are talking about an alloy composition having 62% sugar - let us say somewhere here. Then we see that, it is oversaturated as it cannot dissolve more than 60% at 0° C, the remaining will be present as solid sugar.

Now at the same composition, by the time you increase the temperature, let us say 10° C and 13° C, you have reached the saturation; that means at about 13°C, water can hold 62%. If you further increase the temperature, whatever solid sugar was present before has transformed to liquid solution. So, it has got dissolved in the liquid, because the solubility now is higher than what you have as your alloy composition. This is typically what you must have observed when your mom tries to make some sweets made of sugar; they add sugar and water and put it in a pan - upon heating, after some time the sugar gets dissolved in water.

So, the reason why it gets dissolved in water is because you are increasing the temperature of the solution. With increase in the temperature of the solution, the solubility of sugar in water is increases as seen in this graph (the red line, right?) So, the takeaway is that, at a given composition, the solubility need not be constant, it will be a function of temperature. As you increase the temperature, the solubility in this case is increasing; solubility of sugar in water is increasing. So, the solubility limit increases with increase in temperature for this sugar water syrup. What do we mean by equilibrium? A system is said to be in equilibrium, if its free energy is at a minimum.

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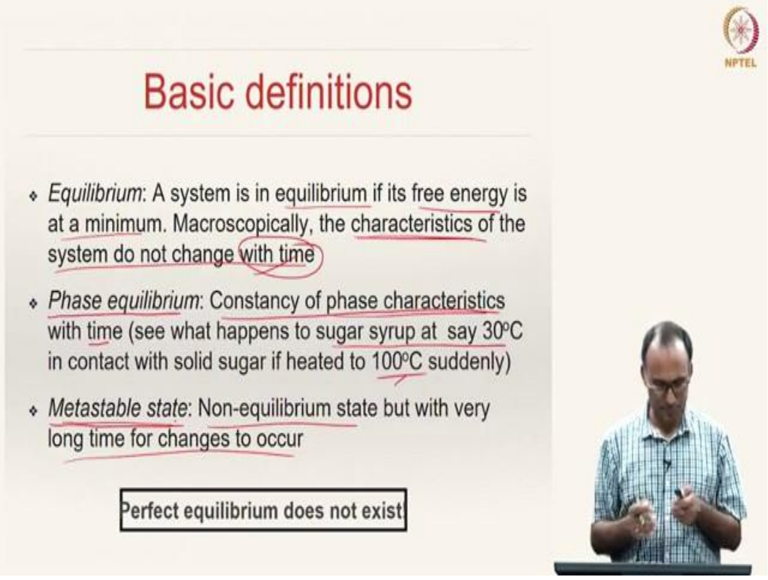

Basic definitions

- *Equilibrium*: A system is in equilibrium if its free energy is at a minimum. Macroscopically, the characteristics of the system do not change with time
- *Phase equilibrium*: Constancy of phase characteristics with time (see what happens to sugar syrup at say 30ºC in contact with solid sugar if heated to 100ºC suddenly)
- *Metastable state*: Non-equilibrium state but with very long time for changes to occur

Perfect equilibrium does not exist

Macroscopically, when a system is at equilibrium, the characteristics of the system do not change with time - that is the key. If you are seeing that component today and come back after hundred years, it will still remain the same, if it is in equilibrium state.

The characteristics of the system should not change with respect to time and such a configuration is called equilibrium configuration or such a system is said to be in equilibrium. What do we mean by phase equilibrium? Phase equilibrium refers to the constancy of phase characteristics.

As we have seen there are in the sugar water solution, you have two phases, liquid phase as well as solid phase. The constancy of phase characteristics means the characteristics of the phases should remain constant with time at a given temperature.

However, for instance, if you increase the temperature of sugar syrup say at 30° C in contact with solid sugar to 100° C, the solubility limit increases and then the phases do not remain the same, i.e., the phases change with respect to time. Then, we say that the phases are not in equilibrium as they are changing with respect to time, when we are increasing the temperature.

Another important concept, the metastable state is a non-equilibrium state, but with very long time for changes to occur; that means it take sufficiently long time for changes to occur. For instance, if you take an iron rod and leave it in open atmosphere, maybe in 1 or 2 days if you come back and see, you may not observe a significant change.

But if you come back and see may be say a month or a year later, you will see that the iron has rusted. Changes are happening to the phases present in the system, because of which the iron is rusting. However, this change happens over a long period of time. Such a state is called metastable state. So, it is a non-equilibrium state, but the changes are happening over a long period of time. Please note that, for any alloy system that we will be discussing, perfect equilibrium does not exist. All the equilibriums that we are mentioning, are usually metastable states; because over a long period of time (may be few hundred years sometimes), but nevertheless, even after few hundred years, there may be some change in the phases. Such a state is what we call a metastable state.

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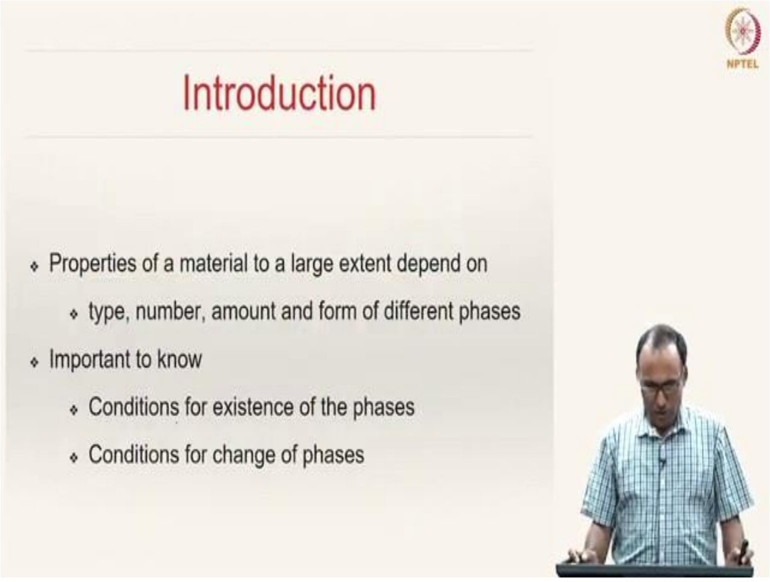

Introduction

- Properties of a material to a large extent depend on
  - type, number, amount and form of different phases
- Important to know
  - Conditions for existence of the phases
  - Conditions for change of phases

We know that the properties of a material or an alloy in this case as we have discussed so far, to a large extent depend on the type, number, amount, and form of different phases. The type of phase it is, number of phases present, weight fractions of the phases, and the microstructure of the phases -- all these determine the properties of the material. It is important to know the condition for existence of these phases.

Let us say a particular phase is going to give you a desirable property; as an engineer, we should know the conditions under which such phases become a reality and the conditions for change of phases. So, you have got some phase, and what are the conditions under which a particular phase changes to some other phase? This information is something that one needs to know in order to be able to use the alloys with the utmost efficiency. Phase changes in many alloy systems is best described by phase diagrams. The phase diagrams are also called equilibrium diagrams or constitutional diagrams - they are synonyms.

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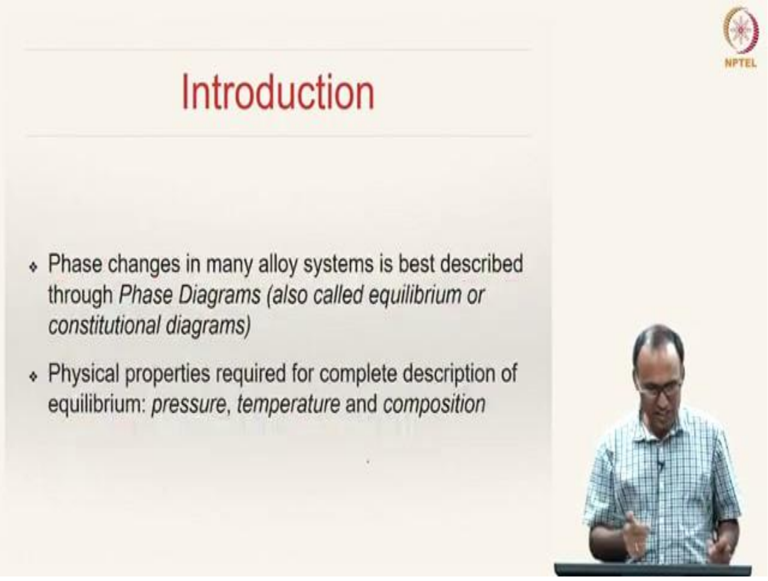

Introduction

- Phase changes in many alloy systems is best described through *Phase Diagrams (also called equilibrium or constitutional diagrams)*
- Physical properties required for complete description of equilibrium: *pressure*, *temperature* and *composition*

We have posed the question in the previous slide: how do the phase changes occur? Phase diagrams provide answers to the question on how the changes occur from one phase to another phase and under what conditions?

The physical properties required for a complete description of the equilibrium phases are pressure, temperature and composition. The phases that we are discussing in an alloy system depend on these three independent variables - pressure, temperature, and composition.

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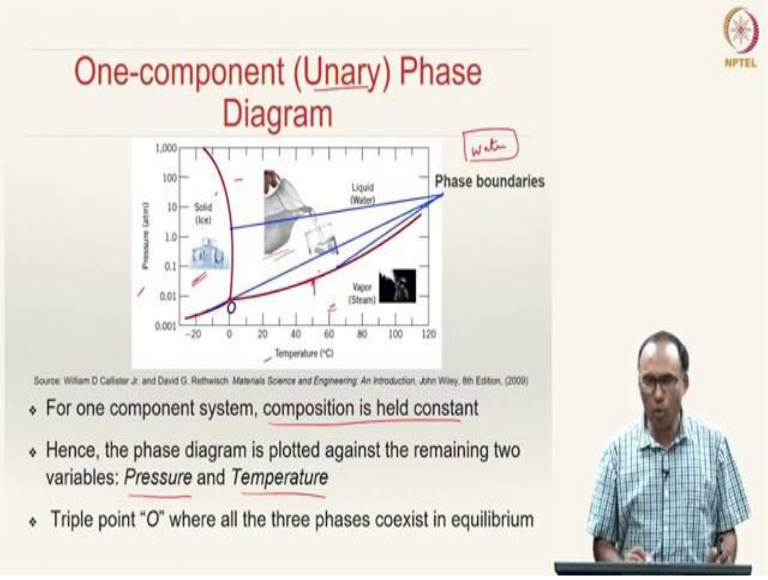

One-component (Unary) Phase Diagram

Source: William D Callister Jr. and David G. Rethwisch. *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

- For one component system, composition is held constant
- Hence, the phase diagram is plotted against the remaining two variables: *Pressure* and *Temperature*
- Triple point "O" where all the three phases coexist in equilibrium

For the sake of understanding, let us now look at a unary phase diagram or one-component phase diagram. Here, we are looking at the phase diagram of water. Because it is a unary phase diagram, the composition does not come into picture (it will always be hundred percent); the composition comes into picture, when there is more than one component.

The composition does not come into picture, and hence the other two variables are pressure and temperature. On the y-axis, we have pressure and on the x-axis, we have temperature in degree Celsius. The boundaries that are shown in red are called phase boundaries; and here on this region you have liquid water, solid ice, and this is vapor region.

For one component system, the composition is held constant because there is no variation of component and hence the phase diagram is plotted against pressure verses temperature.

Here, you can see the triple point O, where all the three phases coexist. On all other boundaries, the two phases coexist. For instance, if you take this boundary -- this is the boundary between solid phase and liquid phase -- and hence on this boundary, both solid and liquid coexist.

This is the boundary between solid and vapor and hence solid and vapor coexist. On this boundary, you have liquid and vapor and hence these two phases coexist on that boundary for various temperatures and pressures.

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Gibbs' Phase Rule

- Criterion for number of phases that can co-exist within a system at equilibrium
- $P+F = C+N$
  - P: number of phases present
  - F: degrees of freedom
  - C: number of components comprising the system $C = 1$
  - N: number of non-compositional variables (temp, pressure) — 2

So, now, what is the criterion for finding the number of phases that can coexist within a system at equilibrium? I am sure that all of you are familiar with the Gibbs phase rule, which says that,

$$P + F = C + N$$

P represents the number of phases present, F represents the degrees of freedom -- we will see what do we mean by degree of freedom -- C is the number of components comprising the system, and N is the number of non-compositional variables. Here non-compositional variables are temperature and pressure.

How many components are there? It is a unary phase diagram and hence $C = 1$. The number of non-compositional variables is 2, $N = 2$. The number of phases present and degrees of freedom are something that we will look at.

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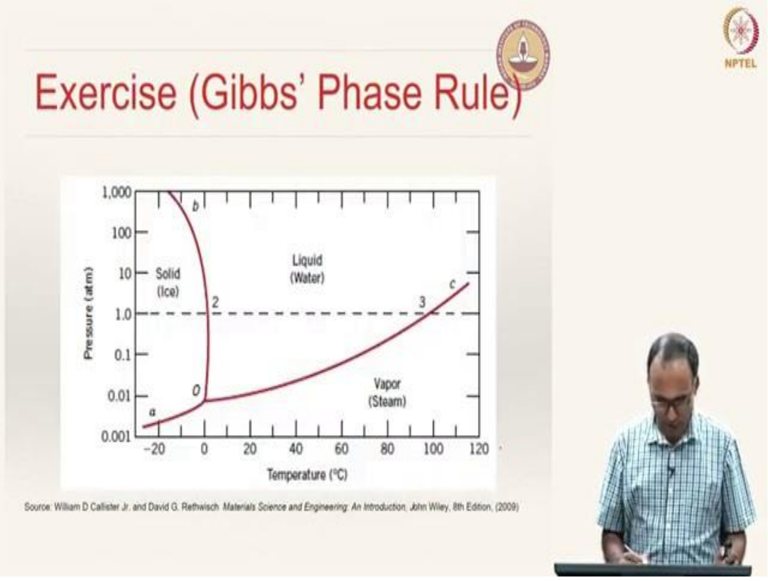

Exercise (Gibbs' Phase Rule)

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

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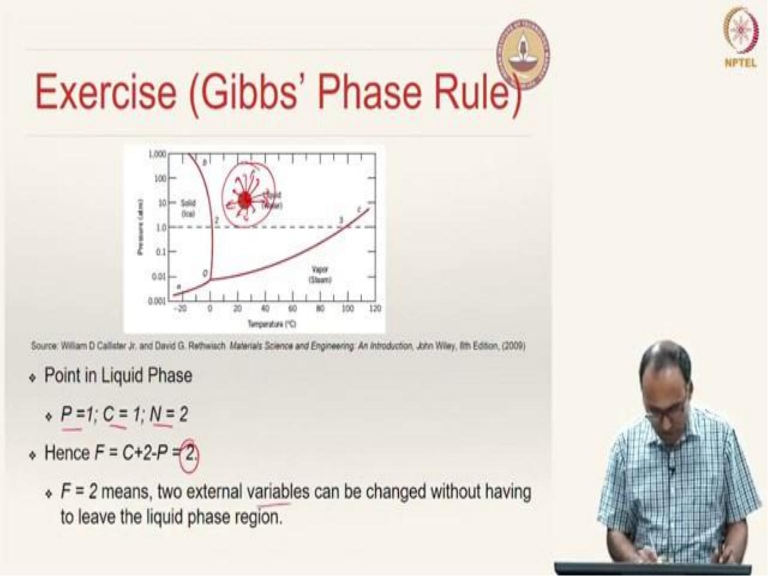

Exercise (Gibbs' Phase Rule)

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

- Point in Liquid Phase
  - $P = 1; C = 1; N = 2$
- Hence $F = C+2-P = 2$
  - $F = 2$ means, two external variables can be changed without having to leave the liquid phase region.

How many phases are present in the liquid phase? Only one phase -- it is a liquid phase. So, $P = 1$, and number of components equal to 1; $N = 2$, N is number of non compositional variables. So, we know that, $P + F = C + N \implies F = C + N - P = 1 + 2 - 1 = 2$. So, in the liquid phase, we have 2 degrees of freedom. That means, from this position, you can move either along the temperature direction or pressure direction independently. You can move in any way -- all these are possible, and you will still remain in the same state i.e., the liquid phase; that is what we mean by degree of freedom. So, $F = 2$ implies that the two external variables, namely pressure and temperatures can be changed without having to leave the liquid phase region.

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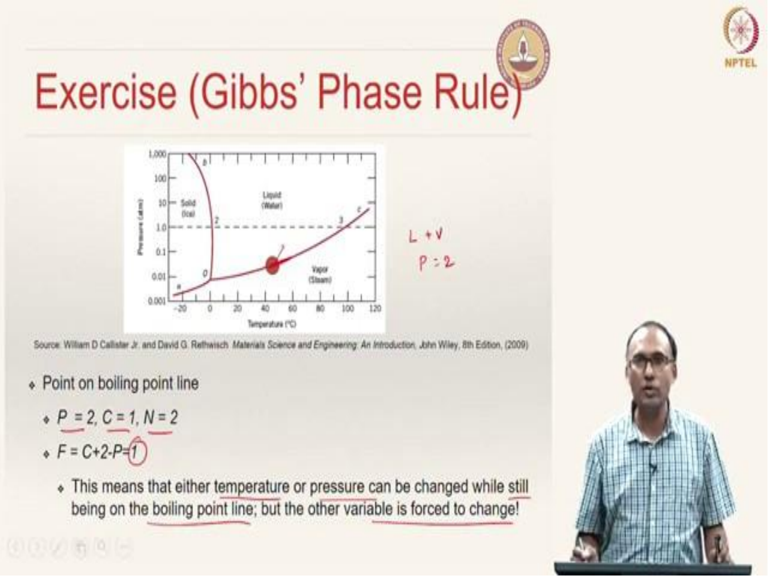

Exercise (Gibbs' Phase Rule)

Source: William D Callister Jr. and David G. Rethwisch *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

- Point on boiling point line
  - $P = 2, C = 1, N = 2$
  - $F = C+2-P = 1$
    - This means that either temperature or pressure can be changed while still being on the boiling point line; but the other variable is forced to change!

Now, you are on the boiling point line, that is liquid-vapor interphase. So, as we know that this is a two phase -- on this line two phases coexist. What are the phases? The liquid phase and vapor phase. So, the number of phases is 2. C and N will be the same. And as a result, $F = 1$. What is the meaning of that? You have only freedom to choose only one of the external variables. This means that either temperature or pressure can be changed while still being on the boiling point line; the other variable is forced to change in its own way.

In other words, you can only move this way. You can choose what should be the temperature change and automatically pressure change should be decided by this line. However, if you want to move in any other way, then you will be leaving the two-phase region. That is what degree of freedom 1 signifies.

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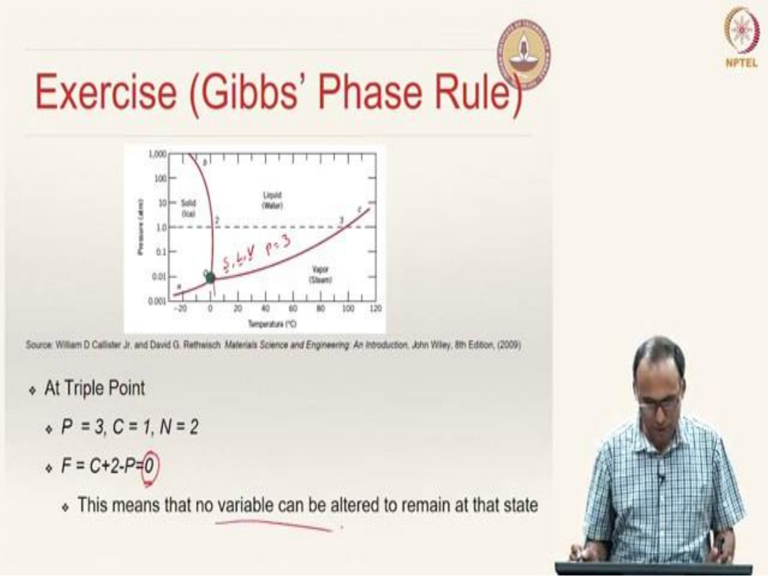

Exercise (Gibbs' Phase Rule)

Source: William D Callister Jr. and David G. Rethwisch. *Materials Science and Engineering: An Introduction*, John Wiley, 8th Edition, (2009)

- At Triple Point
  - $P = 3, C = 1, N = 2$
  - $F = C+2-P=0$
    - This means that no variable can be altered to remain at that state

Let us now look at the triple point. How many phases coexist here? All three phases, i.e., solid, liquid and vapor coexist at the triple point. Hence, the number of phases present are 3, and consequently, $F = 0$; that means you cannot change either pressure or temperature, if you want to be in that region; that is a triple point. Here triple point is only a point.

Hence, you do not have any degree of freedom, you cannot move at all; the moment you move, you are going leave that region and you going to go to another region. So, this means that no variable can be altered to remain at that state.

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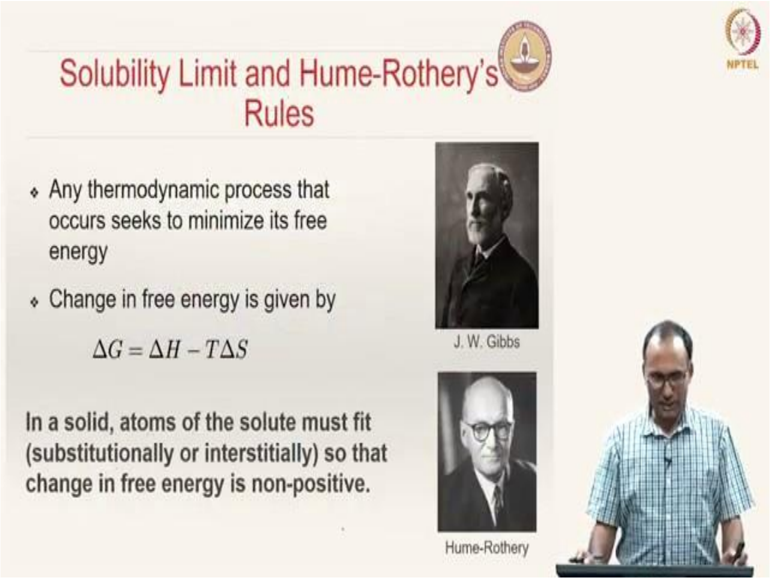

Solubility Limit and Hume-Rothery's Rules

- Any thermodynamic process that occurs seeks to minimize its free energy
- Change in free energy is given by

$$\Delta G = \Delta H - T\Delta S$$

In a solid, atoms of the solute must fit (substitutionally or interstitially) so that change in free energy is non-positive.

We have discussed the solubility limit and there are certain rules put forth by Hume Rothery, which are famously known as Hume Rothery's rules for the formation of solid solutions. First of all, any thermodynamic process that occurs, seeks to minimize it is free energy - that is important. The change in free energy can be written as, $\Delta G = \Delta H - T\Delta S$. A thermodynamic process should happen in such a way that $\Delta G < 0$. Only when ΔG is negative, that is when you are continuing to reduce the free energy, as we have discussed here. In a solid, atoms of the solute must fit either substitutionally or interstitially, so that the change in free energy is non-positive; this is the requirement. When you are adding a solute atom to solvent atom, they should fit in to the solvent cloud, effectively resulting in net reduction in the free energy; only then such a thermodynamic process is feasible.

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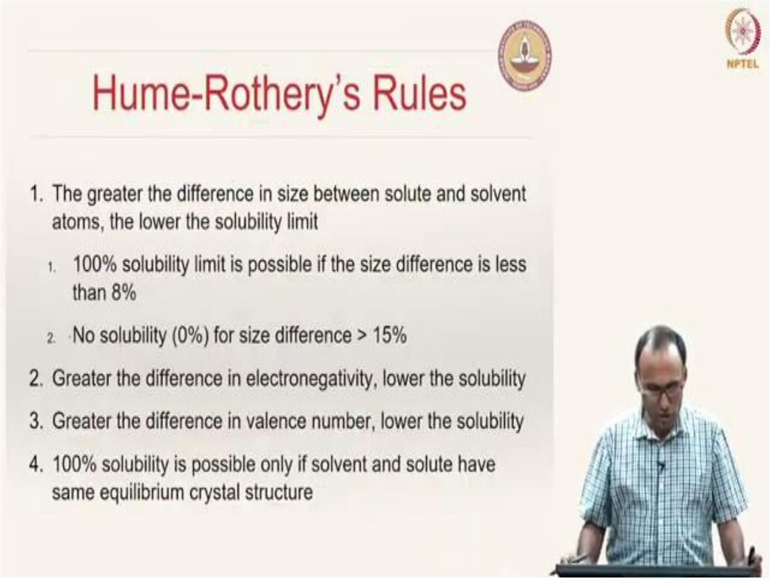

Hume-Rothery's Rules

1. The greater the difference in size between solute and solvent atoms, the lower the solubility limit
    1. 100% solubility limit is possible if the size difference is less than 8%
    2. No solubility (0%) for size difference > 15%
2. Greater the difference in electronegativity, lower the solubility
3. Greater the difference in valence number, lower the solubility
4. 100% solubility is possible only if solvent and solute have same equilibrium crystal structure

What are the Hume Rothery's rules? The greater the difference in size between solute and solvent atom, the lower the solubility. For instance, if we are talking about binary phase diagrams, if you want to have higher solubility, the size of the component atoms i.e., the solvent and solute atoms sizes should be almost similar. 100% solubility of A in B and B in A is possible, if the size difference is less than 8%.

If the size difference between atom A and atom B is greater than 15%, there is almost no solubility. We said 0%, but there is almost no solubility. If the difference between A and B is greater than 15%, then the materials do not get dissolved for them to make a substitutional solid solution. The rules that we are talking about here are true for substitutional solid solutions;the numbers may be different for interstitial solid solutions. Here, we are focusing on substitutional solid solutions just to get an idea. Again, the solubility will diminish, if the electronegativity values of these two atoms are very different.

If you want to enhance the solubility, their electronegativity values also should be very close to each other. The difference in valence number should be very less; that means the valence number of atom A and atom B should be as close as possible in order to have greater solubility.

100% solubility is possible, only if solvent and solute have same equilibrium crystal structure; that is another important thing. If a solvent atom A is FCC, then solute should also be FCC; only then you will have 100 percent solubility; otherwise, you will not have 100 percent solubility.

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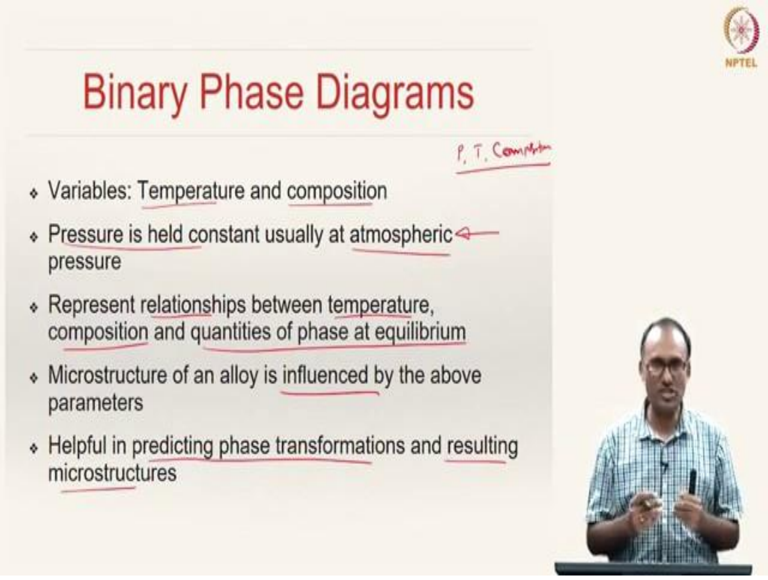

Binary Phase Diagrams

P, T, Composition

- Variables: Temperature and composition
- Pressure is held constant usually at atmospheric pressure
- Represent relationships between temperature, composition and quantities of phase at equilibrium
- Microstructure of an alloy is influenced by the above parameters
- Helpful in predicting phase transformations and resulting microstructures

The Hume Rothery's rules that we have discussed here are primarily suggested based on observations. These four rules that we have written are valid for all the substitutional solid solutions. So, now, let us look at the binary phase diagrams.

When we say binary phase diagrams, you have two components A and B. For describing a phase diagram, you will have three independent variables. What are they? Pressure, temperature and composition.

In this course, when we are talking about binary phase diagrams, the two independent variables that we are choosing are temperature and composition, and typically that is how it is done for most of the phase diagrams. Pressure is usually held constant at atmosphere pressure.

Most of the phase diagrams that you would see in the literature are drawn with composition versus temperature at one atmospheric pressure. When there is change in pressure other than atmospheric pressure, then the phase diagram will change, when you are drawing between temperature and composition.

But most of the phase diagrams that we will be discussing -- not all the phase diagrams that we will be discussing in this class, are done at atmospheric pressure - and that is also true for several phase diagrams that you would come across in the literature.

The binary phase diagrams represent the relationships between the temperature, composition and quantities of phases at equilibrium. What are the different phases and what are their quantities? This is something that will be clearly described by a binary phase diagram.

And note that the underlying microstructure of an alloy is significantly influenced by the above parameters, particularly the composition and the temperature - these two variables are going to significantly influence the microstructure. So, the binary phase diagrams help us in predicting phase transformations and the resulting microstructures.

How a particular phase transforms to another phase and the resulting microstructure through these phase transformations is something that we will understand through binary phase diagrams.

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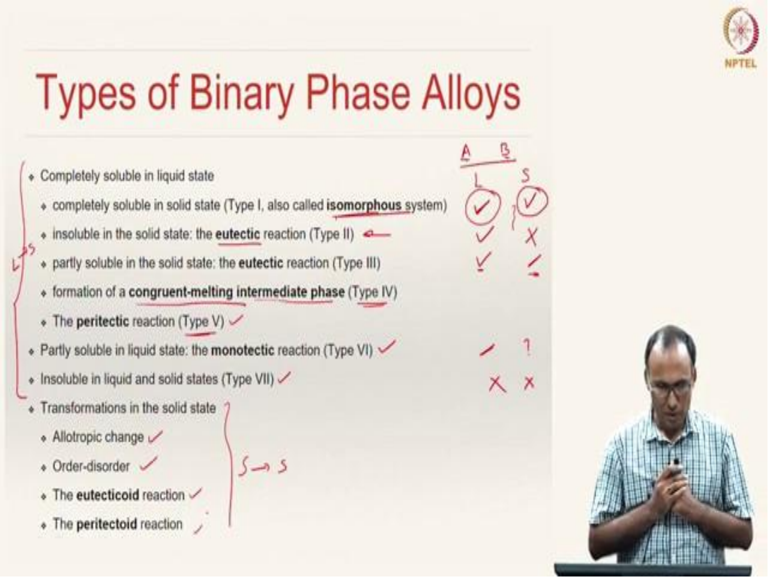

Types of Binary Phase Alloys

- Completely soluble in liquid state
  - completely soluble in solid state (Type I, also called **isomorphous** system)
  - insoluble in the solid state: the **eutectic** reaction (Type II)
  - partly soluble in the solid state: the **eutectic** reaction (Type III)
  - formation of a **congruent-melting intermediate phase** (Type IV)
  - The **peritectic** reaction (Type V)
- Partly soluble in liquid state: the **monotectic** reaction (Type VI)
- Insoluble in liquid and solid states (Type VII)
- Transformations in the solid state
  - Allotropic change
  - Order-disorder
  - The **eutecticoid** reaction
  - The **peritectoid** reaction

In this course, we will be discussing different types of binary phase alloys. Here we have made a classification. So, let us say you have alloy A or metal A and metal B.

We are only talking about metallic alloys, so metal A and metal B. The first classification is that, if metal A and metal B are completely soluble in liquid state; that means there is hundred percent solubility possible for A in B and B in A. When is that possible? When some of the rules that we have discussed before are satisfied.

We are saying that they are completely soluble in liquid state. So, of the materials that are completely soluble in liquid state, now the first type of alloys that we are going to discuss are called isomorphous alloys, which are also completely soluble in solid state. An isomorphous system is a system of alloys in which components A and B are completely soluble in liquid state and completely soluble in solid state; that means A is soluble in B and B is soluble in A completely. And then Type II -- in Type II, we will look at a system, wherein there is complete solubility in liquid state, but there is no solubility in solid state. When we are discussing this type of a system, we will look at an important reaction called eutectic reaction -- these types of alloys are called eutectic alloys.

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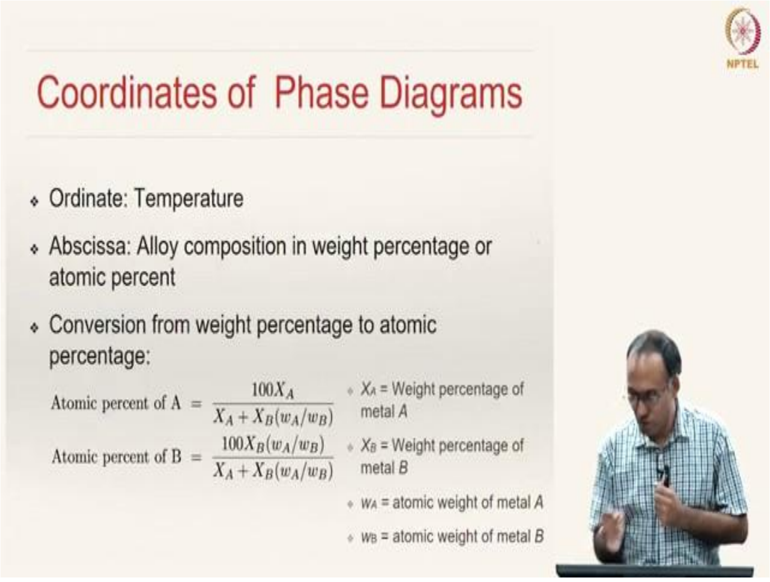

Coordinates of Phase Diagrams

- Ordinate: Temperature
- Abscissa: Alloy composition in weight percentage or atomic percent
- Conversion from weight percentage to atomic percentage:

$$\text{Atomic percent of A} = \frac{100X_A}{X_A + X_B(w_A/w_B)}$$

$$\text{Atomic percent of B} = \frac{100X_B(w_A/w_B)}{X_A + X_B(w_A/w_B)}$$

- X_A = Weight percentage of metal *A*
- X_B = Weight percentage of metal *B*
- w_A = atomic weight of metal *A*
- w_B = atomic weight of metal *B*

Now the third one is somewhere in between these two. You have complete solubility in liquid state, you have partial solubility; that means there is a limit to solubility of A in B and B in A in the solid state, whereas there is no limit to solubility in the liquid state. These are what we call Type III alloys.

Type IV alloys are also completely soluble in liquid state; but here we will see a special kind of a system called congruent-melting intermediate phase. Then, we will look at the Type V alloys, in which we see a special reaction called peritectic reaction. Type I - Type V alloys are completely soluble in liquid state. In the solid state, their solubilities are changing.

We will look at the Type VI alloy, which is having a partial solubility in liquid state. We will look at Type VII alloy, which has complete insolubility in liquid state and solid state. And then, we will also look at the transformations in solid state. Here, all these transformations are liquid to solid; here we will see solid to solid state transformations. The four important transformations called allotropic transformation, order-disorder transformation, the eutectoid reaction, and peritectoid reaction.

With that I will stop here and in the next class, we will look at the isomorphous alloy systems or type I alloys. Thank you.