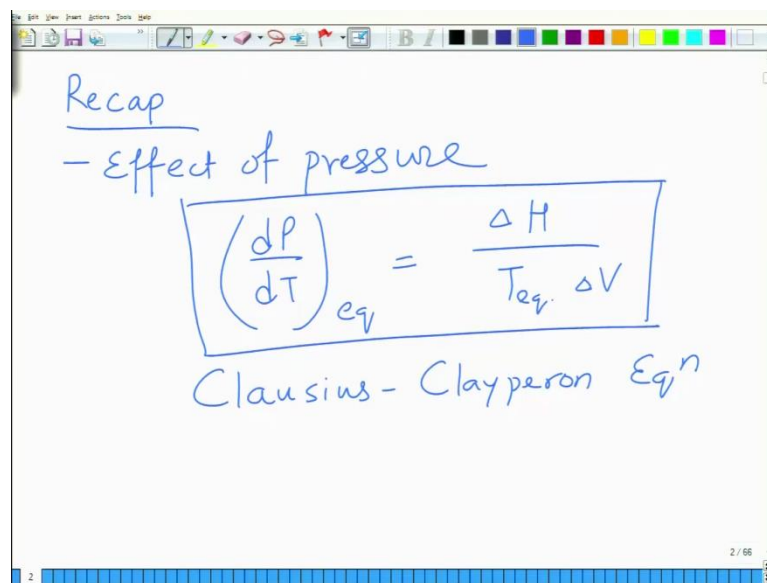


Phase Equilibria in Materials (Nature and Properties of Materials - II)
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Lecture - 05
Clausius-Clapeyron Equation & Binary Solution

We start a new lecture now. So, this is lecture number 5 continuing the thermodynamic basis for phase equilibria. So, let us just recap the last lecture.

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Recap
- effect of pressure

$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq} \Delta V}$$

Clausius - Clapeyron Eqⁿ

So, in the last lecture basically we looked at the effect of pressure, and effect of pressure is very evident in for example, iron phase diagram; where the phase boundaries are not horizontal, the transformation temperature from one phase to another changes as the pressure is changed. And this is because of changes in the molar volume of the phases as the transformation occurs. And for this, we did a simple analysis, and we came up with this expression

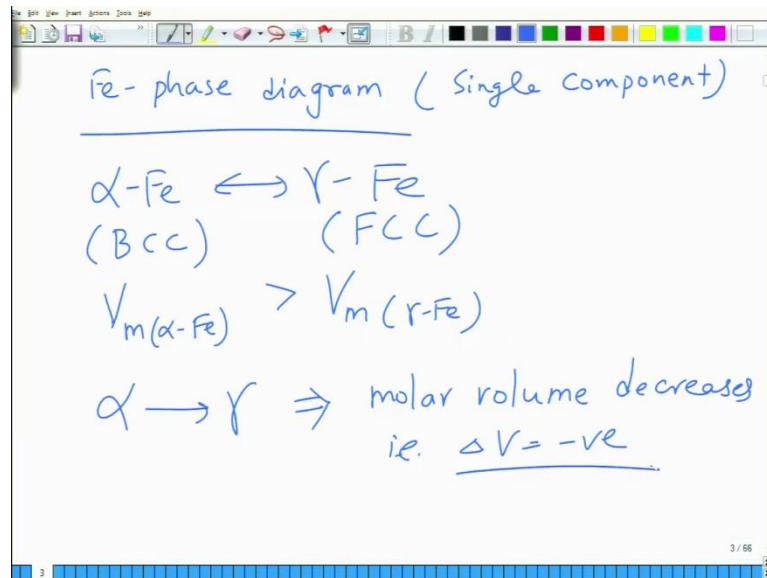
$$\left(\frac{dP}{dT}\right)_{eq} = \frac{\Delta H}{T_{eq} \Delta V}$$

and this equation is known as Clausius Clapeyron equation.

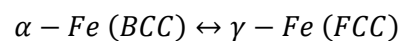
And what basically tells, this tells us is that that change in, as you change the pressure the temperature will change if you have some change in ΔV and as we will see some examples

in this lecture how this works. So, let us know move to variations in the temperature, let us get understanding of that as a function of pressure. So, let us see the example of so, we again go back to iron phase diagram.

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So, it is a same single component iron phase diagram. And so, first we consider



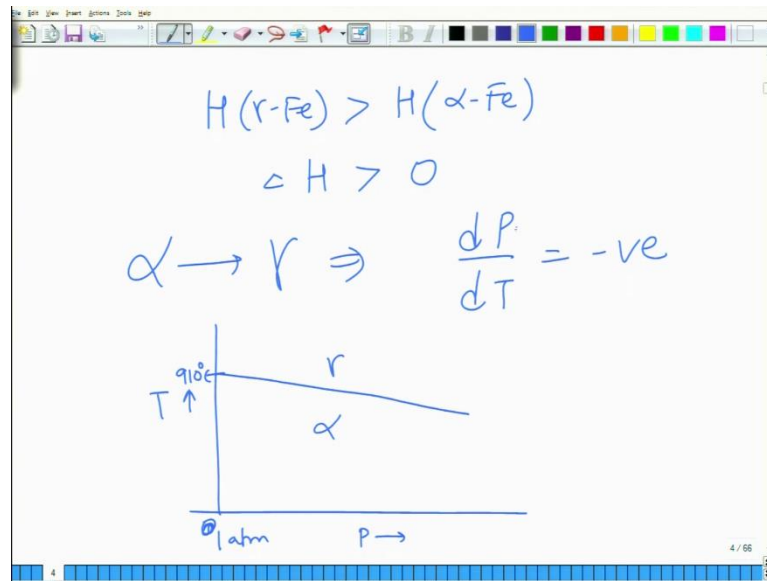
We know that $\alpha - Fe$ is BCC in structure, body centered cubic which is less closely packed as compared to $\gamma - Fe$ which is FCC structured phase which is close packed structure.

As a result, the molar volume so,

$$V_{m(\alpha-Fe)} > V_{m(\gamma-Fe)}$$

So, when you have a phase transformation from $\alpha \rightarrow \gamma$, what it implies is that your molar volume decreases. So, that is your ΔV will be negative.

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So, if your ΔV is negative, in that case now, generally we take H enthalpy of $\gamma - Fe$ to be

$$H(\gamma - Fe) > H(\alpha - Fe)$$

As a result,

$$\Delta H > 0$$

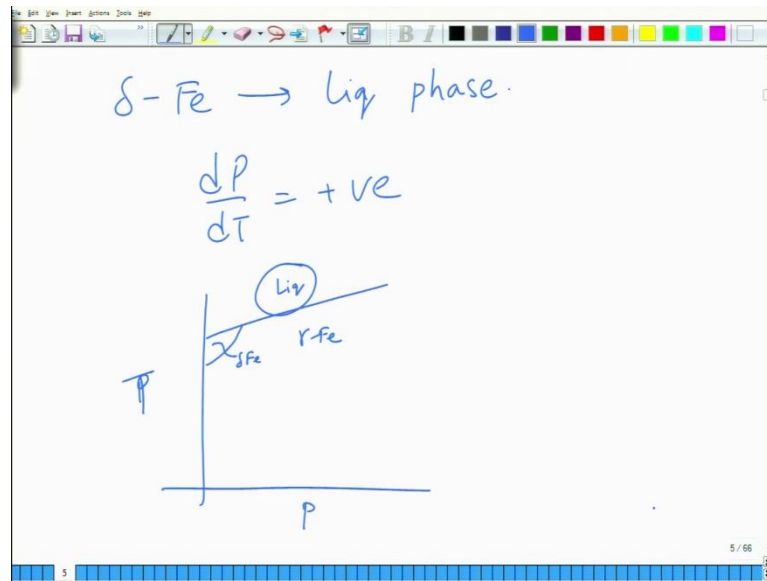
So, when you have $\alpha \rightarrow \gamma$ transformation your

$$\frac{dP}{dT} = -ve$$

So, for every incremental increase in pressure your dT is negative. So, as a result if you look at the $\alpha\gamma$ phase boundary, I am not going to draw a complete phase diagram, but you had temperature on this axis, and pressure on this axis and this alpha gamma phase boundary showed this. So, this is α , this is γ and this is 910 °C at 0 pressure sorry, at 1 atmosphere pressure. And as the pressure increases, the temperature of transformation from $\alpha \rightarrow \gamma$ or $\gamma \rightarrow \alpha$ decreases and this is mainly because of $\frac{dP}{dT} = -ve$

or because of change in the molar volume of 2 phases.

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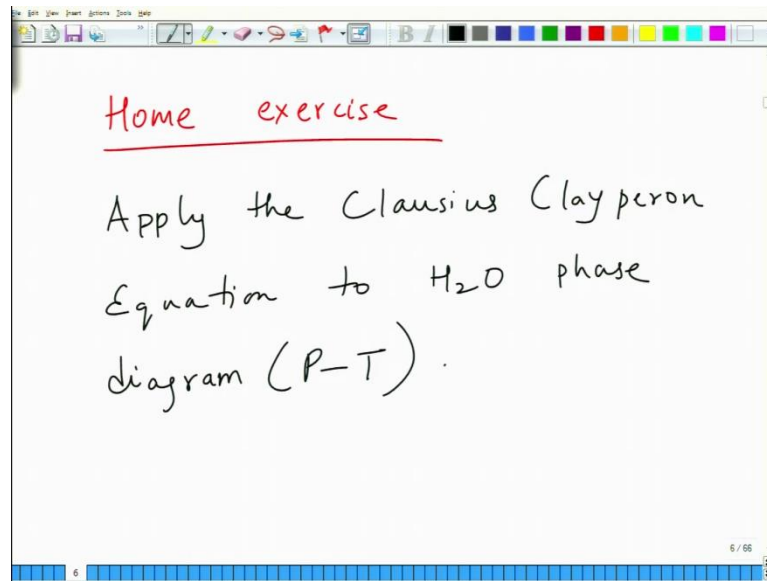


Similarly, if you look at $\delta - Fe \rightarrow liquid\ phase$, the $\frac{dP}{dT} = +ve$. And as a result, at high temperature you see that again when you draw temperature versus pressure, at high temperature the line goes like this. So, this is liquid, and somewhere, we had this we had $\delta - Fe$ and then we had $\gamma - Fe$. So, both of these Δf . So, basically the liquid has higher volume molar volume as compared to $\delta - Fe$ and $\gamma - Fe$, as a result the transformation temperature increases as the pressure increases.

So, this explains the effect of molar volume on the transformation temperature, which is necessary to maintain the equilibrium. So, as a pressure increases if you have changes in the molar volume, the temperature, transformation temperature will either decrease or increase depending upon the corresponding change in the molar volume, and this is necessary to maintain the equilibrium otherwise equilibrium will not exist.

So, let us now move to, you can take another example for example, you can do the same exercise.

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So, as on home exercise you can do, apply the H_2O phase diagram. So, basically you look at the single component pressure temperature phase diagram, for what? For H_2O and then apply the same logic of changes in the molar volume and try to relate it to the changes in the transformation temperatures from, let us say liquid to solid phase and solid to vapour phase.

Now, let us move on to the next topic. So, we have looked at single component system. In single component system, the composition does not change because each phase whether it is $\gamma - Fe$ whether it is $\alpha - Fe$ whether it is $\delta - Fe$ whether it is $\epsilon - Fe$ all of these phases contain only single element that is iron. So, there is no compositional change that occurs; however, most of the engineering materials are not pure, they are impure and they are impure because of certain reasons because addition of purity improves their properties.

So, as a result it is necessary to understand the properties of impure systems or rather, we can say solutions. Generally, what happens in metallurgical systems is, one element is very large, is present in, is a majority element is present in large amounts and other elements are added selectively to improve its properties, they are present in smaller amounts. So, these are called as solutions, and we first begin with what we called as binary solutions.

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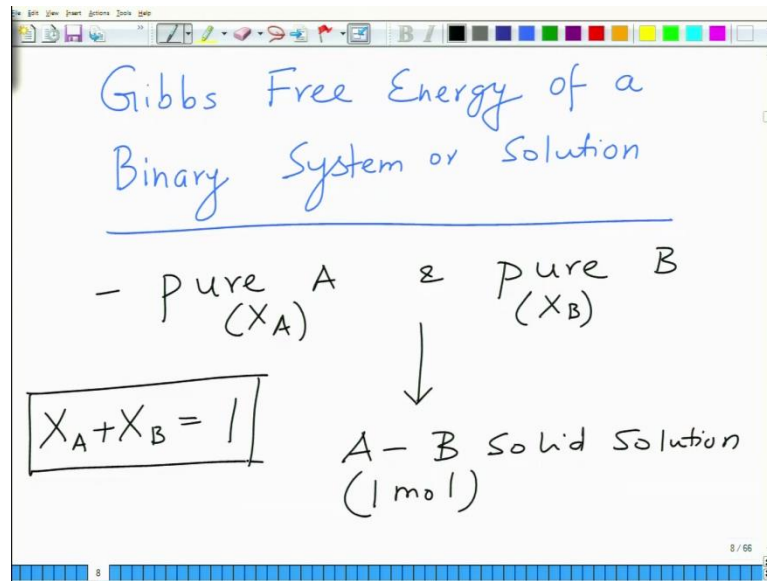
The image shows a whiteboard with handwritten notes in red and blue ink. The title 'Binary Solutions' is written in red and underlined. Below it, there are two bullet points: '- Alloys (Fe-C, ...)' and '- Thermodynamic variables: T, P, C_i'. The equation $G = f(T, P, C_i)$ is written in blue, with an arrow pointing from 'Composition' to 'C_i'. Below this, another bullet point states '- Most metallurgical systems' followed by 'P = constant, $G = f(T, C_i)$ '. The whiteboard has a toolbar at the top and a status bar at the bottom showing '7 / 66'.

Binary solutions as the name itself suggests it is nothing but a mixture of 2 elements; A and B. So, unlike a single component system where temperature and pressure are the only 2 variables, to achieve, to understand the phase equilibrium. In this case, in addition to temperature and pressure you also have composition that makes difference to the thermodynamic equilibrium.

So now getting back to, so, basically binary solutions basically are let say alloys, ok. And for example, you can have iron carbon alloy, which is steel and various other systems you can have copper-gold, you can have nickel-aluminium and so on and so forth. Copper-zinc, copper-tin, variety of alloys are binary alloys. And in this case the thermodynamic variables are temperature, pressure as well as C_i , the composition of i^{th} component. In case of binary system, it will be only 2 of them, let us say if it is A and B, then it is A and B.

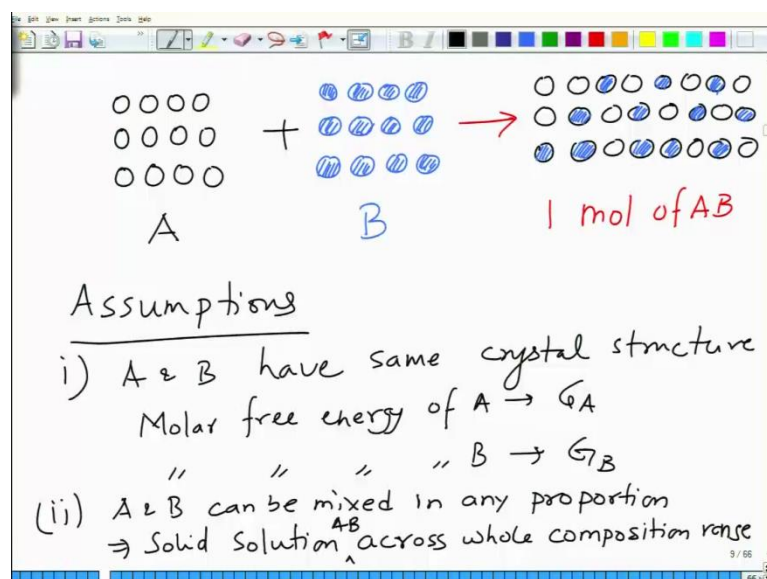
And so, as a result the free energy is a function of temperature, pressure and composition. So, this is composition, right. And for the sake of simplicity, in most metallurgical systems, pressure is generally taken as constant. And as a result, we understand free energy variation only as a function of temperature and composition if pressure is constant and which is true in most cases; in case of engineering materials, transformations related to engineering materials.

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So now let us understand the first topic that is Gibbs free energy of a binary system or solution, ok. So, to begin with, let us consider to pure elements. So, pure A and pure B, the pure A has let us say, pure A and pure B when you mix them together, they give rise to AB solid solution. So, basically you take X_A mole of X_A mole fraction of A. X_B mole fraction of B to give rise to 1 mole of AB. So, what you have here is $X_A + X_B = 1$. This is the equality in which they are maintained, they are present in the in the alloy.

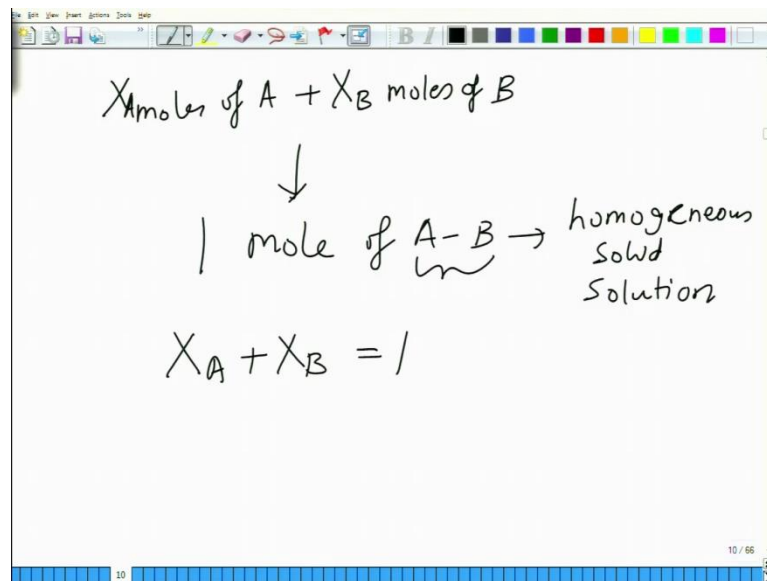
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So, basically what you have is, you have A, let say you have few of these as A. So, this is A, and then you have some of these as B so this is B. And they give rise to a new system. So, let us say if I just make it darker, and they make solid solution which is; now they make a solid solution in such a manner so that A and B are indistinguishable. So, basically what you will have is, this is let us say this will be 1 mole of AB. So, what are the assumptions here?

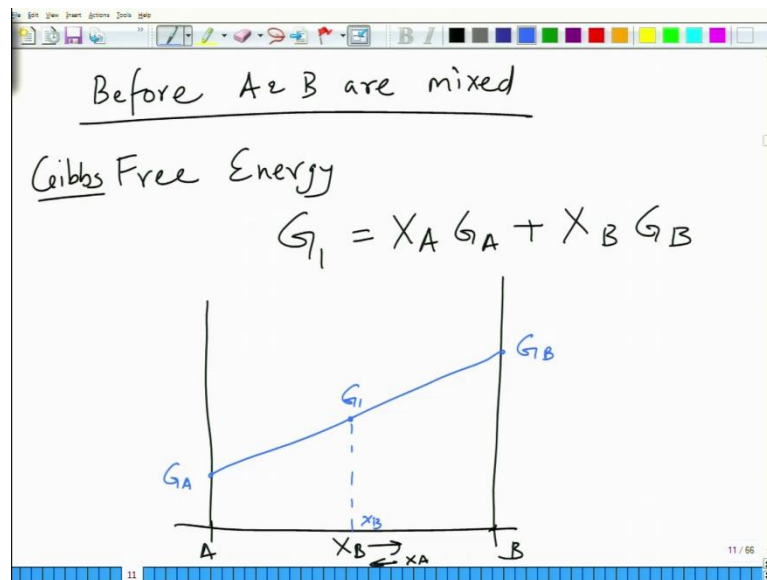
Assumptions are so, first assumption is A and B have same crystal structure. Now this may not be is necessarily a good assumption, but never the less we go ahead with it. And molar free energy of A is G_A and molar free energy of B is G_B . And second assumption is that A and B can be mixed in any proportion. So, basically what it means is that, they are soluble in to each other throughout the composition range. So, you can have pure A, you can have pure B and within any fraction of A and B they are completely miscible into each other. So, they make a solid solution across whole composition range; solid solution AB across whole composition range.

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So, basically as I said we are mixing X_A moles of X_A moles of A plus X_B moles of B to give rise 1 mole of AB, obeying the relation $X_A + X_B = 1$. And AB as a result turns out to be a homogeneous solid solution. Now let us so there are 2 steps, first you bring them together they are not mixed, but just about to be mixed, and then they mix and second step is the formation of a solid solution.

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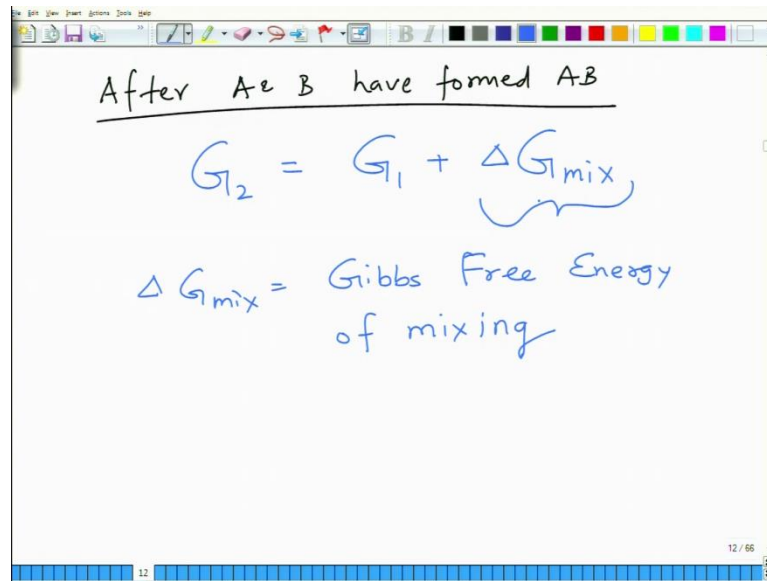
So, before you mix A and B, before A and B are mixed the free energy of system, I can say Gibbs free energy. So, in most cases when I say free energy it is Gibbs free energy, unless I meant, I say that it is a Helmholtz, another free energy is Helmholtz free energy; which we generally do not talk about in our context. So, free energy is

$$G_1 = X_A G_A + X_B G_B$$

And as I said G_A is the mole of energy of A mole of energy of B is G_B , X_A is the mole fraction of A and X_B is the mole fraction of B.

So, if we draw a diagram so, this is A this is B, this is variation of X_B . So, X_A will naturally go in this direction this is X_A . So, if you plot this curve what you will obtain is; so, this is G_A , this is G_B and this would be G_1 the energy of a mixture at a given X_B , ok. Now this is just before mixing, ok.

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Now after A and B are mixed, after A and B have formed AB, the free energy changes, the free energy

$$G_2 = G_1 + \Delta G_{mix}$$

G_2 is G_1 plus a term which is an extra term, which is basically dependent upon the interaction of A and B with each other. Because remember free energy terms consists of terms called as enthalpy; enthalpy built up of inter energy; inter energy is built up of kinetic and potential energy and potential energy is the term which is due to interaction of atoms with respect to each other.

So, in the pure A and pure B you will have only A type bonds, only B type bonds. In case of AB, you will have A-B bonds, you will have A-A bonds, you will have B-B bonds depending upon the nearest neighbor configuration. And this leads to change in the potential energy, as a result you will have an extra energy which is called as ΔG_{mix} . This ΔG_{mix} is called as Gibbs free energy of mixing. And from the definition of stability you will have to realize that this ΔG_{mix} has to be negative if G_2 has to be lower than G_1 ; which means, if the solid solution has to be stable, G_2 has to be lower which implies that ΔG_{mix} should be negative and we will see how it happens.

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The image shows a whiteboard with handwritten mathematical derivations. At the top, it says 'If' followed by two equations: $G_1 = H_1 - TS_1$ and $G_2 = H_2 - TS_2$. Below these, it shows the subtraction: $G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$. A red box highlights the resulting equation: $\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$. To the left of this box, a blue box contains the text 'no change in V_m ' with an arrow pointing towards the equation. Below the red box, there is a handwritten note: ' $\Delta H_{mix} \rightarrow$ heat is either evolved or absorbed during mixing of A & B leading to solid solution formation.'

So, we know that $G_1 = H_1 - TS_1$. And we know that $G_2 = H_2 - TS_2$. And if I define, so if I write this as

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1).$$

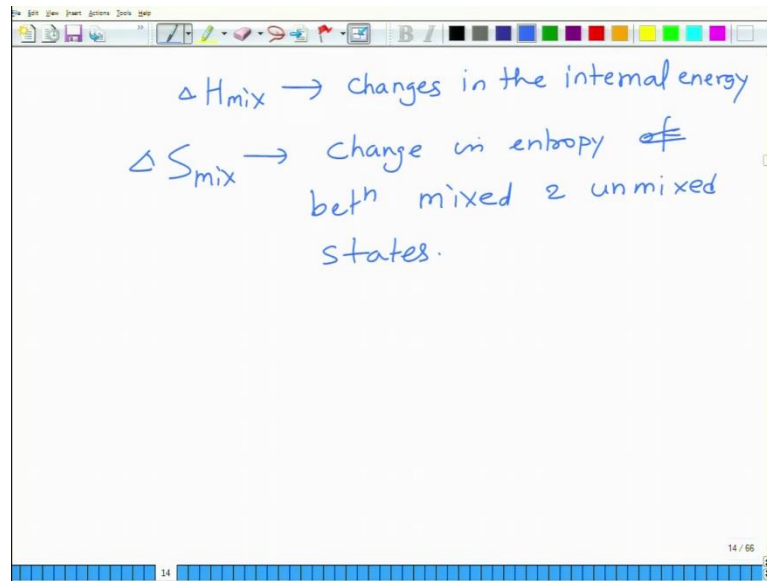
So, which means $\Delta G_{mix} = G_2 - G_1$,

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

So, the free energy of mixing is consists of 2 terms, one is ΔH_{mix} and ΔS_{mix} . And ΔH_{mix} is basically change in the enthalpy, which is due to; which could be manifested in, heat is either evolved or absorbed depending upon the interaction between the 2 atoms, during mixing of A and B leading to solid solution formation, ok.

Now, here we are assuming that there is no change in; so, here of course, we have assumed that there is no change in V_m , so molar volume change is 0; which is not correct assumption in most cases, but never the less. So, basically what we have said is the AB solid solution, volume molar volume is similar to molar fractions of volumes of A and B.

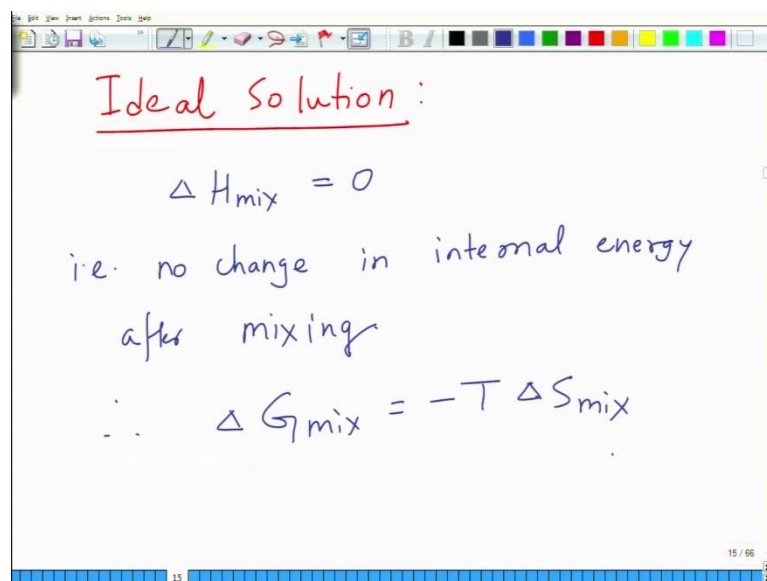
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So, basically here this ΔH_{mix} term; if your molar volume change is 0, then it is basically because of changes in the internal energy. And ΔS_{mix} on the other hand is the change in the entropy it is change in entropy of or between mixed and unmixed states, ok.

So now we will work out what this change in entropy be like. So, so for that, we have to do it in a different way. First is to consider that the solution is ideal, ok.

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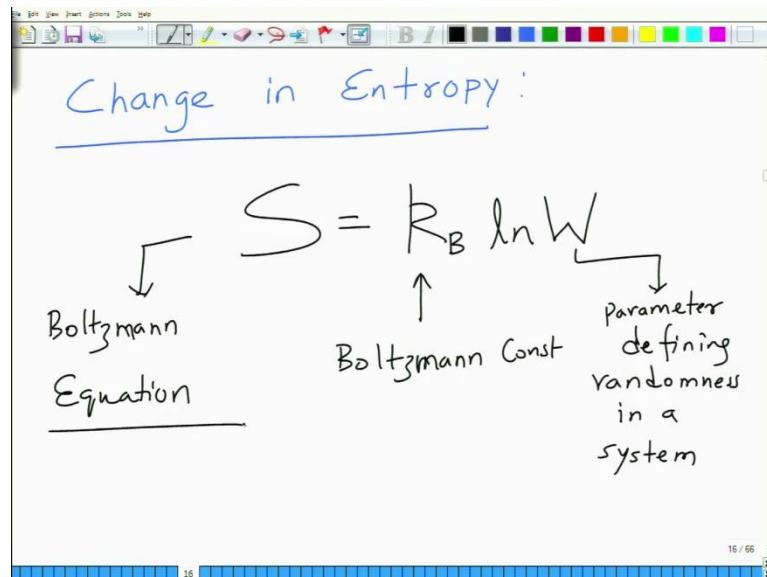


Solution is ideal means, now let me first write that this is ideal solution, ok. Now by ideal solution we mean that $\Delta H_{mix} = 0$; which means, there is no change in internal energy when

you mix A and B and form AB solid solution. Now that is not really a correct assumption, but for the sake of simplicity, let us first assume that this ΔH_{mix} is 0; that means, there is no change in; given the fact that internal energy depends upon the bonding configuration there will be some change in reality.

But let us assume in this case of ideal solution that there is no change in the enthalpy. As a result, what this means is that $\Delta G_{mix} = -T\Delta S_{mix}$, ok. So, basically the change in the Gibbs free energy. So, Gibbs free of mixing is directly related to the change in the entropy after mixing. Now so, let us work out the change in the entropy.

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The entropy is defined as; entropy is generally defined as S , and this

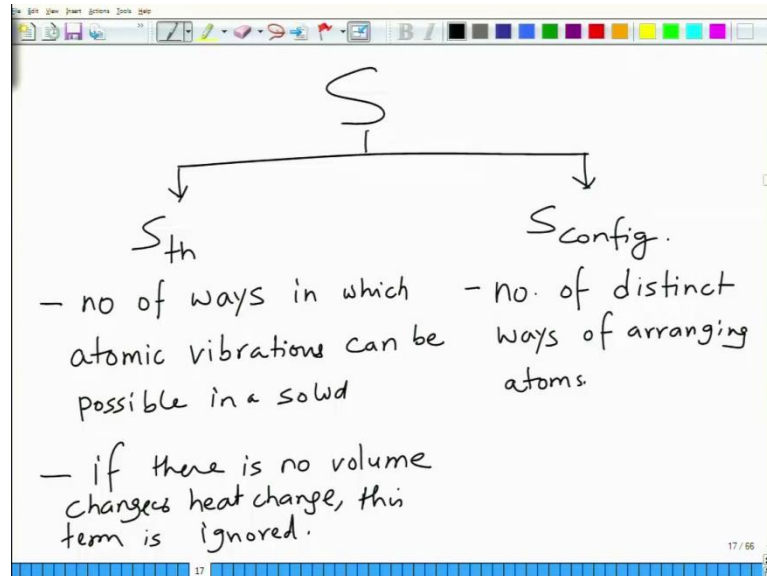
$$S = k_B \ln W$$

Where k_B is Boltzmann constant and W is the; it is a parameter that defines the extent of randomness in the system; so, parameter defining randomness in a system.

So, entropy could be of various kind; it could be thermal; it could be configurational. Thermal entropy would be basically the; because of vibration of atoms. And so, if you have temperature change, your vibrations will change, as a result you will have changes in the thermal entropy. Another entropy is configurational entropy which means configurational entropy which means basically is that how the atomic configuration in a material can be changed. In what many; in how many possible ways you can have distinct

configurations in the in a given material? And this equation of entropy is called as Boltzmann equation.

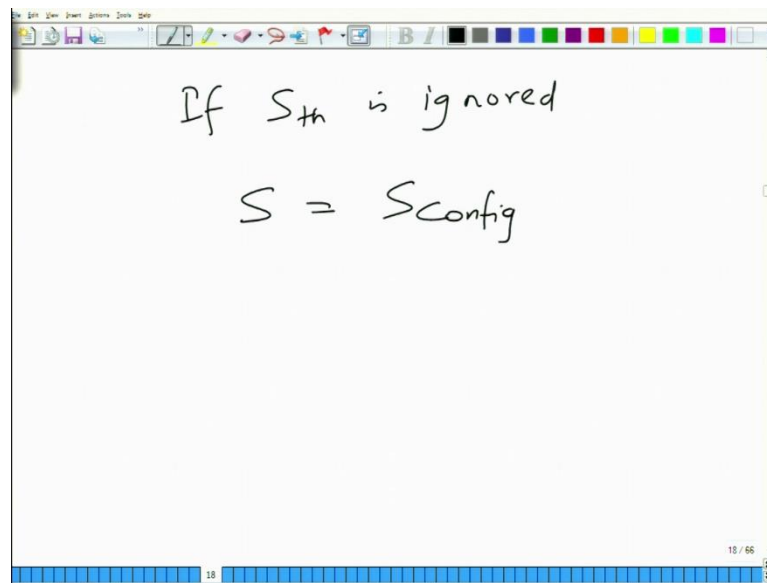
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So, there are 2 kinds of entropies S. So, S_{thermal} is basically number of ways in which atomic vibrations can be present, can be possible in a solid. Or alternatively you can say, number of ways in which thermal energy can be divided among many atoms. And generally if there is no volume change or heat change, then you ignore it. This term is ignored so, this is S_{thermal} . What about $S_{\text{configurational}}$? $S_{\text{configurational}}$ is basically the number of configurations in which; number of in or you can say distinct ways of arranging atoms. So, this is basically the configurational entropy.

So, you can; of course, you can say that if you have a pure metal A then there are only; there is only one way of arranging the atoms. If you have pure metal B, then there is only one way of arranging the atoms because no matter how you put the atoms, provided the crystal structure remains same, it will have only one way of identifying the thing, but when you have solution like AB you can put A and B in different possible configurations, unless it is a regular ordered solid solution.

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So, if $S_{thermal}$ is ignored; so, if $S_{thermal}$ is ignored, then S is equal to $S_{configuration}$. So, in the next lecture we will talk only about the configurational entropy, and see how we can determine it.

Thank you.