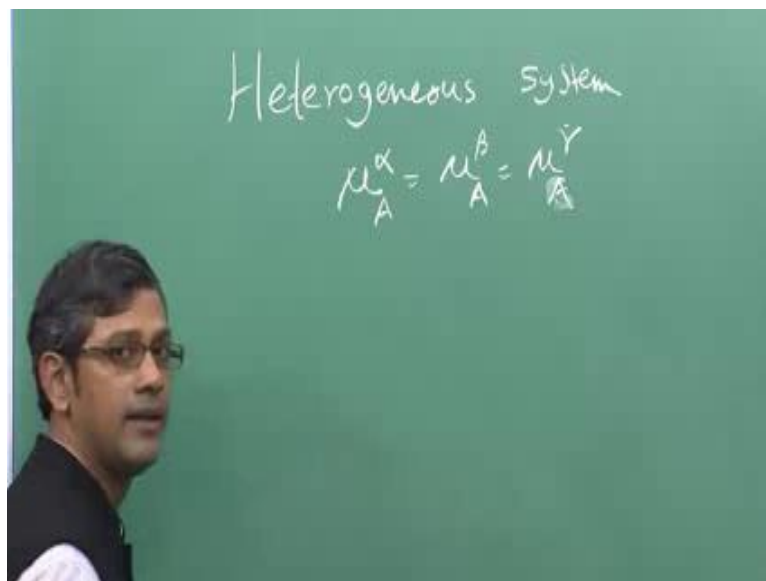


Phase Diagrams in Materials Science and Engineering
Prof. Krishanu Biswas
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

Lecture - 05
Phase Rule-II and Single Component Equilibria

Well, today we are going to start on a topic called single phased phase diagrams or single phase equilibria. Before that, I like to give you recapitulations of the last lecture. I think in the last lecture I discussed with you about the equilibrium heterogeneous systems like mixture of water and ice. What are the thermodynamic rules of heterogeneous equilibrium? Obviously, in heterogeneous equilibrium temperature and pressure must be kept constant. But other than that, one most important rule must be satisfied. The rule is; that rule is known as chemical potential of any component in all the phases must be equal. So, I just write down again this equation.

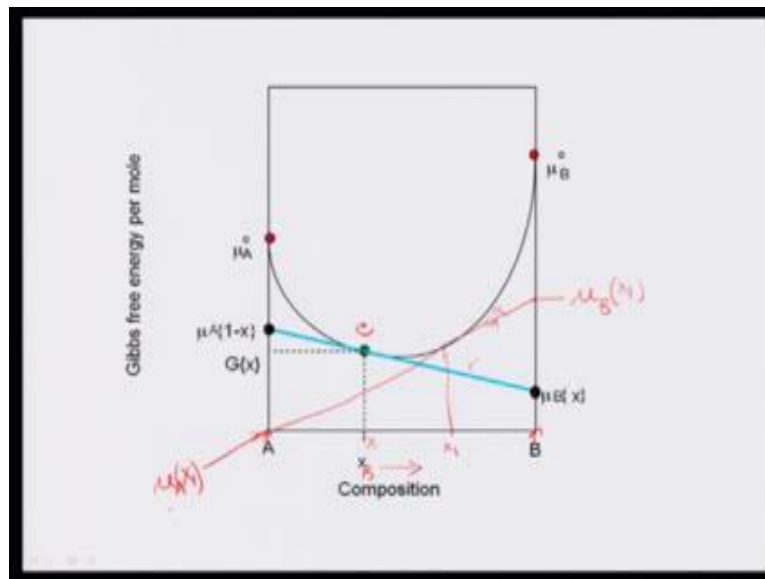
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For heterogeneous system, the chemical potential of any component A must be equal in all phases. Suppose there are three phases, three phases; alpha, beta, gamma, so chemical potential of any component A must be same in all the phases. And, I told you the meaning of the chemical potential. It is the measure of potential of any component in a mixture of many components.

Suppose, you have a phase alpha and this phase contains three components A, B, C, so that the chemical potential of A in alpha means the ability of alpha to react with the other components, in the phase. Or, rather in a thermodynamics sense it means change of free energy, total free energy, when infinitesimal amount of A is added to alpha; that is what is known as the chemical potential of alpha. This is represented by a letter Greek letter known as mu. So, in the pure component chemical potential is represented by mu, but with a superscript zero.

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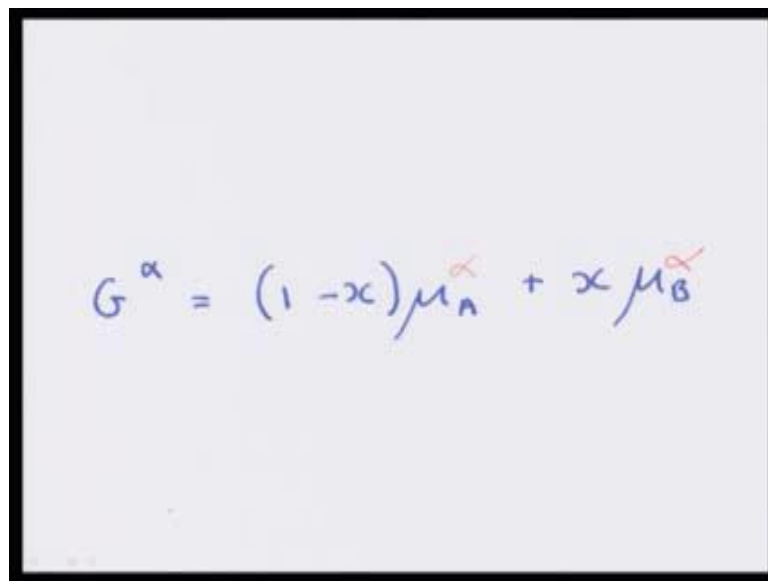
So, let's us now look into this. I just wanted to tell you again that for a system like this, the free energy curve is given by a parabola as a function of composition for a fixed temperature. So, pure ends are given A and B. The chemical potential of pure A is given by μ_A^0 ; chemical potential of pure B is given by μ_B^0 . But, the chemical potential of a component A or B in this phase alpha, can be measured using a construction known as tangent to curve.

How do I do it? Suppose, I have a point A, a point C here suppose, in this case I have marked as by red point C. And, I want to know the chemical potential of A and B in alpha phase, for composition C. So, free energy for the composition point C is given by $G(x)$ because x is the composition of C, given by this point C.

Now, the way I do it is that I draw a tangent to this curve at point C. Now, if I extend this tangent to the both sides, it will meet A and B axis. The vertical axis corresponds to pure

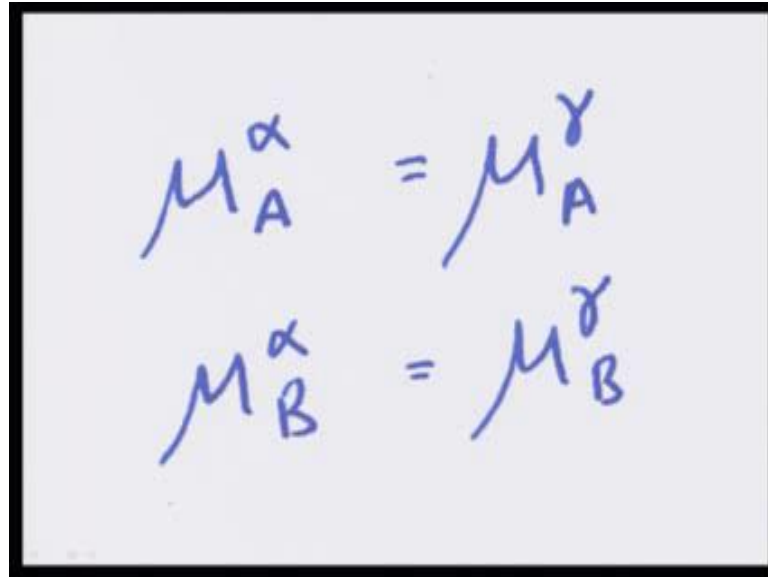
A and pure B. And that means, the cross section of this points at pure A and pure B will correspond to the chemical potential of A and B respectively. That is so it is measured. So, if you want to measure chemical potential, suppose at a point like this X 1 here, I am drawing. So, I can do by drawing a tangent like this. And, so therefore these point will correspond to chemical potential of B at X 1. Similarly, this point will correspond to chemical potential of A at X 1. That is how we do. So if you have the free energy curve, in point of view you can basically measure chemical potential of the components at any composition, by doing this construction. What is the utility of this?

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$$G^{\alpha} = (1-x)\mu_A^{\alpha} + x\mu_B^{\alpha}$$

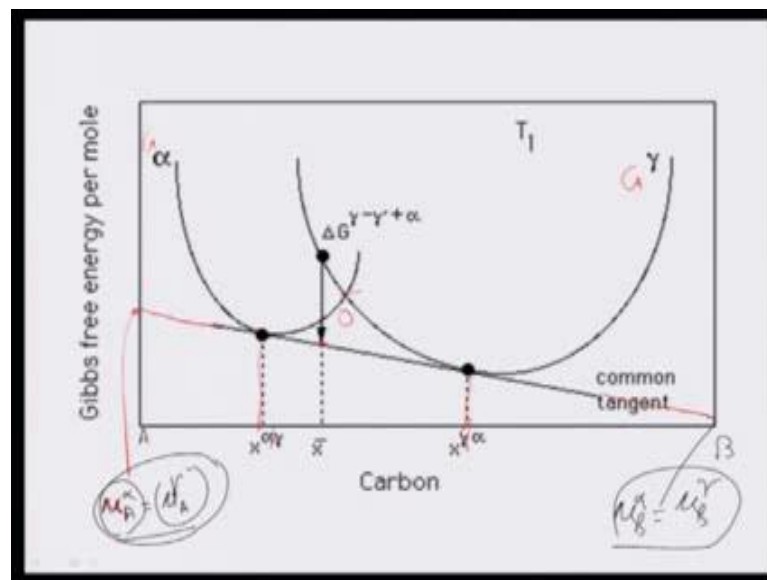
So, this step means we can actually define this free energy curve using chemical potential by this way. Just a line equation. There is a tangent to straight line. We can derive that. What is the utility of that? Let us do that.

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Utility of this is this that we can apply this, this chemical potential equal chemical potential law thermodynamical rule. Rather, $\mu_A^\alpha = \mu_A^\gamma$ $\mu_B^\alpha = \mu_B^\gamma$ for a two phase system.

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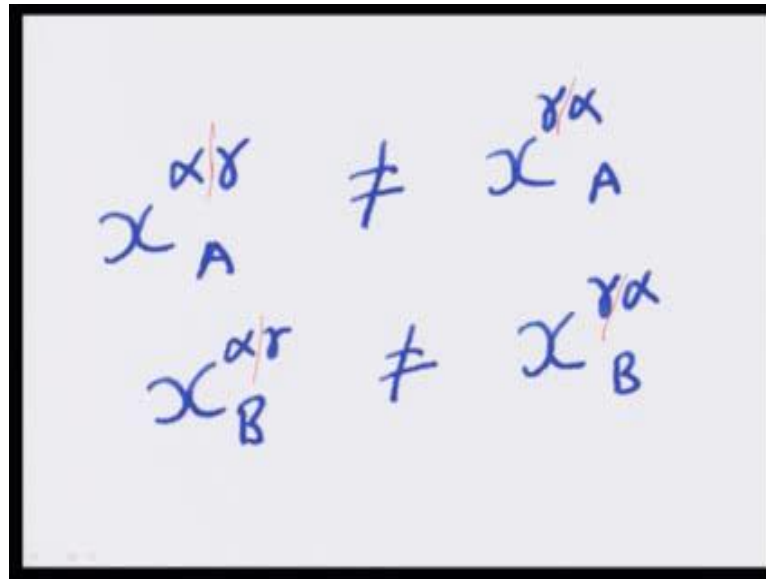
And, find out its equilibrium conditions. So, that is how it is done. Suppose, I have a free energy verses composition curve for two phases of steel; alpha and gamma. Alpha is a BCC solution; gamma is FCC solution. And, it contains carbon as a important solute

element. That is why the free energy plotted as (Refer time: 05:54) carbon. So, there are two curves G_α and G_γ . I marked it at the temperature T_1 , suppose.

So, now if you look at these two curves carefully, these two curves intersect at a point like this, which is suppose O, I marked it. That means that at this point, these two curves have same free energies. Correct. But, you know to find out the equilibrium between these two curves, easiest way to do is by drawing a common tangent passing through the point at which the compositions of the alloy lie. Suppose, the carbon alloy composition X_{bar} . So, I draw a vertical line. And, I draw a tangent between the two curves passing through this point. So, when I extend this tangent to the both ends of A and B, that is carbon end and this is iron end, I can find out that the chemical potentials of A and B. Now, as per the thermodynamical rule for the phase equilibria heterogeneous system, we can always see that this rule $\mu_A^\alpha = \mu_A^\gamma$ satisfied at the A end. Similarly, $\mu_B^\alpha = \mu_B^\gamma$ satisfied at the B end. That is what we always find.

So, this is the way actually we can find out the composition of the phases, which are equilibrium like air; because common tangents like sitting on this two points, this point and this point. So, if do I have vertical down, the composition axis meeting points will be the equilibrium concentration of alpha in equilibrium gamma. Similarly, equilibrium concentration of gamma in equilibrium alpha. So, I can easily find out that. That is possible. So, that is the beauty of this heterogeneous phase equilibrium. And, in a nutshell this gives an idea of the phase diagram. And, we will see how it can be utilized.

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So, what do you learn? We all know that for the equilibrium to be satisfied, there is a common notion; the chemistry or the compositions of a particular phase. Suppose, this is composition of A. Component A means iron; that the alpha gamma interface will be equal to gamma alpha interface. The interface between gamma and alpha should be equal. But, that is not true. That is not at all true. Similarly, for B that is not true. What is true is the chemical potentials. So that means, the chemical potential actually drives any phase transformation process. That is what you must remember. If you want to know about phase transformation phase diagrams and other things, this is very important consequence of the of the derivation, which I have done in the last class. So, that you must not forget in any of the lecture, while going ahead.

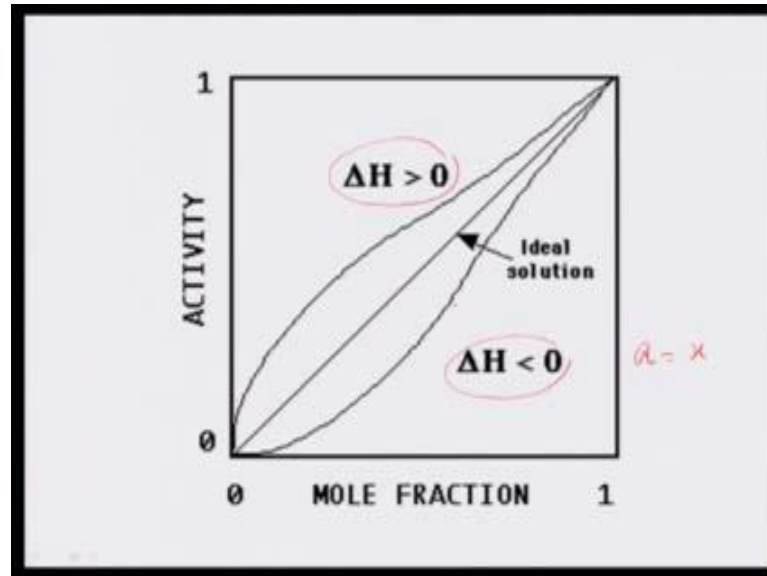
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So, you know, if you look at oceans, there are lot of big ice bergs. We know the Titanic crash because of the collision with icebergs, not direct, by side collisions. Now, what is the factor which stabilizes this ice bergs, in the sea full of water? It is a chemical potential.

So, therefore the chemical potential of the water H_2O as a component is same; mass be same both in water, liquid water and the ice. Similarly, chemical potential were salts sodium chloride, potassium chloride or many other salts, which are present in the ocean water must also be the same in both the liquid water and ice. That is so actually this kind of two phase equilibrium can be attained in vast oceans. And, this is true for our system also. This is very well true in our systems. Why because in our systems, we always know that there are multiple of phases. And, when a multiple of phases present in our system, these multiple phases will always has to be, you know, in equilibrium under the conditions when the chemical potential of a component in both the phases are equal.

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So with this, I will just like to tell you that this is true for ideal solution mostly. But, this can be extended for other solutions like non ideal solutions, where there is a positive deviation or a negative deviation. This is negative deviation; this is a positive deviation. We all know that. Basically, this is the Raoult's law. For the ideal solutions, the activity equal will be equal to the mole fraction. Activity is equal to mole fraction. Correct. But, whenever you have a deviation for a Raoult's law, we can draw this diagram. This kind of plots. So, this can be actually used for. This is, such a large deviations may not allow you to, you know, thermodynamics (Refer time: 10:49) satisfied for such a chemical potential's rule. But for larger composition range, even for non-ideal solution also it is possible.

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$$\mu_A^\alpha = \mu_A^{0\alpha} + RT \ln a_A^\alpha$$
$$a = \Gamma x$$
$$a_A^\alpha = x_A$$
$$\mu_A^\alpha = \mu_A^{0\alpha} + RT \ln x_A$$

Well, normally chemical potential is represented with by this way. How it is done? You see here chemical potential of any component A in alpha is equal to chemical component of a pure A; that is called superscript zero A mu A zero superscript alpha plus R T log A alpha. What is log A? Log A is logarithmic of the activity. So, if the activities are equal to; activity is equal to suppose the mole fraction, then I can write down this equation like this, very easily; mu A zero alpha plus R T ln X A alpha.

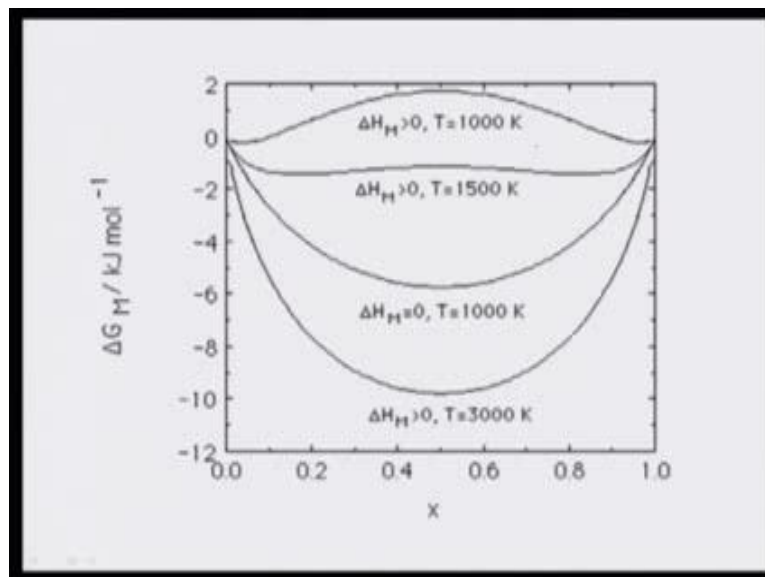
That is for the ideal solution. But for non-ideal solution, the X A will be replaced by activity. And, you also know that activity can be related with this constant gamma in the concentrations. Normally, non-ideal solutions, though therefore we can replace that. So, in that case if this is what is the rule for activity, so and A follows this. Then, you can write down the other equation that is the gamma is equal to mu A is equal to mu A zero alpha plus R T ln gamma X A; that means, it is equal to mu A alpha plus R T ln gamma plus ln A. This can be written. You all know that that is possible. So, that for any ideal or non-ideal solution, does not matter.

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$$\mu_A^\alpha = \mu_A^{\circ\alpha} + RT \ln a_A^\alpha$$
$$a = \Gamma x$$
$$\mu_A^\alpha = \mu_A^{\circ\alpha} + RT \ln(\Gamma x_A)$$
$$= \mu_A^{\circ\alpha} + RT(\ln \Gamma + \ln x_A)$$

We can modify this chemical potential rule and explain the whole stuff.

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I hope you understood that. Now, I just do not want to spend lot of time on this diagram. That you know it is specifically nothing but a delta G value as a function of X. So, the non-ideality or the deviation for ideality will also depend on the H, delta H is mixed. And, the delta H mix is normally if it is negative and like this parabola, this is easy to find out the solutions, what if it is the shapes like that, given then deviation will happen.

We will discuss about this when you derive the (Refer Time: 13:20) approach. Let me just go ahead and discuss with the single phase equilibrium.

So by this, I hope you understood that for any (Refer Time:13:29) you have to be satisfied, the thing which you should understand is that the chemical potential must be equal. So, let me just move ahead with the single phase equilibria. Single component phase system are basically like water, carbon dioxide, oxygen, nitrogen, pure iron, pure silicon dioxide, Sulphur, there are many single component systems. And, we need to understand them because they are the ones which actually satisfy, which gives you very nice idea about how the phase transformation start.

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So, these systems are also known as; this system also known as unary systems because they are single component; unary. We know binary. So, therefore binary means two components; unary means single component system.

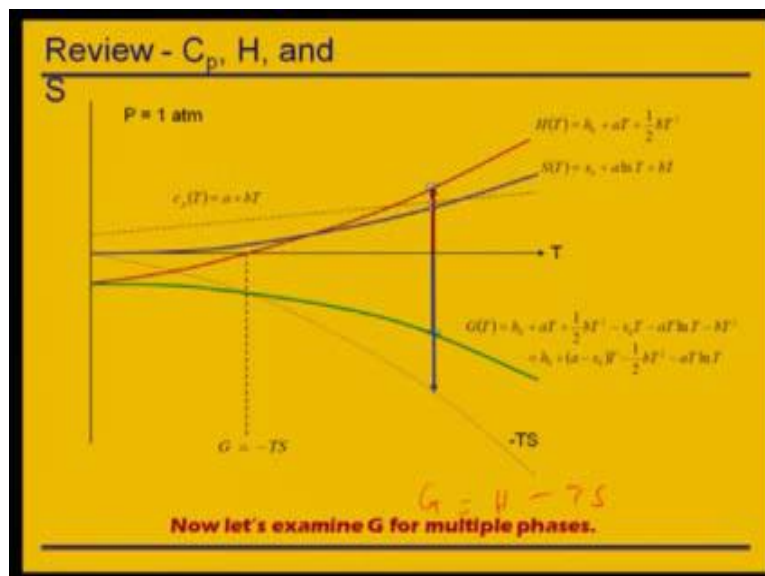
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THERMODYNAMIC PROPERTIES OF THE ELEMENTS*

Elem.	Phase	Temperature of Transition (°K)	Heat of Transition (kcal/g mole)	Entropy of Transition (e.u.)	Entropy at 298°K (e.u.)	cal/g mole·K	cal/g mole·K	cal/g mole·K	cal/g mole·K	A (kcal/g mole)	Ref. 1
Ac	solid	(1090)	(3.7)	(3.7)	(13)	(3.4)	(3.0)	---	---	13.740	(18.7)
	liquid	(2700)	1.95	(25)	---	(8)	---	---	---	30.295	(11.16)
Ag	solid	1234	2.855	2.143	30.20	1.00	1.01	---	0.36	1.488	(9.21)
	liquid	3485	60.52	14.43	---	1.80	---	---	---	21.688	(6.17)
Al	solid	933.5	2.57	2.56	8.709	4.84	2.56	---	---	1.604	(22.26)
	liquid	2600	67.9	26	---	7.0	---	---	---	15.33	(20.81)
Am	solid	(1200)	(3.4)	(3.0)	(13)	(8.9)	(8.4)	---	---	(3.87)	(16.1)
	liquid	2710	51.7	18.8	---	(8.5)	---	---	---	(0.409)	(16.7)
Au	solid	985	5.6	5.6	8.4	1.17	2.54	---	---	1.666	(11.0)
	liquid	1736.16	1.05	2.27	11.32	6.14	-0.173	0.92	---	1.831	(13.6)
B	solid	2313	74.23	23.30	---	1.00	---	---	---	-0.631	(20.99)
	liquid	2313	(3.8)	(3.8)	1.42	1.54	0.40	---	---	0.815	(6.67)
Ba	solid	2800	5	5	---	(8.0)	---	---	---	(-4.500)	(21.4)
	liquid	440	0.14	0.22	16	1.51	1.50	---	---	1.722	(6.1)
Be	solid, α	877	1.83	1.87	---	1.57	1.50	---	---	1.583	(11.9)
	solid, β	1931	33.660	18.63	---	(7.4)	---	---	---	(0.847)	(10.7)
Bi	solid	1576	1.919	1.301	2.28	1.07	1.21	---	-1.13	1.861	(17.67)
	liquid	---	---	---	---	1.27	---	---	---	1.811	(13.68)
Bj	solid	184.2	2.83	4.83	13.6	1.58	2.80	---	---	1.720	(13.8)
	liquid	1950	41.1	23.6	---	1.60	---	---	---	-0.087	(23.8)
C	solid	---	---	---	1.3600	4.10	1.03	---	-2.10	(-0.10)	(-13.30)
	liquid	---	---	---	---	---	---	---	---	1.972	(13.488)
Ca	solid, α	923	0.24	0.22	9.95	1.24	1.20	---	---	1.718	(20.95)
	solid, β	1123	2.2	1.96	---	6.29	1.40	---	---	1.689	(20.0)
Cd	solid	1773	18.6	21.0	---	1.4	---	---	---	-0.187	(20.28)
	liquid	---	---	---	---	---	---	---	---	(-43.055)	(-4.586)
Co	solid	194.1	1.86	2.46	12.5	1.21	2.84	---	---	1.718	(18.8)
	liquid	1040	23.86	23.94	---	7.10	---	---	---	0.798	(26.1)

So, there are many single component system. I just give you some metals, examples like actinium, silver, aluminum, americium, gold, boron, beryllium, bismuth, calcium, cadmium. And, you can see that they exist in all phases; solid, liquid, gas. And, they have all kinds of, you know, they find, solid also they can find alpha, beta. Calcium has two alpha, beta phases. So, to know their phase transformations you must understand the basic philosophy of that.

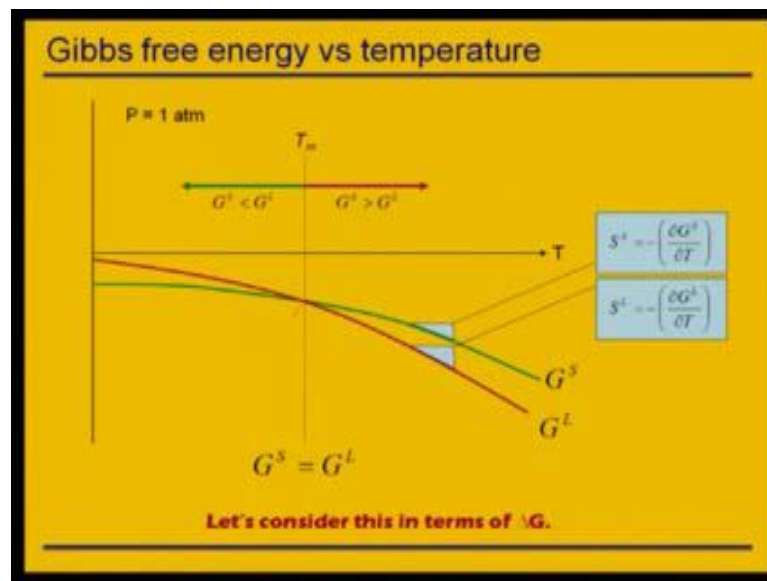
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So, let us first review. Next 10 minutes, I have to review. Before I go for the next class, where I going to discuss about the phase transformation. So, I just here plotted any parameter S, you know, review C p, H and the entropy. So, I know that C p can be termed as a plus b T. So, that is a straight line. a is a constant, b is a constant, b are constant, T is a temperature and absolute. And, this is what is your enthalpy. Enthalpy what? integration of C p, C p T enthalpy. So, if I integrate that function, I get the actual stuff. Now, I can also take the entropy.

Entropy is nothing but integration of C p by T d T. similarly, I can get minus T S; minus T S is like this. So, G will be like this. G is a green curve, which you can see basically H minus T S. G is nothing but H minus T S, which can be obtained for my H and T, H and S easily. So, you can see here that G is equal to minus T S at this point because G and T S are minus equal. And, these are the difference of these values S component T S and H. So, therefore G is basically a real time function between H and T S.

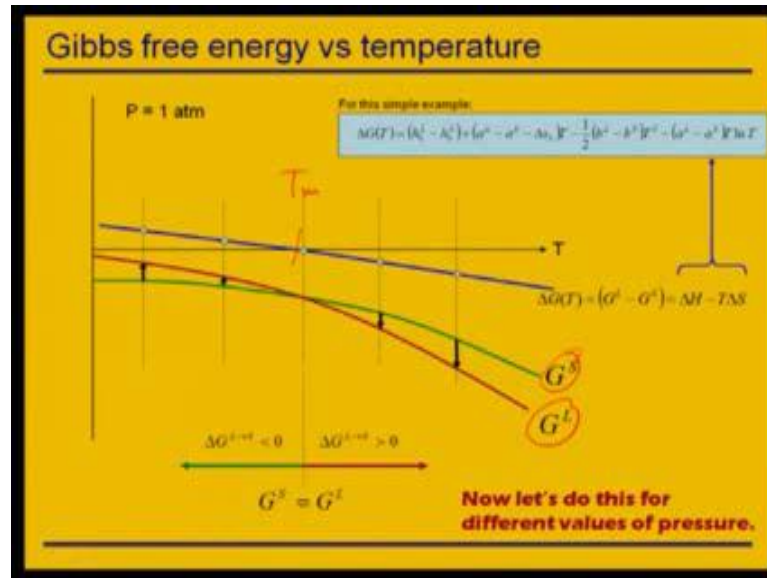
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So, now if I take multiple phases, what happens? I have already done that. If I take a multiple phases, so solid and liquid, then I know that equilibrium will be given by the same value of G and S. And, that is at this point where both solid and liquid should exist. And, therefore the temperature less than this value, the G will be less than G L, G S will be less than G L and solid is more stable. That is what you see here. Solid is lower energy than of liquid, more stable. On the other hand, this side, G S is more than G L.

So, therefore liquid is more stable than the solid. We can do this thing also in terms of your; and this is the melting temperature at which both the curves intersect as slope of the curve basically define the entropies.

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Now, let us consider in terms of delta G. That is very easy. This is G L and G S. (Refer Time: 17:03) too quickly. And, delta G is nothing but difference of these two. This is a straight line equation. And where it will meet, the delta G will be 0. And, if you see here as you go temperature less than this, lower than the temperature at which delta G is zero. You have a resultant delta G values which is positive, and if you go higher than that this temperature delta G will become negative.

And that is why actually, we can actually get idea about whether delta G will be; delta G is change of transformation of liquid to solid less than 0 at temperature less than the melting temperature T m. Above, the temperature is more than 0. And that is why actually it is possible to have solid, liquid become solid lower than the melting temperature; solid become liquid at the above the melting temperature because sine of delta G actually tells you exactly the transformations, the direction change which way this transformation will happen.

Now, before I go into the next lecture, I just wanted to tell little bit about this. See, normally we have done all these calculation function of temperature keeping the pressure constant. Why? Because if I change both the variables together, I cannot have a good

handle on the stuff. So that means, the pressures is always kept at one atmospheric pressure or as temperature are varied.

And, all the free energy functions, entropy and enthalpy and free energies are actually measured as a function of temperature. If that is what is true, then we can actually easily, you know, do this calculation at one atmospheric pressure. But, if you want to do this phase diagrams for the single component system, we need to understand what is the effect of pressure on the transformation temperatures. That is why we actually need to know the effect of pressure, which I will do in the next lecture.