Phase Equilibria in Materials (Nature and Phase Properties of Materials – II)

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Lecture – 02

Basic Thermodynamics: Gibbs Free Energy

The first lecture we just learnt about some basic definitions related to essential thermodynamics that will make us understand phase equilibria. So, in this lecture we will again continue building on that and we will see some more thermodynamic co-relations. So, we were studying about how phase equilibria is an important understanding phase transformation.

For example, I give the example of water in which H 2 O molecules go from, H 2 O molecules are present in liquid phase at temperature slower than 100 degree centigrade, but as you go beyond 100 degree centigrade, phase transform into gaseous phase. The reason for that lies in the thermodynamic equilibrium because at higher temperature higher temperature the vapour phase in the equilibrium state whereas, at lower temperature the liquid phase is the equilibrium state. And this is determined by what we call as free energy. The free energy of liquid phase is slow at lower temperature has compare to vapour phase whereas, converse is true at high temperatures

So now let us look at the aspect relate to phase stability.

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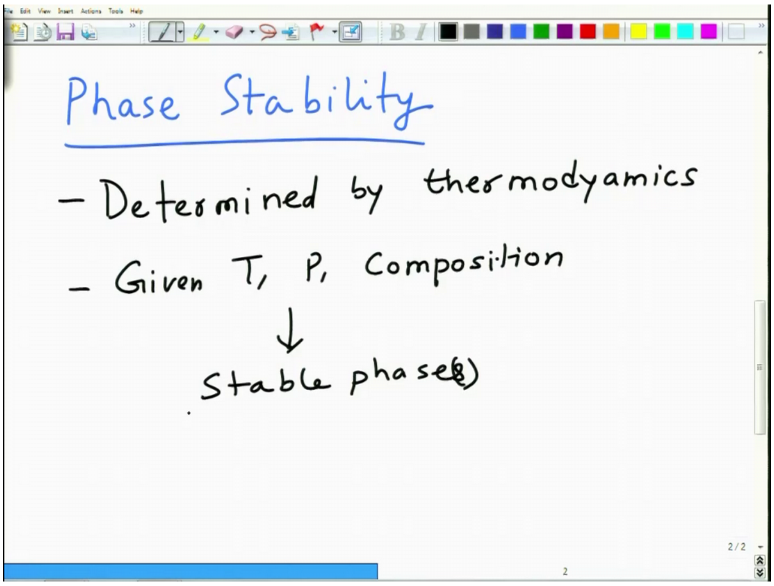

Phase Stability

- Determined by thermodyamics
- Given T, P, Composition

↓

Stable phase(s)

So, we look at what we call as phase stability. Phase stability basically determined by thermodynamics. And in particular a so, basically what we are looking at a given condition of given temperature, pressure and composition. What are the stable phases? And this is what is phase equilibria.

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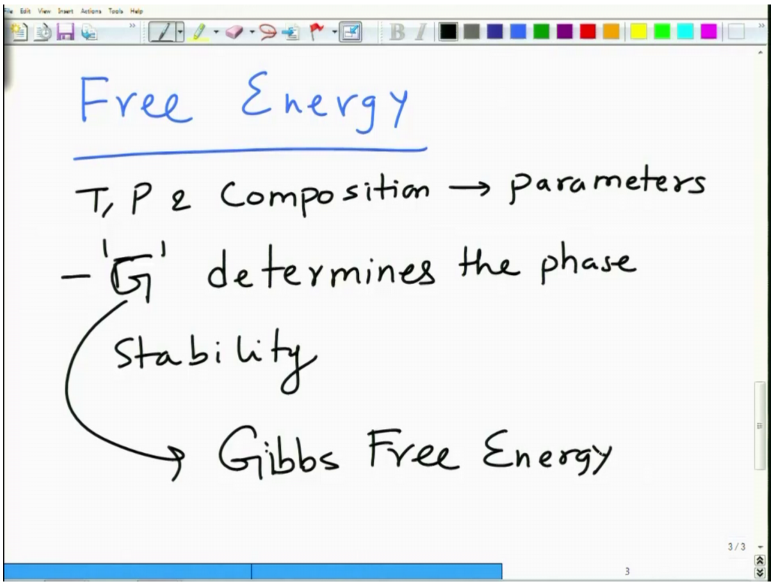

Free Energy

T, P & Composition → parameters

– 'G' determines the phase

Stability

→ Gibbs Free Energy

So, let us first define the term called as free energy. So, I assume that you have basic knowledge of elementary thermodynamics, which is useful to understand the course. So, free energy so at a constant at a given temperature and pressure as well as composition, free energy G, let us G determines, determines the phase stability an alloy, and G is called as Gibbs free energy.

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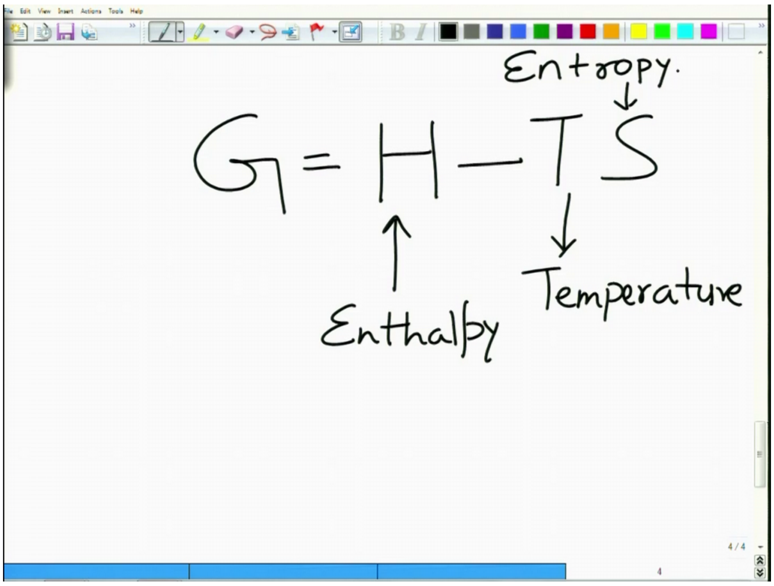

And this G is written H minus T S. So, H is called as enthalpy, T is the temperature and S is called as entropy. So, let now let us just look at the definitions of these components.

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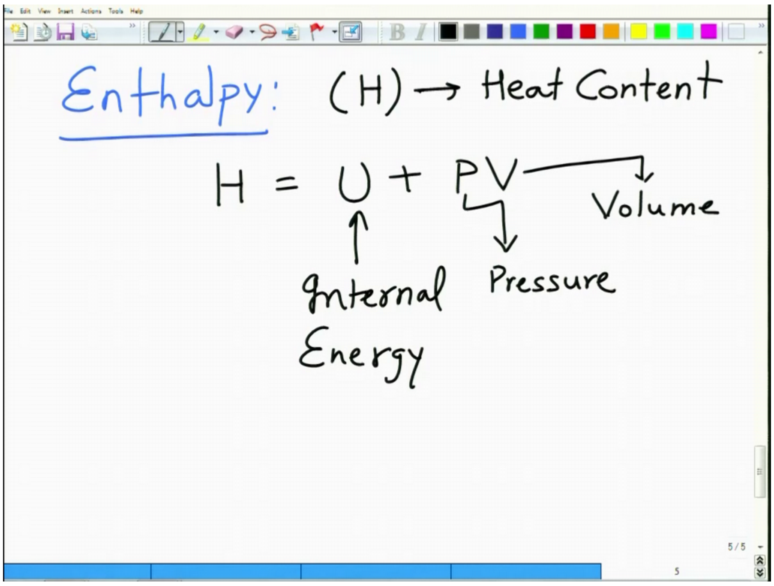

So, let us first look at what is enthalpy. So, enthalpy is essentially defined as H, ok. It is essentially defined as heat content of a given system. And H is defined as further U plus PV, where U is the internal energy, P is the pressure and V is volume. And this U essentially so they basically it is the enthalpy can say the total energy inbuilt in a system; which consists of the internal energy, and it consists of the pressure and volume terms the net amount of work which is done by the system or on the system. That will determine the total heat content of system. So, let us now first look at the internal energy.

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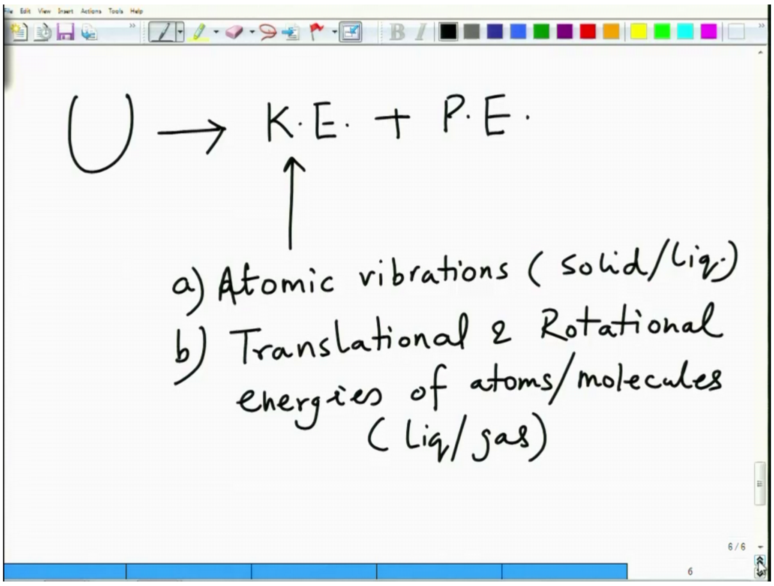

$U \rightarrow K.E. + P.E.$

a) Atomic vibrations (solid/Liq.)

b) Translational & Rotational energies of atoms/molecules (Liq/gas)

This U is basically some of all the kinetic energy contributions and all the potential energy contributions. So, kinetic energy may arise from let us say a, atomic vibrations, b it could be due to so atomic vibrations in both solid and liquid phase it could be because of translational and rotational energies of atoms or molecules. So, it again could be within the liquid phase or gas phase generally these are more of significant liquid and gas phase whereas, atomic vibrations are more in gaseous phase. So, this is the kinetic energy term. The potential energy term on the other hand is composed of one due to; you can say the bonding atomic slash molecular interactions in a system.

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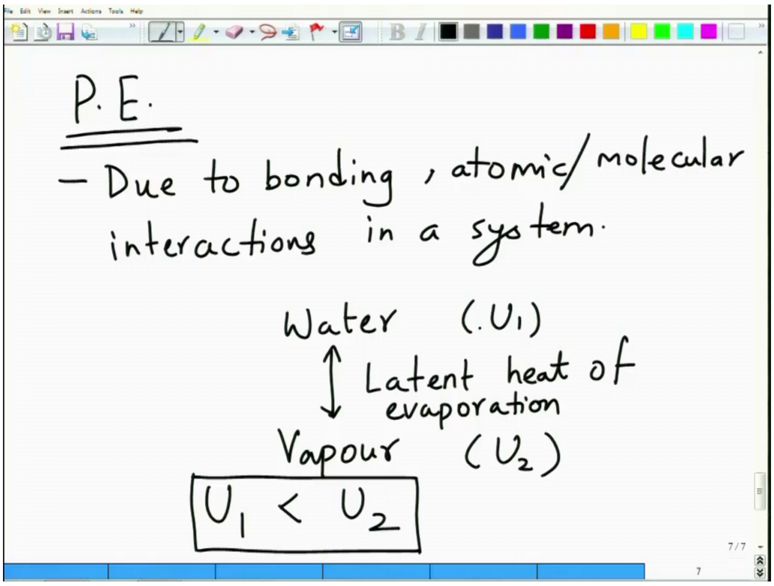

P.E.

- Due to bonding, atomic/molecular interactions in a system.

Water (U_1)

Latent heat of evaporation

Vapour (U_2)

$\boxed{U_1 < U_2}$

So, basically, you can say when you transform from one phase another let us say water again the evolution of evolution or absorption of heat is determined by changes in the internal energy of the system. So, let us say when you go from if you look at water for example, and you go to vapour phase, water and. So, when you when you when you go from water to vapour phase the heat is when you go from water to vapour the heat is released. Whereas, if you when you go from so this way the heat is released and this way the heat is so this would be minus Q, and this would be plus Q the heat is absorbed.

So, in this case what happens is that, that the internal energy of internal energy of water as compared to vapour is so, you are saying that this is let us say U 1, and this is let us say U 2 and U 1 is smaller as compared to U 2. The internal energy of water is lower as compared to internal energy internal energy of vapour. So, when you heat water to vapour, you can say the latent heat of evaporation is U add, right. So, you when you go from water to vapour, you are you are saying so just correct this I think this was, I just make a modification.

I just say this is latent heat of, ok. So, as you go from water to vapour phase the water having lower internal energy as compared to the vapour phase, results in or it is because of addition of latent heat of evaporation as you go from water to vapour phase. On the other hand, when you go from vapour to water phase upon cooling, then the so that is why you know the vapour sounds, vapour contains more energy with it. On the other hand, when you go from vaupor to water pahase the heat is so, you have to supply this much heat. In this case you have to the heat that much heat is released out of the system. So, water is at lower energy as compared to vapour phase. So, it is because of absorption or release of latent heat of evaporation, and this is because of difference in the internal energy of water and vapour.

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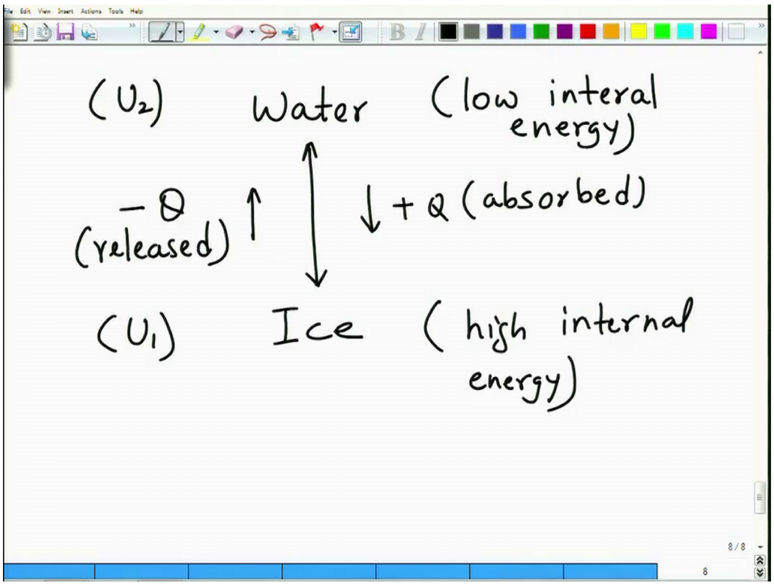

(U_2) Water (low interal energy)

$-Q$ (released) ↑ ↕ ↓ $+Q$ (absorbed)

(U_1) Ice (high internal energy)

So now, similarly you can say in the case of water to ice, when you go from water to ice, ok. Now ice let us say has a internal energy of U 1 water has an internal energy of U 2. Water is at low internal energy, because there are very little atomic interactions. And then ice has high internal energy, because it is in solid phase as a result the potential energy component is higher so high internal energy. So, when you go from water to ice, this is reversible process. So, as you go from water to ice, you say the heat is absorbed.

So, and as you go from you can say this case minus Q the energy is released. This is the and so, if you compare the internal energies of the 2 water at 0 degree centigrade and ice at 0 degree centigrade, if I make a comparison between the 2, let us say this is the kinetic energy part.

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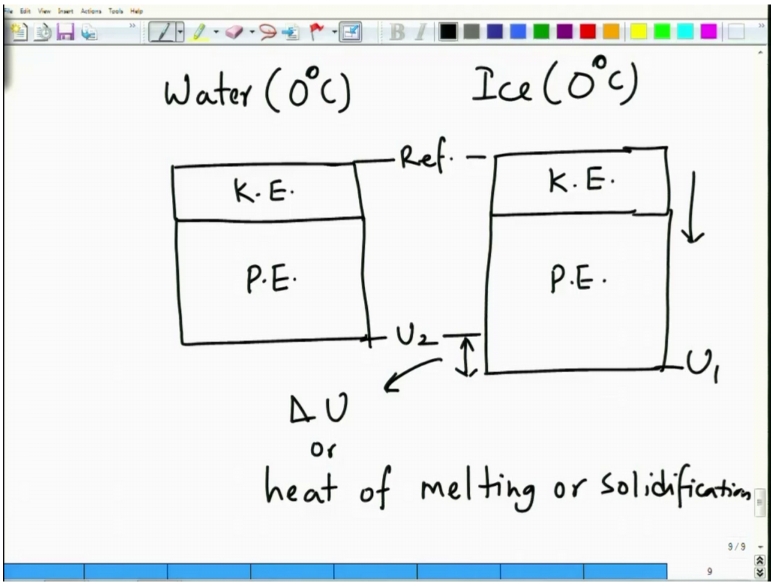

A kinetic energy are nearly equal in both phases. But the potential energy part so this is the potential energy part. So, this is the difference, basically it becomes more and more negative. If you look at a scale so this is a reference level. Let us say you are starting from 0 here. So, the potential energy decreases in the ice phase because of further addition of negative potential energy, leading to total energy reduction. So, this is let us say U 1 and this as U 2, and this is the difference between the 2 which is what is the delta U or you can say the heat of melting or solidification, ok.

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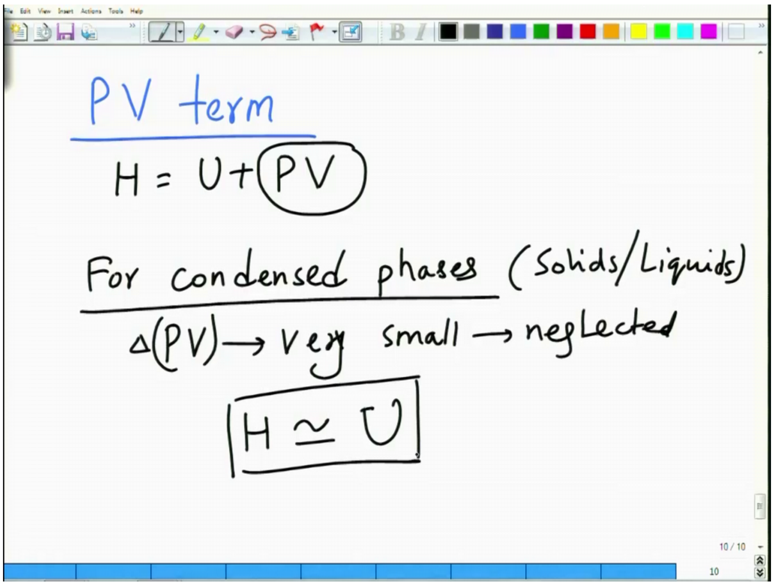

PV term

$H = U + \boxed{PV}$

For condensed phases (Solids/Liquids)

$\Delta(PV) \rightarrow$ very small $\rightarrow$ neglected

$$\boxed{H \simeq U}$$

So, basically the ice has higher potential energy term, than water and this is because in ice in the solid phase the water molecules have stronger interactions with each other as compared to that, in the liquid phase as a result of potential energy is more negative as compared in the water phase. So, when I say higher internal energy of solid, it means that it is more negative internal energy as compared to the liquid phase.

Now, second thing that we talk about is the PV term. The PV term is of importance because phase changes are affected by the change in the volume or the pressure. So, when we say H so this P when we say H is equal to U plus PV. So, at this term which acts or which adds for which becomes plus or minus has come depending upon the what the magnitude as this term is. So, a basically for mostly condensed phases general for condensed phases condensed phases by this I mean generally liquids and solids. Delta PV term is generally very small. And hence is generally neglected. So, for condensed phase is generally H is nearly equal to you can say U if this delta PV term is very small and finally, we come to the third term in G minus TS; that is what is called as entropy.

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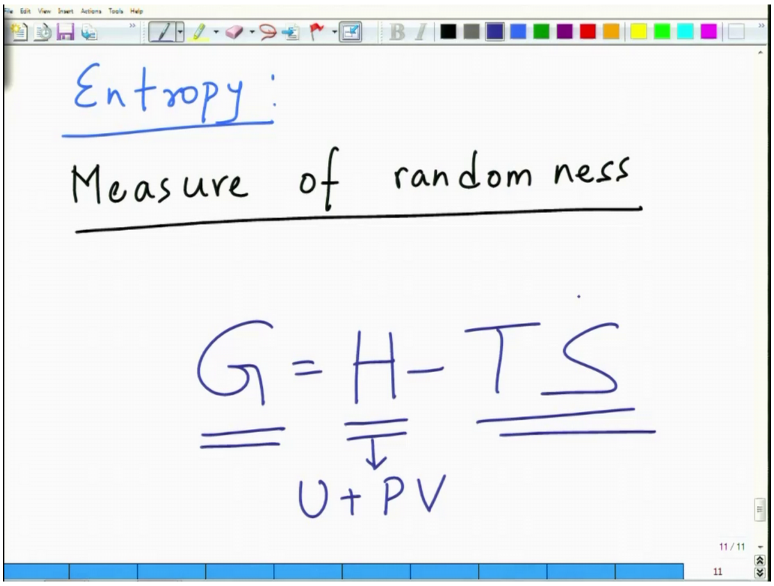

Entropy:

Measure of randomness

$$\underline{\underline{G}} = \underset{\downarrow}{\underline{\underline{H}}} - \underline{\underline{TS}}$$

$$U + PV$$

And this entropy is nothing but a measure of randomness, measure of randomness of measure of disorder of species within a given system. And this is again this again has a strong bearing on the overall stability of the system. So, as now become to the first expression again G is equal to H minus T S the free energy of a given phase is affected by the overall heat content H which is equal to U plus PV. In most cases it is equal to U for solid phases and then TS term. So, whether enthalpy increases or decreases or the entropy term increases or decreases under given set of thermodynamic conditions will determine whether G will increase or decrease as a function of temperature pressure for a given system.

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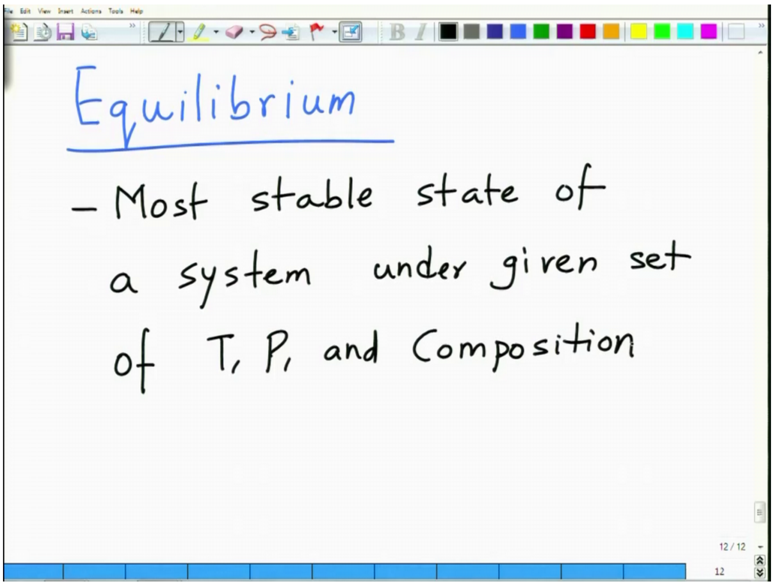

Equilibrium

- Most stable state of a system under given set of T, P, and Composition

Now, let us look at the definition of what we call as equilibrium. So, what is equilibrium? Equilibrium is defined by generally we defined as equilibrium as the in a context of materials, the most stable state that is no change happens if you leave the system on its own under given set of parameters. So, basically you can be defined equilibrium as most stable state of a system under given set of temperature, pressure and composition.

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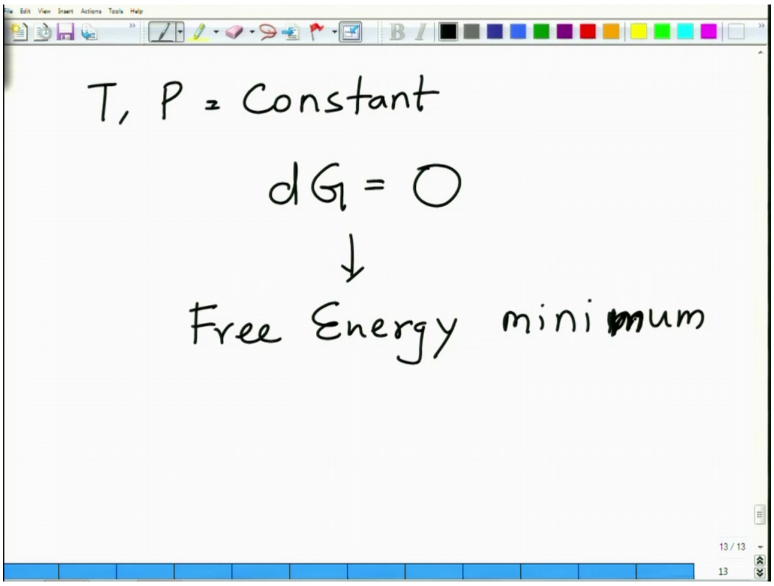

T, P = Constant

$$dG = 0$$

↓

Free Energy minimum

So, basically if T and P you can you can define these are constant, then d G is equal to 0, and what it means is that free energy has a minimum under those conditions, ok.

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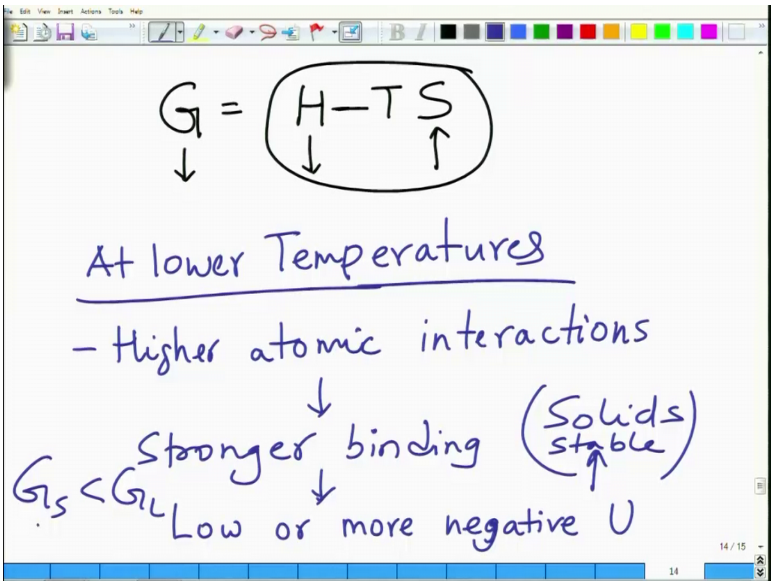

$$\underset{\downarrow}{G} = \boxed{\underset{\downarrow}{H} - T\underset{\uparrow}{S}}$$

At lower Temperatures

- Higher atomic interactions

↓

Stronger binding (Solids stable)

↓

Low or more negative U

$G_S < G_L$

So, generally if you look at again G is equal to H minus TS, ok. So, G will decrease when H is small. So, if you decrease H your G will decrease and when you increase entropy G will decrease what there is a negative term. So, generally speaking, the free energy free energy decreases when enthalpy decreases or entropy increases. Because minus TS term goes as negative and H term of course, it has to decreased for the, but overall is a combination of these 2 which will govern weather free energy will increase or decrease um for a given system and generally what we are interested in knowing what is a relative change in free energy for given phrases. So, it might happen that you have 2 phases, and as the function of temperature the free energy of both phases decreases.

But if the decrease in the free energy for one phase is happening at a higher rate as compared to the other phase, then we may come across the temperature at which the free energy of the phase for which the pre energy decrease rate was higher may lead to lower free energy as compared to the other phase. So, we will see those changes later on.

So, generally so let us say at lower temperatures generally what happens is that at lower temperatures, basically at lower temperatures you have higher atomic interactions, ok. And higher atomic interactions will lead to higher binding, stronger binding and this generally leads to low or more negative you can say internal energy. Because and that is why solids have lower internal energy or more negative internal energy as compared to the liquid. Gases have or if we compare solid liquid and gases. Solid will have the most negative internal energy whereas; liquids and gases will have higher more positive internal energy as compared to the solid.

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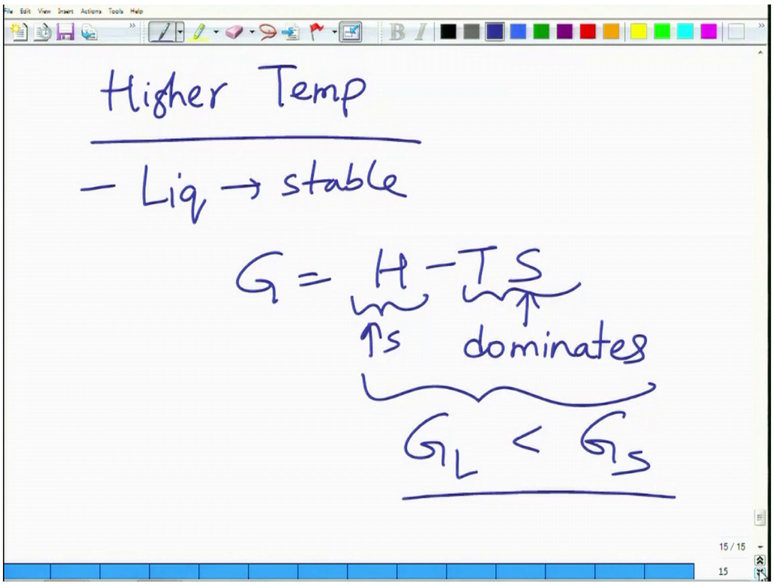

Higher Temp

- Liq → stable

$$G = \underbrace{H}_{\uparrow s} - \underbrace{TS}_{\uparrow \text{ dominates}}$$

$$G_L < G_S$$

So as result generally because of the sink decrease in the internal energy negative internal energy of the solids; solid phases are more stable at lower temperature. So, we can say if you go to (Refer Time: 21:07) this is what makes solids stable. Whereas, at higher temperature converse happens at higher temperatures your solids have your liquid and gases have although they have so if you look at higher temperatures, higher temperature we see just generally liquids are stable, right? This happen is equal to H minus TS, although there H is positive, although there is more although the H is more positive as compared to the solid the entropy is higher.

So, again this entropy term dominates, this term dominates over the H terms. So, H increases, but S also increases. So, the competition between these 2 makes lower than G S whereas features G S is lower than G L in general. So, we will look at various systems a few systems later on. So, at higher temp term dominates lower temperature the enthalpy term dominates giving rights to stability of solids and liquids at lower and higher temperatures.

Similarly, you have a pressure volume effect as well. As we said generally pressure volume effects are not generally considered, but; however, if they are present they have to be considered and hence the systems with the smaller volumes are preferred as compare to system with higher volumes because of lowering of PV terms. So, if we look at this H is U plus PV.

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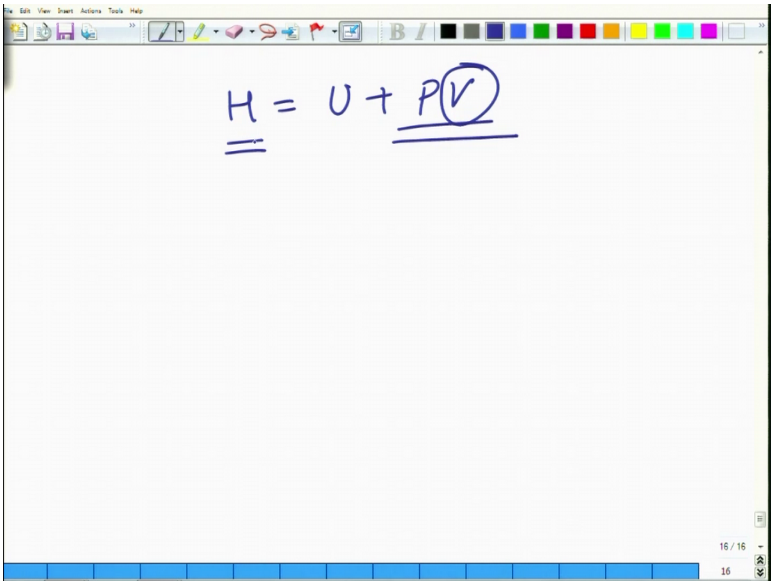

$$\underline{\underline{H}} = U + \underline{P\boxed{V}}$$

So, this volume time comes into picture at a given pressure if you have 2 phases the phase with small of volume will be preferred as compared to phase with higher volume. And this is because of changes in the corresponding changes in enthalpy. So, if your enthalpy has to at higher. So, if you have 2 phases, another one phase with lower volume that will have lower enthalpy as compared to the phase with the higher volume. So, more negative enthalpy has to be will be preferred or lower enthalpy will be preferred as compared to the as compared to the other phase.

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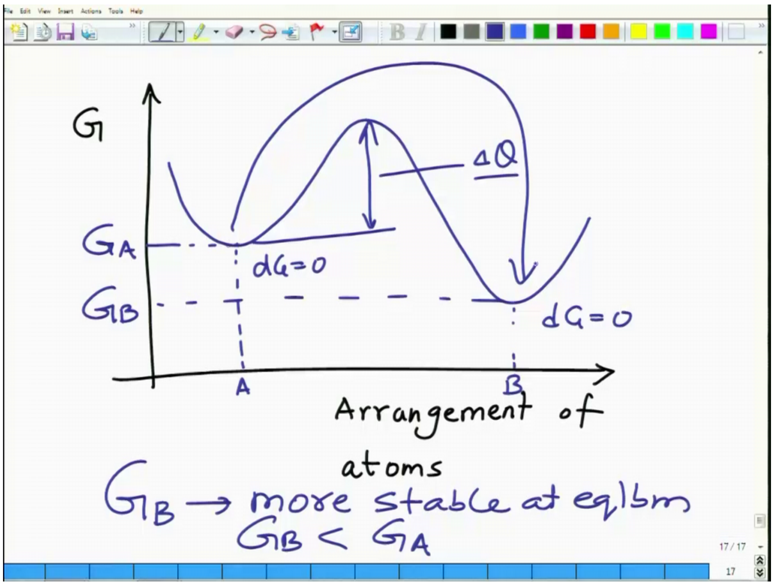

$G_B \rightarrow$ more stable at eqlbm
$G_B < G_A$

So, when we define equilibrium in totality; the equilibrium in totality is defined as, you have you plot G as a function of let us say arrangement of atoms. So, if I make a plot of this. So, this is for example, the situation, you have a state A and you have a state B. So, we can see that there are too minima here. So, d G for this is also 0, d G for this is also 0; however, in totality if you look at that free energy landscape, this B state has lower energy as compared to; so, this is let us say G B, and this is let us say G A. So, G B is more stable at equilibrium, because G B is lower than G A. So, if we leave the system for long time to achieve equilibrium system will move towards achieving G B.

However, in many system such as in glasses there are on in polymers there are meta stable states which have local minima. So, this local minima is often stable, because this is also at energy which is small at a give at this arrangement. How it to reach from here to here it has to overcome energy barrier so, this is energy barrier, ok. Delta let say Q, this energy has to be overcome for system to again achieve a lower energy state. So, as a result typically some sort of impetus has to be provided, for system to move from this state to that state. So, this happens generally in glasses in glasses there are local minima in energy and the system stays in that energy because the delta Q can be quite large for system to achieve the proper equilibrium.

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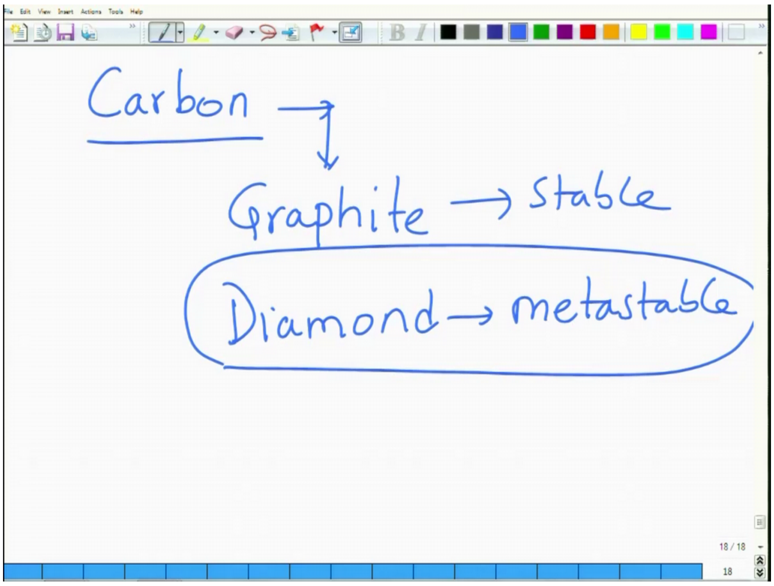

Carbon → Graphite → Stable

Diamond → metastable

However, for many crystalline systems for many solids the minimize achieved quite fast. So, minima how fast or how slow minimize achieved that is determined by the kinetics, or the time dependent rate processes within the system. But generally the tendency of a system if you leave it enough for long enough time it will achieve the equilibrium with lowest free energy state.

So, for example, if I give you a I will give the example of diamond the carbon. So, carbon if you leave it for long time, the thermodynamic state stable state of carbon is it has 2 forms one is graphite, second is diamond. Diamond is the metastable form and graphite is a stable form. But we do see diamond exists. We do see that diamond exists and, however, if you leave diamond long time for very long time diamond will eventually convert to graphite. So, if you so, but the process is so slow that for virtually for very long times, for virtually for eternity the diamond is appears as if it is stable, but within size of earth the timeline of earth is very long as a result the phase transformation that happen from diamond and graphite. They do not happen in our lifetime they take million years to for them to happen similarly glasses.

The crystalline glass is more stable as compare to a amorphous glass, but what we see in front of us is mostly amorphous first class, because the time scales at which amorphous glass is converted into crystalline glass are huge, there the way beyond our imagination. So, that is why you see these metastable states appear to us as of the other stable phases; however, since these are local minimas and free energy which you are not absolute minimum as a result they are they that is why they are called as metastable states, which do exist for long times in front of us.

So, we will stop here today. What we have learnt is basically in this lecture. If you go from the beginning we learnt the concept of free energy, what free energy is, what are the terms, which are included in free energy. So, free energy is required to understand the phase stability. And free energy consists of 3 terms and enthalpy temperature and entropy. Enthalpy is basically the heat content of the system. So, heat content depends upon the internal energy in the PV term, buy and large it is governed by internal energy itself. So, internal energy is sum of potential energy and kinetic energy. And these are kinetic energy comes from atomic vibrations and translation rotational energy of atoms molecules; whereas, potential energy is primarily because of binding or bonding between the molecules.

So, it is a competition between enthalpy and entropy which gives rights to eventual loading free energy in the system, determining the final phase stability entropy. As I said is the measure of randomness of a given system. So, in the next few lectures we will again expand on these and establish a basis of phase equilibrium.

Thank you.