Solid State Chemistry
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Lecture – 02
Solid State Thermodynamics

Now, I will go to lecture 2, of week 1 of this course. So, in the first lecture of week 1, we learnt about the solid state of matter and we looked at different solid state materials. We looked at some elementary properties and some bonding some characteristics of bonding in solids. In this lecture that is the second lecture, I am going to talk about the thermodynamics of solids. So, this is week 1, lecture 2, we are going to discuss Solid State Thermodynamics.

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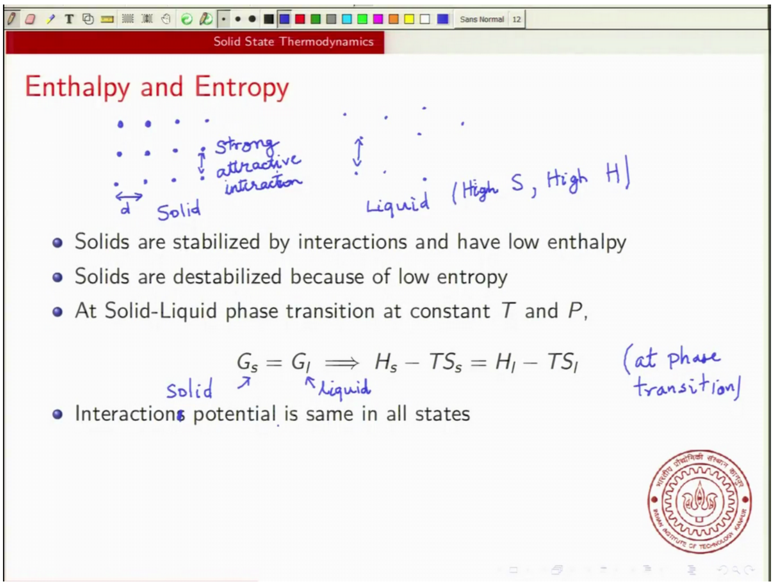

Solid State Thermodynamics

Enthalpy and Entropy

- Solids are stabilized by interactions and have low enthalpy
- Solids are destabilized because of low entropy
- At Solid-Liquid phase transition at constant T and P,

$$\underset{\text{Solid}}{G_s} = \underset{\text{Liquid}}{G_l} \implies H_s - TS_s = H_l - TS_l \quad \text{(at phase transition)}$$

- Interactions potential is same in all states

So, some very basic thermodynamics of solids can be understood by looking at enthalpy and entropy we mentioned that solids are characterized by or stabilized by interactions and have low enthalpy, ok. On the other hand, they are destabilized because of low entropy. So, what do we mean by this? So, if you take any solid material, then the constituent particles; let us say if there are atoms, then these atoms would be arranged in a regular order and the distance between the atoms would be very small compared to in a liquid.

So, if you look at typical solid you have various particles and they are arranged in some order. I am just I am just taking hypothetical example of a of a solid where everything is arranged like this and this distance is very small, so this distance in solid is much smaller than in a liquid, ok. So, compared to a liquid ok, liquid you will have particles that are quite far apart typically and they would not be arranged. They would not be ordered in any fashion, they would just exist far away from each other.

So, now, what happens is that since the particles are very close to each other there is an interaction between these between these particles, ok. So, there is a strong attractive interaction, ok. So, there is a strong attractive interaction between the particles I am emphasizing the attractive part because of this attractions the enthalpy, the energy of the solid is lower, ok. So, the enthalpy of the solid is lower and this is what I mean by solids are stabilized and have low enthalpy. However, because the particles are very close to each other they do not have so much freedom to move around and therefore, they have low entropy ok.

So, a low entropy state is actually less stable. So, the solid is stabilized by enthalpy, but destabilized by entropy whereas, a liquid has lower entropy or higher entropy High S and it also has High H enthalpy. So, the enthalpy is higher, so, it is less stable, but the entropy is higher so that so entropically the liquid is more stable. So, now, what happens at the solid liquid phase transition at some temperature and pressure what happens is that the free energy of the solid and the liquid are identical at the phase transition. So, at the phase transition that would be the melting point of the solid ok.

So, what happens is that the free energy is a combination of enthalpy and entropy and there is a factor of temperature that appears. So, the enthalpy minus T times entropy of the solid, ok. So, this is this refers s refers to the solid and l refers to the liquid. So, the enthalpy of the solid minus T times entropy of the of the solid of the solid should be equal to the enthalpy of the liquid minus T times enthalpy of the liquid this is at the phase transition at phase transition and I emphasize this part that this is only true at the phase transition, ok.

If you go below the phase transition then the free energy of the solid becomes lower, ok. So, the solid becomes more stable. If you go above the melting temperature above the phase transition then the liquid has a lower free energy ok, but at the phase transition the solid and liquid have the same free energy, and what we said is that the solid has a lower enthalpy, but it also has a lower entropy, ok. So, the factor that you subtract from the enthalpy is also lower whereas, a liquid has a higher enthalpy, but it also has a higher entropy. So, the factor that you subtract the entropy is actually higher. So, that is why at higher temperatures the entropy term becomes more important and the liquid becomes more stable at higher temperature.

A point to make is that the interaction potential in solids and in liquids is the same. So, what you mean is that even in a liquid the particles are interacting with each other, and if you get two liquid particles very close to each other let us say you get them a distance D apart the interaction energy will still be the same. The interaction is the same whether you have solids liquids or gases, ok. It is only that since the particles are far away, ok. The interaction is weaker, ok. So, there, but the potential of interaction is the same in all the states.

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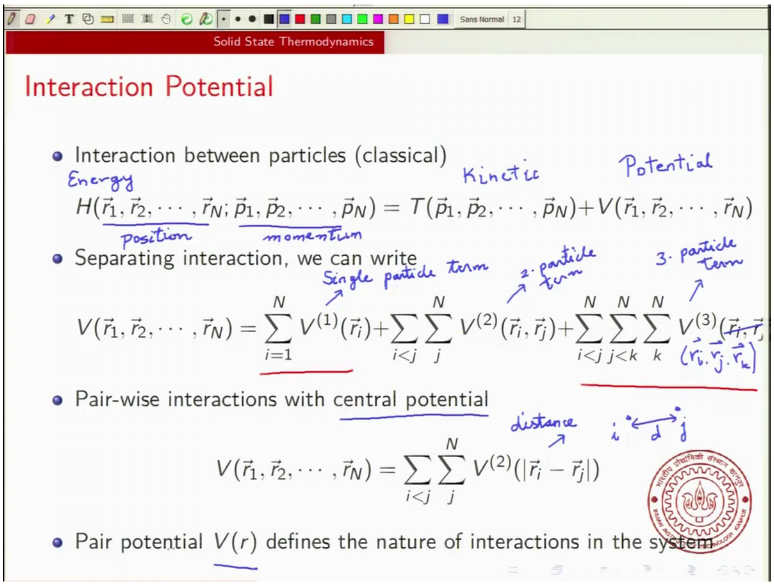

Solid State Thermodynamics

Interaction Potential

- Interaction between particles (classical)

$$\overset{\text{Energy}}{H}(\underbrace{\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N}_{\text{position}}; \underbrace{\vec{p}_1, \vec{p}_2, \cdots, \vec{p}_N}_{\text{momentum}}) = \overset{\text{Kinetic}}{T}(\vec{p}_1, \vec{p}_2, \cdots, \vec{p}_N) + \overset{\text{Potential}}{V}(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N)$$

- Separating interaction, we can write

$$V(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = \underline{\sum_{i=1}^{N} \overset{\nearrow\ \text{Single particle term}}{V^{(1)}}(\vec{r}_i)} + \sum_{i<j} \sum_{j}^{N} \overset{\nearrow\ \text{2-particle term}}{V^{(2)}}(\vec{r}_i, \vec{r}_j) + \underline{\sum_{i<j}^{N} \sum_{j<k}^{N} \sum_{k}^{N} \overset{\nearrow\ \text{3-particle term}}{V^{(3)}} \cancel{(\vec{r}_i, \vec{r}_j} \, (\vec{r}_i . \vec{r}_j . \vec{r}_k)}$$

- Pair-wise interactions with central potential

$$V(\vec{r}_1, \vec{r}_2, \cdots, \vec{r}_N) = \sum_{i<j} \sum_{j}^{N} V^{(2)}(\overset{\nearrow\ \text{distance}}{|\vec{r}_i - \vec{r}_j|}) \qquad i \overset{d}{\longleftrightarrow} j$$

- Pair potential $\underline{V(r)}$ defines the nature of interactions in the system

Just to clarify that, ok, we will discuss a little bit more in detail about the interaction potential ok. So, here let us look at we are trying to see what is the interaction between particles and let us take a very classical picture where the particles are just particles that obey laws of classical mechanics. The total energy is this is the total energy, and can be written I will just I will come to details of this can be written as a sum of a kinetic energy and a potential energy.

So, the total energy can be written as a sum of a kinetic energy and a potential energy and now what I am showing here is that in classical mechanics the energy is a function of the positions. So, r 1, r 2 up to r n represents the positions of all the particles and p 1, p 2 represents the momentum; so, momentum or if you can think of it as a velocity of the particles, ok.

So, each particle so, if there are n particles in the system, then the total energy is a function of all the coordinates all the positions of all the particles and all the momenta of all the particles and when you separate the total energy into a kinetic part and a potential part the kinetic energy function that is T that depends only on the momenta of the particles it depends only on the momenta. So, the kinetic energy is half mv square. So, V or you can write this as p square by 2 m for each particle.

So, the total kinetic energy of the of the entire system of particles, entire collection of n particles the total kinetic energy is just sum of individual kinetic energies of each of the particle. However, the total potential energy that depends on the coordinates of each of the particles and this potential energy typically comes because the particles interact with each other, or there might be an external field, ok.

So, now let us look at this potential energy in a little bit more detail. So, is what we will write is that this total potential energy that is the energy due to the due to the positions of the particles can be written as a sum of different terms. The first term has this is called a single particle potential, and this is just a one particle potential and what it means is that this term, this is a single particle potential, ok. So, this is a single particle term what it means is that this is a term in the potential energy that depends only on the coordinates of one particle, ok. So, i goes from 1 to n. So, this will have this is a sum from i going from 1 to n. So, it will have a term that looks like potential energy of the first particle plus potential energy of the second particle and so on.

Now, such a term only comes into play when you have the system in an external field. So, if there is an external magnetic field or any or an electric field that effects each particle individually then you would have this kind of term. The second term k is V 2 that depends on coordinates of two particles i and j, and i should not be equal to j, and this is called a pair potential, ok. So, this is called a two particle or a two particle term, and this comes because two particles a pair of particles interact with each other.

So, particle i and j they are interacting with each other and what is the energy due to their interaction is what is governed by this pair potential. You could also have higher particle terms this got erased a little. So, this should be V of V of r I, r j, r k. So, it should be a it should depend on these three coordinates ok. Now, this is a three particle term, and what it means is that is that if you it depends on it is a term in the potential energy that depends on coordinates of all that of three particles three particles at a time and you have to take all sets of three particle groups,. Now, usually we are interested in cases where there is no external field.

So, this term goes to 0, then we ignore the higher order interaction. So, we say that the particles interact only through pairs and if you make that assumption then the total potential energy, is written as just the sum of the pair particle terms only of V 2 and further if you assume that it that all the particles interact with a central potential, ok; that means, that the potential energy due to interactions of particles at i and j just depends on the absolute value of the distance. So, this is the distance between particles.

So, therefore, way it is like saying that if you have this is the distance. So, it is like saying that if you have if you have one particle at i and you have other particle at j then the interaction the potential energy due to interaction between these two just depends on this distance between the two particles. And you can so, this V 2, becomes a function of just one scalar distance and typically you call this the pair potential V of r, that that tells you what is the nature of interactions in the system, that tells you like how this interaction will change as you change the distance between the particles ok. So, the pair potential is what tells you what is the interaction between the particles are, ok.

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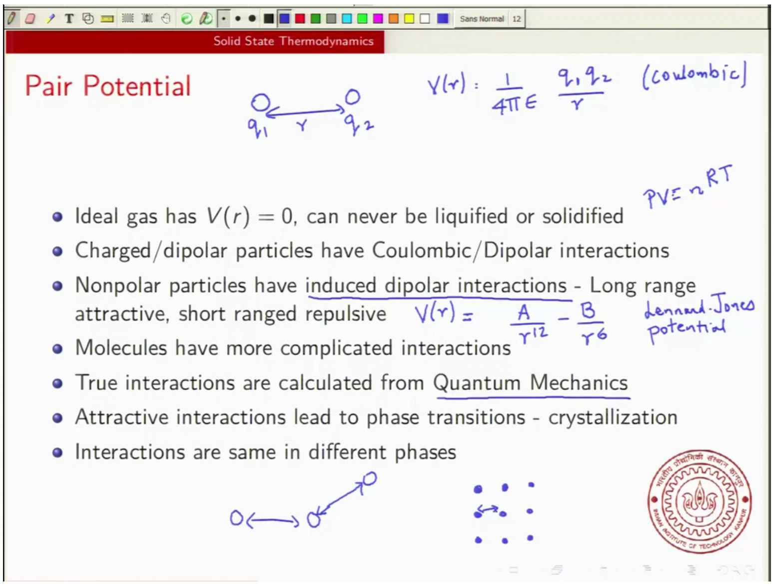

Pair Potential

$q_1 \xleftrightarrow{r} q_2$

$V(r) : \frac{1}{4\pi\epsilon} \frac{q_1 q_2}{r}$ (coulombic)

$PV = nRT$

- Ideal gas has $V(r) = 0$, can never be liquified or solidified
- Charged/dipolar particles have Coulombic/Dipolar interactions
- Nonpolar particles have induced dipolar interactions - Long range attractive, short ranged repulsive $V(r) = \frac{A}{r^{12}} - \frac{B}{r^6}$ Lennard-Jones potential
- Molecules have more complicated interactions
- True interactions are calculated from Quantum Mechanics
- Attractive interactions lead to phase transitions - crystallization
- Interactions are same in different phases

And, what I want to Emphasize is that this pair potential is what describes various system. So, suppose you have an ideal gas then the pair potential is 0; that means, you take two particles, and you keep separating them and you know you get them closer and closer to each other and they will never interact and the potential energy will never increase, ok. So, ideal gas has V of r equal to 0, and as a consequence it can never be liquefied or solidified. It is always a gas, ok. You always have PV equal to nRT and that never changes.

So, so PV equal to nRT is always valid at whatever temperature you go, ok. So, for an ideal gas if you just look at the form of the ideal gas, it just says PV equal to nRT independent of temperature there is no nothing that causes of phase transition from gas to liquid or solid, and this can be understood as a consequence of the fact that the particles in an ideal gas do not interact with each other at all,.

Now, suppose you had charged or dipolar particles, they would have Coulombic or dipolar interaction. So, if you had if you had particles in your in your system having, let us say let us say some particle has charge q 1, other another particle has charge q 2, then the and if they are separated by a distance r, then the potential energy due to this interaction looks like 1 over 4 pi epsilon q 1 q 2 by r.

So, so, the potential so, the pair potential, this is a Coulombic pair potential, this is Coulombic. So, so what you have to do if you go back to the pair potential if you go back to the description you have to sum over all pairs of particles, ok. So, so there is a sum over all pairs ok; it is written as i less than j just to make sure that you do not over count the pairs, ok. So, V between 1 and 2 is same as interaction between 2 and 1. So, it should not be over counted. So, we put a condition that i should be less than j in the second sum the j goes over all the particles,.

So, now, what is so, if V of r has this form ok, then you can write the pair potential. You can write the total interaction as sum of all these pairs. You could have other cases where you do not have charged particles because that are dipolar you could have particles that are that have both charges and dipoles, ok. So, you could have you could have many different interactions, ok.

If you have completely non-polar neutral, particles then you can also have what are known as induced dipolar interactions and I want to emphasize this induced dipolar interactions, ok. So, suppose you have something like argon gas and inert gas, ok. So, inert gas if there is not really much polarization that happens and you still have interaction you can still liquefy all these inert gases, and this let me write it right here.

So, if you take I will just write it here. So, the V of r in this case the if you have neutral non-polar particles, and then what would happen is that there would be an attractive interaction that goes like I will just say 1 over r to the sixth ok. So, the way the attractive interaction goes as 1 over r to the 6. So, it is. So, this is and then and then you have repulse typically you will have some short range repulsion, ok. So, this is the, this 1 over r to the 6 ok, so this represents the attraction due to the induced dipolar interactions.

Now, if you get the particles very close there will be some repulsion, and a very common form of this repulsion, ok. This is not the only form by any means ok. So, this is referred to as Lennard Jones potential ok. So, this is what happens when you have neutral particles and you have induced dipolar interactions and this is typically what happens in inert gases ok.

Now, of course, you know real if you take if you take atoms of metal then the interactions are much more complicated. If you take molecules you will get even more complicated interactions and typically these interactions if they form a bond, then you will have a interaction due to the bonding which will be either a Morse potential or a harmonic oscillator potential. But, in any case the point is that if you take particles in any solid, then they can have very complicated interactions.

And, if you actually want to go ahead and take any two particles and calculate the interaction between them then you have to do you if you want to do it correctly you have to do a quantum mechanical calculation,, but nevertheless we say that at the end of this calculation you get some pair potential of interaction.

Now, what is important is that if you just had particles, if your system just had particles; let us take a gas, and let us take a gas that is not ideal ok. Now, if since the gas is not ideal then we say that the gas particles interact with each other and if they interact with each other now if there is some attractive interaction, then that could lead to phase transition; that means, if there is some attractive interaction then by cooling down the gas you could get into a liquid state. If there was no interaction you could never liquefy or solidify it that is what we said. For an ideal gas there is no interaction.

So, you can never liquefy or solidify it, but if there is some attractive interaction then you can actually cool the gas and at some point the particles will try to come close to each other. Now, what should be kept in mind is that the interactions are same in all the phases. So, whether you have a solid, liquid or the gas the interaction potential V of r will be the same ok, it just depends on what the constituents are what atoms or molecules are there in this in that system, ok. And, therefore, when we say that a solid, as a solid has low enthalpy, what we mean is that is that these particles are at such a distance from each other that there is a strong attractive interaction ok.

So, the distance between these particles are such that there is a strong attractive interaction in a solid, ok. When you heat it then the entropy term, it becomes more important and therefore, the even though this there is a tendency to be close to each other, because at high temperatures the entropy term becomes important and so and so the liquid state becomes more stable, alright.

So, what I want to emphasize through this discussion is that solid, liquid and gas have the same pair potential. If you take for example, iron and you heat it and heat it, the interaction the pair potential between any two atoms in iron will be the same. You heat it above the melting temperature it will become a liquid, even liquid iron will have the same pair potential. But, because the temperature is so high entropic effects become more important.

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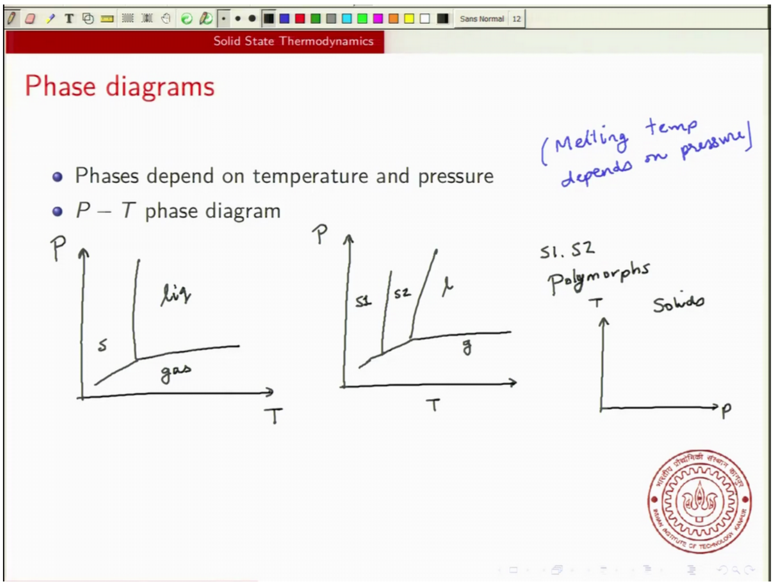
Solid State Thermodynamics

Phase diagrams

(Melting temp depends on pressure)

- Phases depend on temperature and pressure
- $P - T$ phase diagram

S1, S2 Polymorphs

Next, I will talk briefly about the phase diagrams, ok. What should be kept in mind is that your melting temperature depends on the pressure, ok. So, your melting temperature depends on pressure, ok; that means, if you take ice and at normal atmospheric pressure ice melts at 0 degree centigrade ok, but if you increase the pressure then ice will melt at much higher temperatures.

So, now this dependence of this behavior of the system on pressure and temperature is encapsulated the pressure-temperature phase diagram and you have all seen this in your thermodynamics course. So, I will just briefly mention some key characteristics. So, if you look at a typical phase diagram of any simple material, and I will show you the P-T phase diagram, ok. So, let me show the pressure on this axis and the temperature on this axis,.

Now, as you increase the pressure ok, then the phase that will that you will get is the solid phase, and at as you as you increase the temperature you will get the gas phase, ok. So, the typical phase diagram will look something like this where you have a gas phase here, we have a solid phase here and in between you have the liquid phase, ok. So, this is what the pressure versus temperature phase diagram will look like for a typical material that has only three phases a solid, a liquid or a gas.

Now, if your solid is a crystalline solid, then you could have multiple phases on the solid. So, the solid itself could have many different phases. So, so in these different phases are typically referred to as polymorphs. So, in this case you have a solid, you have a gas, sorry this is your gas you have your now what you have is you have your liquid here, and your solid you can have different phases of the solid.

So, you could have you could have solid in the first phase. Solid in the second phase and these are called polymorphs. So, S 1, S 2 are referred to as polymorphs of the solid ok. So, you could have different polymorphs in the solid and these would corresponds to different phases of the solid, ok. So, your phase diagram could get much more complicated, and this is quite common in lot of materials typically these polymers they are seen at very high pressures ok.

And, often the phase diagram is actually shown the other way it is shown as a it is shown in terms of temperature and pressure, ok. So, for solids usually when you go to very high pressures, then you will see you will see lot of these polymorphs, ok. So, often this phase diagram for solid temperature and pressure, and typically you need to go to very high pressure to see different phases in solids, ok.

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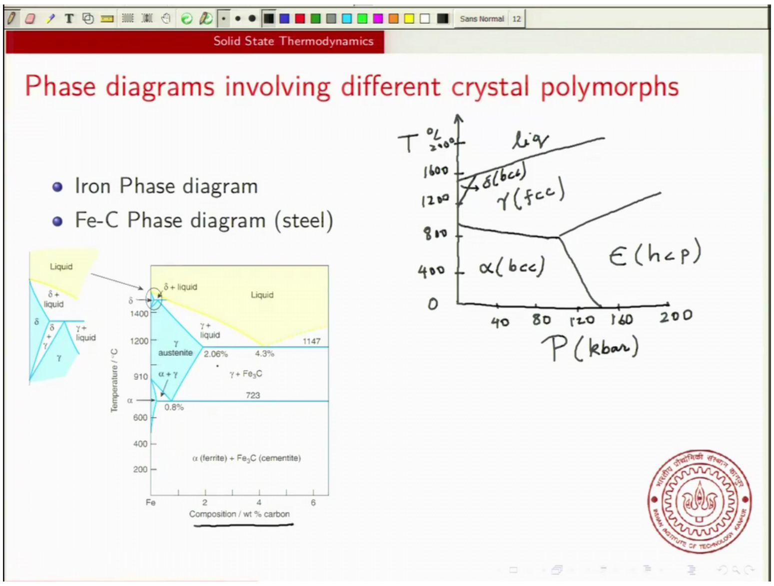
Solid State Thermodynamics

Phase diagrams involving different crystal polymorphs

- Iron Phase diagram
- Fe-C Phase diagram (steel)

And, now if you go to let us take an example of first we will go to the iron phase diagram. So, the pure iron if you just look at pure iron, then the phase diagram I will just sketch it schema I will just sketch it, ok. So, this is approximately there is an approximate sketch. So, if you this is 40, so, this is a pressure in units of kilo bar, ok. So, 1 bar remember 1 bar atmospheric pressure is about 1 bar. So, this is in many kilo bars, ok. So, it is really thousands of bars. So, it is very high pressure.

So, if you go to very high pressures, and let us say you look at temperature, in degree centigrade and let me take a gradation where I have 400, 800. So, I go from 0 to about ok. So, so, obviously, if you go to much this is 0 degree centigrade. So, if you go to lower temperatures then you will just have the same solid phase. Similarly, if you go to lower pressures ok, if you go to you know very low pressures, then you will just have the usual solid phases.

But, if you take iron and you look at the various phases as a function of pressure, when you increase the pressure to very high values ok, then you will see some interesting behavior, ok. So, I will just show it schematically it is approximately drawn, ok. So, you will see things like this. This is the usual phase of iron that is a bcc phase it is called the alpha phase ok. But, if you go to very high temperatures; so, if you go beyond about 900 degree centigrade then you get what is called a gamma phase of iron which is an fcc phase, ok. So, it is the same iron solid all these are phases of solid iron, ok.

So, this is a phase diagram of this is also solid gamma fcc is also solid if you go beyond about 1500 degree centigrade, then iron will melt and you will get liquid phase, and if you go to very very high pressures very high pressures greater than 100 kilo bar you will get an epsilon phase which is actually hcp iron, hexagonal close pass flat iron, this is a body centered cubic, this is face centered cubic and hexagonal close pack ok.

So, you can see that just this part of the; if you go back to our phase diagram you just had a solid, liquid, gas, ok. So, we are just looking at this solid and liquid region and we see that there are we are just looking at this solid liquid behavior at very high pressures and we see already we see a lot more complications, ok. Now, if you see this phase diagram, you there is one other one other phase that has been observed experimentally that is right around here there is this delta phase which is another bcc phase of iron ok, high temperature bcc phase of iron.

So, so you can see we are just taking pure iron metal and we are getting all these faces, just most of this is s only in the solid region. Now, what happens if we take iron-carbon phase diagram, for this is typically very important for steel ok. So, , here if you take if there is more than 1 atom and iron and carbon if this is a phase diagram of iron and carbon and now what happens is in addition to pressure and temperature ok, you also have the percentage of carbon.

So, let us say so, you have you have an additional variable which is a composition or the weight percent of carbon. So, in this case what happens is that the as you change the composition of carbon and you change the temperature you get several different phases, ok. So, at low temperature you have this ferrite a mixture of alpha ferrite and cementite,. As you as you go to higher temperatures, then you get alpha phase and alpha plus gamma, austenite steel and so on.

And, melting is again much higher. Melting is only at this very high temperature as you increase the percentage of carbon the melting temperature decreases, ok. You can see already that there is the phase diagram becomes very complicated when you have different crystal polymorphs ok. So, so, I will stop this I will conclude this lecture here, and then and this will be the end of lecture 2 of this course.

Thank you.