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Lecture - 02 Define Phase, Equilibrium

So, in this lecture we are going to take recap. Many things probably you have learned, but to buildup the course we need to relook some of these aspects. Otherwise you have to refer every time to book. Then the phase transformation materials has 3 important words. First one is obviously materials which I assume you know because world is full of materials, they are classified into 3 parts mostly 3 parts, but they can be made in 5. So, metal ceramics and polymers, polymers can have 2 things 2 parts one is elastomer other one is plastics.

Similarly, you can also have composites or hybrids, but we are going to concentrate mostly on metals and ceramics not on polymers. Second important thing is phase and third is transformation. Transformation will be our main point of interest, but what is this phase there is lot of misnomer about phase in the literature. Some people say phase is nothing but a solid state of matter. Yes, if you consider very simplest way it is nothing but another term for solid liquid or gas.

Like if I take a ice in water, ice is solid H2O water is liquid H2O. Similarly, vapor is gas H2O. Obviously, there is a distinct difference between gas and vapor. I am not going to clarify it now, but on the root on a crude manner we can always consider these 3 things are presence when you have a ice on a water in a confined environment. So, therefore, these 3 things are in thermodynamically stable condition if you know the pressure temperature. Similarly, if I have soap bubbles; this is nothing but air inside the bubble. Then what is a bubble it is a liquid film. So, therefore, gas and liquid are in coexisting situation in a soap bubble correct.

But suppose, if I have oil in water both are liquid. So, if I consider oil and water both as a state of a matter in liquid, then it should be a single phase because they are liquid. Unlike in the first case of the last case, but that is not the true whenever we have 2 liquids not mixable each other we call them separate phase. This is very important thing you must remember. Whenever we have 2 liquids not mixable atomically we call them separate

phases, but what about that is about the solid liquid gas does not distinguish whether it is one gas or multiple gas it is single phase whereas, air is consisting of so many different entities like oxygen, nitrogen, carbon dioxide, carbon monoxide many moisture organ.

But they are considered as one gas mixture consists one gas. So, one phase we never distinguish between different components of the gas as separate phases. For the liquid we distinguish liquids are different phase when they are not mixable to give you. Simple example if I take milk, add coffee into it or tea into it, the mixture is a single phase because add coffee and milk will mix atomically. Similarly, if you mix tea with milk it will mixed completely.

Therefore, we call them not. So, separate phases, but a single phase, but if I had 2 oils, 1 oil in water then they are not mixable. They never will mix that you can do the same simple experiments or you have done it in a school days. So, we call them separate phases. So, that is for the liquid, but what about the solid is a most complex stuff. Let us see.

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Let us consider a first a case of a metal. That is what we always keep pure iron and is a god's gift pure iron is a solid and it is consisting only iron, but if you look at from room temperature to melting temperature iron melts at 50 139 degree Celsius temperature. It exists in 3 different crystal structures specifically that exist in 2 different crystal structures, but we always consider the existing 3 different crystal structure what are they

a room temperature to 900 and 10 degree Celsius temperature, that is what is shown here. That is what is shown here I am sorry it is in bodies in the cubic structure BCC. And once it goes to above 910 degree Celsius temperature, it transform to FCC. That is what we call gamma iron alpha becomes gamma and this gamma iron remains stable till 19 1300 94 degree Celsius temperature above 1394 degree Celsius temperature again it transform to a BCC iron known as delta correct.

So, you can see clearly a single solid different phases exists in different crystal structure. So, the connecting phase in solid is the crystal structure, if I change the crystal structure I change the phase whether it is a pure or it is an alloy. So, that is what you must understand the moment you change the crystal structure, you have making a new phase in solid the crystal structure dictates the phase, but what happens in this of alloy. So, that is pure iron is still understandable remember beta iron is nothing but high pressure phase which is not shown in the one atmospheric pressure system, that is a normal stp we never show beta iron, but it is sometime people call beta sometime people call epsilon iron, but this is a high pressure phase that is why beta is omitted here now what about alloy.

If you consider simple example a steel because iron is related to steal a steal is nothing but iron carbon alloy you add a little amount of iron little amount sorry carbon into iron to produce steel, but if you do that you create a complex so called complex microstructure which looks like a lamella consist from many lamellas. And one if one does careful understanding of these is well known to everybody. Now that this is what is known as pearlite it looks like a parallel. Let us why it is called pearlite it consisting of 2 phases one is alpha iron solid solution, it is almost pure alpha iron carbon concentration is very low other one is a compound Fe 3 C.

Similarly, you can see I can create a different chemical entity if I have an alloy by adding carbon into it. So, Fe 3 C whether it has a different structure or not, because it is the different compositions, it must be a separate phase, but here it like it very clear the Fe 3 C has the atomic structure it does not match with alpha beta gamma iron.

So, by anyway it is also a different phase, but it need not be if it is a different chemical compositions, but even if it is a similar crystal structure, it will be a separate phase because it contains a carbon lot of carbon as compared to alpha iron. So, that might it must be a separate phase that is what you see in the different phase diagrams like if you

consider copper and silver both are FCC structure, but the moment you formed mix them they form eutectic copper and silver both are solid solutions both are FCC, but they have different chemistries both contains copper and silver, but they have different chemistries.

Therefore, crystal structure is one factor, other factor is the chemical composition that is makes different phases. So, it you will clearly see that is why the students always do mistake when they try to figure out whether it is a phase or not a phase. So, these are the point you might understand. So, again I want to point it out to you because these are the very basic concepts, you should know for a gas it does not matter how many components are present in the gas mixture, it is always a single phase air is a single phase. Or if you consider mixer between a different gases of which used in cooking gas methane or some other things, that is also a single phase liquid if 2 liquids are mixable we call as a single phase, if they are immixable. We call as a separate phase solid 2 important factors which remark it a phase one is crystal structure, second one is a composition.

So, the pure metal there is no compositional change. Therefore, crystal structure what dictates you to phase and am I clear. So, that is what you must take away from these lectures. Now to give an examples I always teach, this in the class if I have sand and salt are they separate phases. Yes, because sand and salt will never mix each other milk.

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And coffee single phase, if I mixed milk in coffee they will mix atomically that is what (Refer Time: 09:33) to the test coffee and sugar mixed completely, if add sugar into

coffee stir it will mixed. Therefore, it is a single phase liquid, but if coffee beans are used solid coffee and if I adding sugar into it they will now mix each other. Therefore, they are 2 separate phases salt and water no question is to be asked, because this is in simple mixture we will call it brine and it is a single phase. So, you must able to ask this question yourself when answer this questions because phase is very important in the phase transformation or phase diagrams.

Let us move on to the next thing, that is what I told you in this lecture again retitling, first solve it first solve.

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It chemically and structurally distinct things are called phases for liquid miscibility dictates the phases gas is always a single phase. So, phase is always a chemically homogeneous physically distinct mechanically separable portions of it is of it is system or a material is called a phase chemically homogeneous, why because? It should have a same chemical composition. That is why chemical homogeneous physically distinct looks different.

You can see under microscope or you can see by naked eye, it will look distinctly different from the other things. That is why in pearlite one phase is in white, contrast other phase is black contrast they look different. And mechanically separate we can separate them like ice, and water I can simply separate them, but I cannot separate salt and water mixer salt and water cannot be separated mechanically. They are mixed atomically that is why they cannot be separated atomically.

So, this is this definition is you know many times is not understood properly that is why you have to provide examples to make you clear; more discussion in my course, now transformations. The second the third important word; first of all, why phases will transform; that means, they are not stable that is why under certain condition, that is why they transform why ice transform to water because we know ice will melt above 0 degree Celsius temperature and normal atmospheric pressure. So, the moment you keep it in temperature condition more than 0 degree Celsius water dissipation it will melt down, but if you keep it at less than 0 degree Celsius temperature it will not. So, there is something which makes them unstable not unstable. Not stable actually unstable is the very difficult word they are not stable under certain experimental conditions that is why they do get transformed.

So, that to understand that what under what condition they will be stable or meta stable or unstable we must have an idea about equilibrium, because equilibrium is something which allows you to differentiate between these 3 important aspects. That is why I say concept of equilibrium is of fundamental importance.

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But you know nothing is at equilibrium in this world. Everything is away from equilibrium, but still from a theoretical perspective we must know or must have an idea

if equilibrium. Thermodynamic equilibrium is very important concepts. Thermodynamic equilibrium has 3 important aspects because we are going to deal with thermodynamics.

One is a mechanical equilibrium what is mechanical equilibrium we will discuss in the next slide. Second one is the thermal equilibrium. Thermal equilibrium means is a conditions arising from absence of any temperature gradient. See if I have a piece of metal or else piece of steel or piece of ceramic, there must not be existing any thermal gradients in anywhere in the sample; that means, temperature has to be uniform, but making temperature uniform means that gradients to be 0. That is why you always define thermal equilibrium in terms of absence of temperature gradient in the material.

Third important aspect for a thermal equilibrium is the chemical equilibrium. Chemical equilibrium is obtained when no further reaction occurs between the reacting substance; that means, forward and backward reactions rates are equal. Remember you cannot stop reactions, but visibly speaking you cannot say reaction is over or not. Unless and until you know the reaction rates are the forward reactions or the backward reactions are same it very simple if I consider A plus B going to C.

So, this is the forward reaction backward reaction is C going to A plus B. What it says is that the reaction rate of A plus B going to C must be same as C going to A plus B. The A plus B going to C is forward reaction C going to A plus B is a backward reaction. So, when the rates are same you will not see in any change is happening in the system. And that is what you say chemical equilibrium.

So, this is under stable thermal means there will be a no temperature gradient, chemical means there will be no resultant waxing rates. Reaction rates they forward or backward reactions will be same. What about chemical equilibrium, sorry mechanical equilibrium it is very easy to understand if I consider match box.

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Mechanical means energy means kinetic plus potential energy. We know that in any material will be atoms will be having both potential and the and the kinetic energies. So, when the energies of these system is at the minimum both the energies together, that we call as mechanical equilibrium.

If you considered a match box match box has 6 phases. There are 2 broad faces and 4 short faces. If I keep the match box in one of the 2 broad faces on a plane on a suppose table like this table then it is becomes or it better to show you this this is exactly same as a match box. This is a duster has 2 flat faces, one this other one is this see. If I keep it like this, then on this table or if I keep it like this then we will call it at equilibrium. Why? Because if you see that is on the broad face nothing will happen even if I do something some force applied energy is at minimum potential plus kinetic energy, but I can also keep it on one of the short faces like this or you can keep it like this, when you know see it stands, but this is not at equilibrium, global equilibrium. Why? Because if I apply a little force it will fall back it is gone inside does not matter it will fall back that is what is happen?

That is see basically the problem with all these all these structures. Now if I keep it like one of the edges and leave it will immediately fall, so that is called unstable situation you can see it is on the edge it will not be standing, even it will fall you can do all these experiments yourself, but if I keep it on this it can still sit on it I do not whether it will sit, but it should be able to sit, but because height is longer so; obviously, potential energy is higher kinetic energy may be same, but potential energy is higher with respect to these plates, then this configuration. Therefore, this configuration is called equilibrium. This configuration is called meta stable equilibrium and this configuration is called unstable equilibrium. These are 3 equilibrium mechanical equilibrium concepts.

So, in thermodynamic equilibrium, system has to be mechanical equilibrium under mechanical equilibrium under thermal equilibrium under chemical equilibrium. When all the 3 things are satisfied we call the system is at equilibrium. So, in phase transformation you are taking out the system from the equilibrium that is why it is transforming to something else. That is why equilibrium is the central point of discussion in the all these things. Once you know very clearly that my system is at equilibrium under certain experimental condition, and then you can be sure there will be no other phase transformations, but this equilibrium can be meta stable or stable that we will look into it much later because this is a very beginning of the lecture.

Now, there is another important aspect, I must tell you equilibrium can also be define in terms of the energy landscape. Energy landscape means energy in those systems in terms of space.



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If I plot energy of the system like air in terms of the space variable space is xyz, you can consider one of these also it is. And suppose I have a well like this kind of well in a energy consists coordinates or the or the distance diagram. So, if I keep a ball here and drop it will simply fall and settle there. And it will not come out because this is a well it is a very deep well energy well and it is gone there. Similarly, if I keep a ball and set it will fall back on the same positions. Whatever I do even if I take this ball from this position and put it here it will again fall back. So; that means, system is at this position system is at the global equilibrium; that means, system is having lowest or minimum energy. Am I clear?

Now we can also have such a kind of local minima such a kind of things possible. So, if I drop a ball here, it should have fallen back here, but it is not it is going and settling here. Because there is a locally hump or locally some space to occupy this ball. Only when I if I give a push like this, it will fall back to be global once it is fall back here it cannot be again taken out there. Unless and until I simply apply a force and put it there. So, this is what is known as meta stable equilibrium; that means, when the way of moving somewhere it finds a local equilibrium or local minima rather and it got stuck there, that is what is known as meta stable equilibrium. This is very important in steel you will see it in the class that is what known as meta stable equilibrium.

Now what is a unstable equilibrium first, there are 2 things unstable and unstable equilibrium you must have a very good idea about that. Suppose an energy landscape is like this inverted parabola. And if I put a ball here it will simply fall this way or this way it will not stay. This what is this situation it will either fall this way or fall this way or if is on the edges correct, but still this is a equilibrium, because it is not dissipating energy, but suppose if I have a path like this on a hill let us imagine a situation you are can not up the tower hill. And you are gliding on the hill, basically it will simply glide down and every time it will glide down it will dissipating the energy. So, therefore, this is not in equilibrium this is known as unstable or instable, whatever the situation you call unstable is a better word.

. So, therefore, if system is dissipating energy we cannot call it at equilibrium, but this stable Meta stable or unstable. System must not dissipate energy to be in equilibrium conditions it can be varying from stable meta stable or unstable, but the moment it dissipates energy; that means, it is losing energy, then it is no longer in continuously losing energy basically; that means, no longer in equilibrium.

So, this is something which you also understand. There will be many such situation where you want the system to be at global equilibrium, but system will not it will try to remain in Meta stable equilibrium. Similarly, there will be situation where system is unstable equilibrium immediately, it will transform into 2 products there is where the third situation material walls actually exactly same at this pictures.

There are materials, if I simply change pressure and temperature conditions they will be going into unstable equilibrium conditions and immediately, they will transform into some stable products. Similarly, there are materials which will not transform into the global equilibrium product or Meta stable equilibrium product. And remain there peacefully for long, long time. So, that is why this equilibrium concept is very, very important for you.

I think we should stop here. And in the next lecture we will discuss in more details about this things.