Advanced Metallurgical Thermodynamics

Prof. Dr. B. S. Murty
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture No. # 01

Basic Definition

Today, I want to just know how much we know about free energy. I want to see how many of you have heard this term, all of you must have heard. Let see what is your understanding of free energy?

This is the energy of the system which is available to perform some work.

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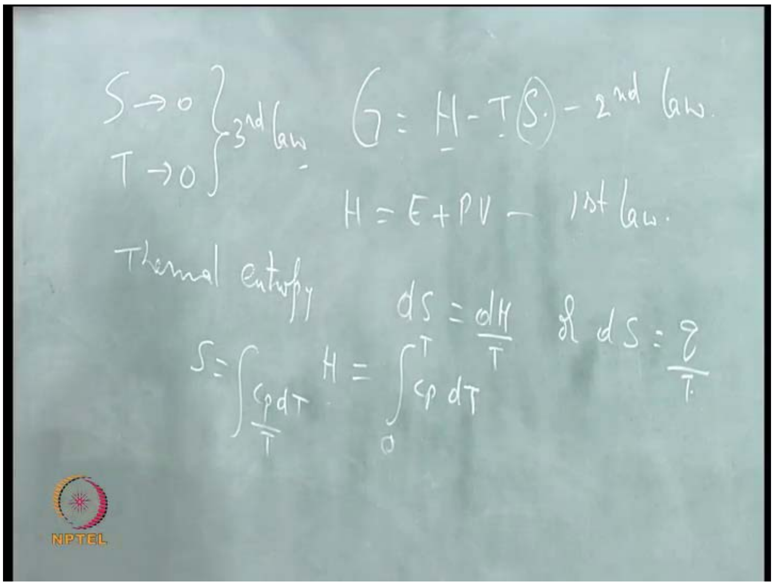

Some work; that is the reasons - why we call it as free energy. And Gibbs has a defined it as you all are aware as G is equal to H minus TS. This is something every one of you should known and must have gone through it; where H is enthalpy and T is the temperature and S is entropy. And this also coupled with the other equations, this comes actually from the second law of thermodynamic all of you are aware of it. And because the entropy concept of entropy is actually comes from the second law.

First law basically talks about what is what is first law how many of you?

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Conservation of energy is the first law, for example, H equal to E plus P V - this is what we call it as first law. This is let us say say one way of calling the second law, if you want to say. And then we also have something called third law of thermodynamics, how many of you are aware of the third law? What is third law?

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Correct. So, entropy S tends to 0 as T tends to 0 - this is, what is third law, this is what we say, am I right? And there one point that you all have to remember, whenever we say entropy which is basically entropy is the degree of randomness in a material. And this degree of randomness can come into a material because of two important factors, one is called thermal; another is called configurational. For example, at any temperature there are vibrations inside a material and these vibrations would cause some kind of randomness inside the material and that particular randomness that you see is what is referred to as thermal entropy.

And we defined that particular entropy in terms of, how many of you known this? How is entropy defined?

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Yes. In fact, if you see the second law definition of entropy is dS equal to dH by T or we can it also comes out as q by T, actually this is how this is how the first at the beginning the people have defined the entropy. And because we known under certain condition, under what conditions q can be taken as dH?

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Constant pressure, so we take it as dH and it becomes dH by T. And H in principle enthalpy, enthalpy is related to what?

Enterology

Enterology, H equal to E plus P V we have already written, but how do we measure H. If somebody wants to calculate the enthalpy of a material, how does he from the specific heat? So, H is nothing, but integral C p dT from anywhere from 0 let us say to some temperature T. So, H is integral C p dT and basically C p is what we know is a heat capacity of a material at constant pressure and that is basically nothing but the amount of heat. How one does defined the heat capacity? Tell me.

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Correct. Not hold the amount of heat that is required, required that it is need to raise the temperature. That is how we defined and once we defined H, S, C integral C p dT, S automatically turns out to be because dS is dH by T, so you can see that S is nothing but integral C p dT by T.

So, these are the basic equations that one needs to remember when we are talking about the entropy and the enthalpy. And in principle one can even find out how the entropy increases with the heat capacity. In fact, if you carefully observe this, the heat capacity of a material itself is not a constant term. How does a heat capacity change as function of temperature? Do you know?

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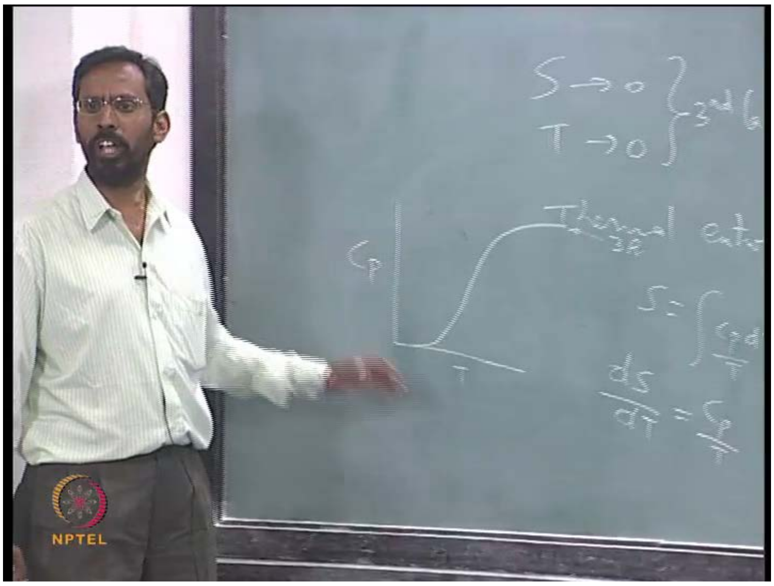

Increases with temperature.

Increases with temperature, what kind of a shape it has, if I plot let us say heat capacities as a function of temperature, how does the plot look like?

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Yes it is start like this and then saturates somewhere and this value where it saturates is what we usually take it as, how much? Some of you have remember from your earlier studies, it is 3R one can one can derive that and show. And as you can see that C p actually goes to 0 and absolute 0, because there are no vibrations at absolute 0. Heat capacity comes because of vibrations and because the atomic vibration vanish as you go to 0 the heat capacity goes to 0 and that is why you will see the entropy also actually goes to 0 and that is what the third law of thermodynamics.

So, you can see that the C p more or less is very, very small at and then it increases and as a result because this increases if I try to see what is dS by dT; that means, the rate of change of entropy with temperature that can be given as what? dS by dT will be C p it will actually turn out to be C p by T. So, that means, you can see that the rate change of entropy with temperature is C p by T and; that means, the entropy always increases with increase in temperature. When I say dS by dT how does the entropy change as you increase the temperature is it positive, is it negative, or is it does not change.

If you look at it, if C p was 0 then we can say ds by dt is 0. d s by dt being 0 means what? That entropy does not change with temperature at any temperature material will always have the same entropy. And again I am talking in terms of thermal entropy here. We are not yet come to what is called configurational entropy, configurational entropy comes into picture when you take more than one type of atoms and try to put them together in one place (( )). Something like you take a box and try to put red balls and the white balls together certain number of them and depending on how you can arrange these red and white balls, there is some randomness associated with that particular configuration and this is what we call it as a configurational enthalpy.

And you will see slowly as we go along materials which are ordered will have very low configurational entropy, and in fact, one can even prove that that if a material is perfectly ordered, have you heard about ordered compounds? For example, sodium chloride is an ordered compound. You will see every sodium will have a chlorine atom around it, and every chlorine will have a sodium atom around it, because of the ionic bonding. You have also in metallic system also you have inter metallic compounds, things like if you have heard of compounds such as Ni 3 Al. do you know where Ni 3 Al is very important?

Super alloys.

Super alloys - the strengthening in super alloys basically comes from that particular phase which is called gamma prime phase Ni 3 Al. Ni 3 Al is ordered and if it is in a perfectly ordered condition an ordered material also can have some disordered inside it - we call it as partially ordered. If it is perfectly ordered then in such a case we can prove as we go along we will do in this course that we can prove that it is actually we will have 0 configuration entropy. And in that case the material can only have one more entropy which is the thermal entropy. Thermal entropy is bound to be there whether it is a ordered or disordered structure. Only difference between the two is, if it is perfectly ordered, it will not have configuration entropy; it will have only one type of entropy which it is thermal entropy. Otherwise if it is a disordered, it will have both of them.

And for a pure metal, if I am considering in principle I will not talk about the configuration entropy because there is no second element there. In fact, if you go deeper people even talk in terms of the the vacancies inside the material and talk about configurational entropy arising because of the presence of vacancies, but in general for normal study we usually consider for pure metals that only thermal entropy becomes dominant and configurational entropy does not come into picture only when I add a second element - a binary system or a ternary system or a quaternary system and so on, we start talking about configurational entropy.

In that room temperatures will that be perfectly ordered this

Of course, In fact, particularly ionic solids if to introduce a disordered into them is not so easy, for example, if you want to remove one of the fluorine atom the bodies are disturb you need to maintain what is called charge balance. And if you cannot maintain the charge balance you are in the system is at a high level energy state. So, here to keep the system at the lowest energy state, system prefers to have every sodium atom would like to have a chlorine atom around it because of the the the shape, the basically the exchange of the electrons in the particular material.

So, you would see that in when I am talking about the thermal entropy you would see that thermal entropy because C p is positive. C p is never negative we have seen from here C p the lowest value C p can take is 0. So, that is the absolute 0 at any other temperature the C p has a positive value. If this is positive then this ratio is positive. Is it not? So, this particular rate of change of entropy with temperature is always positive, so entropy increases with increase in temperature. And what is the rate at heat increases depends on the material for for some material which has the high C p you would see that you will have the rate at which increases is higher you will have a steeper entropy.

If I plot entropy verses temperature you would see a steeper curve there which we will see it possibly in the next class as we go along. So, this is something which you need to understand before you start discussing about the free energy I think with that we will stop for today.

(( )) easy temperature one shot it not becoming right. So, in order might not be in a certain temperature.

True, but that particular entropy that you are getting here can also be talked in a terms of thermal entropy. So, that is why it is a it is a little tricky issue to say this particular entropy that is generated in the material is it because of a thermal or not?

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Configurational entropy is assumed to be constant, once you have fixed the amount of the second element as you go along you will see. How many of you remember the configuration entropy expression?

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klnW. And klnW if you derive it further it is turns out to be minus r x i ln x i.

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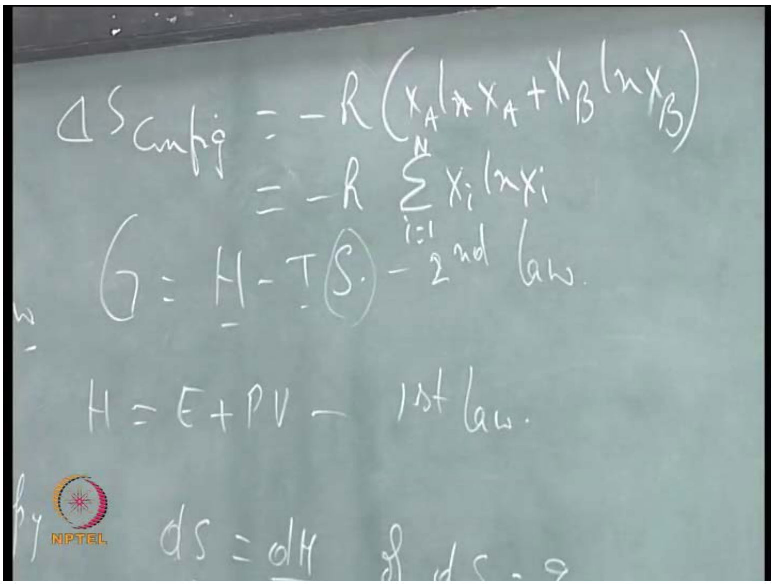

$$\Delta S_{config} = -R\,(X_A \ln X_A + X_B \ln X_B)$$

$$= -R \sum_{i=1}^{N} X_i \ln X_i$$

$$G = H - T\,\textcircled{S} - 2^{nd}\ \text{law.}$$

$$H = E + PV - 1^{st}\ \text{law.}$$

$$dS = dH$$

For binary system we can easily show that it is delta S configurational is nothing but minus R X A ln X A plus X B ln X B. Some of you might have seen this and you can see that this is the function of only composition. And once you fixed that, and in fact, you can clearly see that this would; obviously, would go to 0 when you go to a pure metal side. If you put any one of them as one either X A as 1 or XB as 1, you would see immediately that the function goes to 0. So, that the configuration entropy is 0 for the pure metal and it comes into picture only when you have more than one element. And in principle, if it is more number of elements, we write it as X i ln X i where i equal to 1 to 2 whatever it is in N, so any number of elements you can continue that expression. We will talk about multi component system as we go along and there you will understand as we go along. We will stop now.

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Additional Input

Third Law of Thermodynamics:

- The third law of thermodynamics can be stated as "Entropy of a system tends to zero as the temperature tends to 0K".

  we can express this as, $S \rightarrow 0$ as $T \rightarrow 0$ K

- From second law of thermodynamics we know that $dG = VdP - SdT$ and hence $dG/dT = -S$ at constant P

- Thus we can express third law of thermodynamics as

  $dG/dT \rightarrow 0$ as $T \rightarrow 0$