

Physics of Functional Materials and Devices

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Lecture-24, Week 6

Heat Capacity

Welcome to the third lecture of this week. In the previous lecture, I had talked to you about the expansion in solids. We had talked about the phenomena of negative expansion coefficients in solids and you must have also seen the large number of applications which these negative expansion solids are finding and you must have realized that you can make materials easily and you can tune these thermal properties and then finally, the application can be modulated. The next topic which we will start and you will see that they also have large number of applications is the specific heat and latent heat. These phenomena's are basically related to the concept of heat transfer. What do I mean by heat transfer? Basically, how heat transfer occurs in solids from one point in the particular solid to the other point and is there a mechanism by which you can change the way heat transfer will take place or there are various mechanisms by which this process can be modulated.

Therefore, you can have heat capacities at constant volume or at constant pressures. Along with that you can see that you can modulate or you can change various thermodynamical parameters and you will get different heat transfer mechanisms in these solids. So, you can relate the specific heat at constant pressure or constant volume and you can find out what is the relationship between the two. When you move from specific heat to heat capacities, then there are various models.

The basics were introduced in the initial lecture of this week. And we will spend some more time on these two concepts namely the Dulong-Petit's law and the Einstein model of heat capacity in solids. Why should heat transfer take place? Let us have two objects object 1 and object 2. They are at different temperatures T_1 and T_2 . Now you bring them together.

If you bring them together two independent objects then there is a boundary which is formed. Heat is basically defined as the energy that is transmitted over this boundary because of the heat is defined as the energy that is transmitted over this boundary as a result of what? As a result of temperature difference that means T_1 and T_2 are not equal. If they are equal then we are talking about an equilibrium position or condition and at that point

or when you have the equilibrium condition there is no heat transfer taking place. And when you have two objects which are coming together the heat is transferred from the warmer object to the cooler object. And when you reach the thermodynamical equilibrium heat transfer becomes 0, but how will this heat get transferred? So, how will the heat transfer take place? The heat transfer is classified into three types.

This means it is not random. There are well defined mechanisms which will drive this transfer of heat from one point of the body to the other. The first is heat conduction or thermal conduction. Here the transfer of energy from one medium particle to the another is in a way when these particles are in direct contact with each other. So, that is the way the thermal conduction takes place.

Now, suppose you have a solid which has high density. So, you can see I am drawing a solid where the particles are closely packed and then I make another solid, but having the same molecular formula. So, let us say we have been talking about a common example like ABO_3 structure. So, I will continue taking it as an example. So, an ABO_3 structure and the solid which is built using the unit cell that has ABO_3 type configuration has high density.

So, the densification is quite high. Now, for the same system I make a configuration where the particles are quite far apart. What do you think will happen? Will the heat transfer in the two systems be same or will they be different? Please note in heat conduction you are transferring energy between the particles who are the nearest neighbors. So, if the particles are slightly far apart then the conduction would be lower than when they are in a highly dense condition. So, have I told you a way to tune the heat conductivity of a ABO_3 type ceramic? Yes, please remember what did we discuss in the previous class? If you sinter the ceramics, the densification occurs.

That means, you densify the What does it mean? That you bring the particles closer and closer and you have a high density. Now, suppose you take a material. For example, we took calcium titanate as one of the examples in the previous lecture. You sinter it at 900°C , then you sinter it at 1000°C and you go on like this 1300°C . You will find that the density of the material will change because you are giving different time for sintering as well as for different temperatures.

Once you change the density what have you changed? You have changed the conduction mechanism that is heat conduction mechanism in these solids. So, just by tuning the synthesis parameter while keeping rest everything same you can easily tune the thermal conductivity of a ceramic. So, now you have an idea of how to tune thermal conductivity and get novel materials which have different orders or different magnitude of thermal conduction. The next mechanism for heat transfer is the convection or thermal conduction. Here we are mostly talking about the influence that the movement of the particles causes the heat transfer.

And the heat because of this movement of the particles in a fluid the heat transfer takes place from one location to another. And finally, you have the radiation or thermal radiation. It is the energy emitted by matter in the form of photons or electromagnetic waves. If you look into a very common phenomena which we experience daily, you have heat coming in from sun in the form of radiation which comes and heats the ground, the ground heats the air which is in contact or is covering over the area which is under consideration and that heating occurs because of conduction. And finally, the warm air rises and then heats the atmosphere above and that is by the process of convection.

So, you have three types of mechanisms which we already know. Similar things can occur in solids. So, let us start with the first quantity that is specific heat. What do we mean by specific heat? It is the quantity of heat that must be added to a substance in order to raise its temperature by 1°. Again, the same example, if you have highly dense material.

Or you have a porous material, will you be required to give same magnitude of heat so that its temperature can be increased by a degree? No, you will have to have different magnitude of heat being given. So, you also know how the specific heat changes in the same material, but if that material is prepared under different synthesis conditions. Specific heat is defined as

$$Q = C m \Delta T.$$

With a SI unit of joule per kg per Kelvin. Q is what? Is the quantity of heat adsorbed body.

M is the mass of the body, ΔT is the rise in temperature and C is the specific heat of the substance. And you must now understand that specific heat capacity of a substance will depend on the nature of the material of the substance. So, if you take a copper block, if you take aluminum block or if you take water then they have different specific heat capacity and hence you have different application for these materials, but even for the same material let us say copper. You can make various forms of copper and you can tune the specific heat of the substance which was being fabricated or built on a copper-based material. In addition to specific heat, the second term is latent heat.

Latent heat is the energy absorbed or released by a substance during a change in its physical state and this occurs without changing its temperature. So, if you remember we had talked about occurrence of phase transition in lead calcium titanate in the previous lecture. lecture and we had plotted the variation of a, b and c parameters as a function of temperature and you had seen that as you heat the system you have the c parameters. this is c parameter; this is a or b parameter it one increases with the temperature and then at the transition temperature they show a distinct change and then a positive expansion is observed and c then merges with a and b because you are going from tetragonal to cubic cell and then they show the positive thermal expansion. But at T_c in this kind of system there must be some

release in energy because you are transforming from one state to the other and this absorbed energy or released energy at this point is called the latent heat.

So, the latent heat produced by melting a solid or freezing a liquid is a common example which we have been studying. So, two types of latent heats are mostly considered heat of fusion or heat of vaporization. Fusion means what? You have transformation from ice cube to then going to water vaporization going to liquid. liquid to gaseous form. So, solid melting then liquid up to certain point then vaporization and then gas in the heating cycle and in the cooling cycle gas condensation taking place it transforming it to liquid up to a certain temperature it remains liquid you cool it further freezing takes place and beyond a certain temperature you have the solid forming once again.

So, these are the concepts which you should remember. Specific heat at constant volume or constant pressure are two concepts. What happens? You can change thermodynamical parameters as volume, temperature, pressure or entropy. But here let us start with volume and pressure as the two thermodynamical parameters which we will consider. Now the rate of change of specific internal energy with respect to temperature when volume is held constant is called as specific heat at constant volume given as

$$C_v = \frac{\Delta U}{\Delta T} \text{ at constant } V$$

Where U is the internal energy, T is the temperature and V is the volume Similarly, specific heat is what? It is the rate of change of enthalpy with respect to temperature when the pressure is held constant.

$$\text{Therefore, } C_p = \frac{\Delta H}{\Delta T} \text{ at constant } P$$

Where H is enthalpy, T is temperature, V is volume in the previous case and P is the pressure in the case of specific heat at constant pressure. Now, if you look into heat capacity at constant pressure, this is greater than the heat capacity at constant volume because when heat is added at constant pressure the substance expands and work takes place. The sum of the internal energy and product of pressure and volume of a thermodynamical system is what? It is written as

$$H = E + PV.$$

That is what? H is enthalpy, E is the internal energy, P is the pressure, V is the volume. So, you can take two conditions.

You have a system having an ideal gas. Now, you heat this system and what will happen you will heat the system the internal energy will increase and now you will see that gas expands due to pressure on the piston and creates a new volume. So, there is a change in volume. Enthalpy is a property or state function that resembles energy. It has the same

dimensions as energy and derives all its value from the systems composition, temperature and pressure.

So, you must now clearly have an idea. as how you can change the enthalpy, you can change the composition of the material, you can change the temperature at which you are evaluating the performance or you can change the pressure. Now, the system can actually be looked into it from another aspect. The enthalpy change is what is it is exactly equal to the heat imparted to the system when only work involved is the change in volume at constant pressure. So, if you are giving heat to the system and it is only the work which is involved.

And that is the change in volume at constant pressure then that is called as enthalpy change. Let us see what is the relationship between C_p and C_v . We have seen

$$Q = (n C \Delta T),$$

But at constant pressure,

$$Q_p = n C_p \Delta T$$

and similarly at constant volume you have,

$$Q_v = n C_v \Delta T.$$

The value is equal to change in enthalpy this is what we have seen in the previous slide.

$$\text{So, } Q_p = n C_p \Delta T = \Delta H.$$

If you go from the change in terms of volume that means, you talk in terms of Q_v this equal to what that change is equal to

$$\text{So, } Q_v = n C_v \Delta T = \Delta U$$

Now, we know for one mole of an ideal gas $\Delta H = \Delta U + \Delta(PV)$. We can write the same equation as

$$\Delta H = \Delta U + \Delta(RT)$$

$$\text{or } \Delta H = \Delta U + R\Delta T$$

This is what we can derive. Do we know what is the value of ΔU and ΔH ? Yes, we know from the two equations discussed earlier. So, we can write

$$C_p \Delta T = C_v \Delta T + R \Delta T$$

What this gives?

$$C_p = (C_v + R)$$

$$\text{or } (C_p - C_v) = R$$

Where R is the gas constant, C_p is the specific heat at constant pressure, C_v is the specific heat at constant volume, Q is heat, T is the temperature and U is the internal energy which we had discussed in the earlier equations.

So, this is important relation which you should remember. If you go to heat capacity ratio, this is also known as adiabatic index. The ratio of specific heats is the ratio of heat capacity at constant pressure to heat capacity at constant volume. you can easily derive the equation and you will get heat capacity as $\gamma = C_p / C_v$ and you can then from there relate

$$C_p = \frac{\gamma R}{(\gamma - 1)}$$

$$\text{or, } C_v = \frac{R}{(\gamma - 1)}$$

And this relation has important implications and is utilized while we use the phenomena of thermodynamical reversible processes in materials to design certain devices. Dulong Petit law states the classical expression for molar specific heat capacity.

Now, let us talk about molar specific heat capacity. According to this law the gram atomic heat capacity that is the product of specific heat capacity and the atomic mass of an element remains constant. This law actually gives you good prediction of heat capacity of many elementary solids, but at higher temperatures. This you should remember that it is at higher temperature that this law is able to predict the heat capacities. In addition, please remember you are talking in terms of atomic mass.

Now, if you have a material and then you use some kind of a dopant that means, you change the composition of the material. What will happen? Then you are changing the atomic mass of the material. Once you change the atomic mass of the material, what is going to happen? You are going to change the specific heat capacities and that is the way how you get different types of materials finding applications in various devices where heat capacities play the critical role. So, Dulong Pettit's law is

$$C m = k$$

$$\text{Or, } C m = 3R$$

Where C is the specific heat capacity, m is the molar mass, k is a constant. You can write the same expression by considering the molar mass M .

You can write

$$\frac{CM}{m} = 3R$$

$$\text{That is } \frac{C}{n} = 3R$$

$$\text{or } C = 3nK_B.$$

n is the number of moles; R is the gas constant and is K_B the Boltzmann constant. Dulong-Petit's law gives the prediction about the behavior of materials at higher temperatures. at lower temperatures it actually fails to predict the behavior and this was then taken care by the Einstein's model. and here the quantum mechanical behavior of harmonic oscillators was considered and the harmonic oscillator behavior at low temperatures were considered.

That means you have the harmonic oscillators at low temperature means you are giving less $K_B T$ that means you are talking the motion of harmonic oscillators but with low energies. In Einstein model, the atoms are independent quantum harmonic oscillators. Each atom has the same frequency and then you can write the heat capacity per harmonic oscillator

$$C(T) = K_B \left(\frac{T_E}{T} \right) \text{ the expression written within the brackets,}$$

where T_E the Einstein temperature given by

$$T_E = \frac{\hbar\omega_0}{K_B}$$

T_E is temperature and K_B is a constant. So, now, we have talked to you about various such as heat capacities and latent heat in today's lecture. My question today would be how can you tune these properties.

Just look into the aspects which have been taught in this course from first week onwards. So, if you are understanding the lectures then you will be able to answer this question very easily. I will give you a hint the answer lies in tuning the material. Second question which I would ask is if you have a given material where you can tune its heat capacity then where would you use such a material. I have already indicated in today's lecture as well as in the previous lecture where such materials are routinely used.

Just think and you will get the applications where such materials are being utilized. So, let us conclude today's lecture and I hope you have seen what is the driving force of heat

transfer in solids, what are the concepts of specific heat and latent heat and how the Dulong-Petit law along with Einstein model have predicted the heat capacities in solids. These are the books which you can refer to for developing further understanding and I thank you once again for listening to this lecture 3 of week 6. Thank you very much.