

Physics of Functional Materials and Devices
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Lecture – 18, Week 5
Thermodynamics

Hello, welcome to the first lecture of week 5. What have we seen till now? We have seen that there are various types of materials. We have seen that the materials can be classified under various categories. Then we went on to see the synthesis protocols which are there to make these materials. And most of these synthesis protocols can be classified under two broad headings which are the top down approaches or the bottom up approaches. Each of them have their own advantages and disadvantages or I must say certain limitations.

So, depending upon the material which you require, the property of the material which you require, you can choose amongst the synthesis protocols that would be beneficial for the work. Then we went on to focus lot of attention on various types of crystalline materials which had periodicity and because of the periodicity you went on to have materials such as metals, insulators or semiconductors. Then, we had seen that the band gap which originates in insulators or semiconductors is strongly dependent on the inter atomic distances or you may say the lattice parameters if you talk in terms of 3D lattices. Immediately then you will understand why did we spend significant amount of time on crystal structures.

You have 14 Bravais lattices in 3D. That means you have various combinations of lattice parameters a , b and c along with the angles α , β , γ and based on that you can bring all the crystalline materials to fall under one of these 14 Bravais lattices. Now my question comes, how will you choose a material which has a slightly different property than what your friend has synthesized or is using? You would say I would make a material which has a lattice parameter that is slightly different from the one which is being used by my colleague. For example, if you have a cubic or a tetragonal lattice which I am unit cell which I have just drawn here you can clearly see the c axis is much larger than the other two axis which are nearly same. So, $a = b \neq c$.

Now if you change the values of a and b that means you have let us say for first example you had 3.5 \AA as a and b whereas c was 5 \AA . Then you have a different size tetragonal unit cell and if you make a material which has a tetragonal parameters as 3.9 \AA as a and b parameters and c is approximately 4.01 \AA .

They are nearly same, but different clearly they are different. So, what is the thing which you are seeing? The tetragonal cell is moving towards the cubic cell because then the c parameter is also moving towards the a and b parameters. So, if you move from the

tetragonal cell to a cubic unit cell what will you call it? You will call it as if there is a transition occurring transition of what you are transforming from a tetragonal unit cell to a cubic unit cell and this is called as transformation and such kind of transformations can lead to various modifications in the properties because by now you already understand that materials with different types of unit cells that means the arrangement in the lattice will have different properties. Hence, phase transitions and phases play a very important role in deciding the range of application of the material and the properties which a material will behave in a given temperature range and in comparison to a range which may be above the transition temperature. You will see that I am stressing quite a lot on temperature because temperature is one of the factors which drives this or these kind of phase transitions in materials which we are investigating or understanding in this course.

And the moment I stress upon temperature then the concept which becomes very important and must be understood or revised once again is thermodynamics. That means how the temperature changes the dynamics of a system and what are the consequences. Hence, let us start this week with revising the basics of thermodynamics, the laws of thermodynamics, the Maxwell's relations in thermodynamics and how those will become very useful for the people working in the field of materials and devices which use these materials and they are going to be used in areas where temperature would be one of the parameters that can vary significantly. What have you understood till now from your school days what is thermodynamics? It is basically a study of energy, heat and work and their interconversions in various systems. So, when you move from one form to the other, one phase to the other what happens and what are the driving forces which drive these transformations is the concept or concepts which you understand in thermodynamics.

So you will understand that as you change the thermodynamic parameters which are S, P, V and T. S is entropy, P is pressure, V is volume and T is temperature. So as you change any one of these thermodynamical parameters there are modifications in the properties. It can be physical properties or it can be chemical properties or it can be both that means physio chemical properties. And these modifications are then used in different types of applications such as power generation, refrigeration, air conditioning, batteries, supercapacitors, solar cells or you can have other sensors which would be using the interconversion or interplay between these parameters.

So if we go back to our knowledge and quickly revise what are the parameters that we are going to use, what are the parameters or terminologies which we should remember. First of them is what is a system, the boundary and the ambient surroundings. In terms of thermodynamics, the word system is associated with the macroscopic part of the universe that we select for study. So if I am sitting in a room then if I select this room then this becomes the system. So macroscopic here means that it is made up of large number of particles which is much more than the Avogadro's number.

And this is a very important parameter or concept which you should understand because the temperature is not going to affect just one particle but a group of particles or a system as a whole will get impacted if temperature, pressure, entropy or volume is changed. Second surroundings. This is simply the vicinity of a system. For example, if I sit on a chair and if there are lot of heaters put around the chair then The temperature which I will feel would be very different. In the second case if there are ice bricks which are put all around then the temperature which will be appearing around the system that is me in this example which I just took would be very different.

So surroundings would also be playing a very important role in thermodynamical systems. and generally what we believe that the surroundings are much larger than the system itself and hence they will not be treated in the same way as the system. So the properties of the surroundings and systems are different and when you have a system surrounded by the boundary each of them having their individual properties you will form a interface and this interface is called the boundary. Then you have the total system which is a thermodynamical system which will be considered as an isolated example to a good approximation. So you will take the whole system that means system boundary surrounding and then as an isolated body this total system is not being impacted by its surrounding and the system is not getting impacted by the surroundings which is impacting the the total system and that is why you have these concepts.

So you have system, boundary, surrounding and the total system. So, once again please remember there is a difference between a system and total system. What is a thermodynamical equilibrium? Everybody talks in terms of equilibrium. What does an equilibrium means? Generally, equilibrium is explained if all of its thermodynamical variables for example, S, P, V, T are well defined, they have the same value throughout this system and they do not vary as a function of time. So if an external factor is there then that factor is also not impacting the properties of the system and then that system is called in thermodynamical parameters.

One way to visualize this is by drawing the PV diagram. So you have pressure versus volume diagram. You have two conditions at a given point you can have P_1, V_1 as the thermodynamical set and at the other you can have P_2, V_2 as the set. What will happen? In thermodynamics you will have to explain the concept using an additional factor that is equation of states. An equation of state in thermodynamics is what? It is equating equation which relates the state variables which characterizes the state of matter under a given set of physical conditions.

What do we mean by this complex statement? It is a thermodynamic equation. So thermodynamic equation means it is somehow going to relate the thermodynamical parameters. You have the variables which are associated with the given state. So the state of matter means what? It has a well-defined state under a set of physical conditions. So the

equation of state would be doing what? If I am talking in terms of thermodynamics it is going to relate the thermodynamical parameters.

Mostly we talk in terms of pressure, volume, temperature and then how are they related. But the fourth state entropy is also as important as any of these. But to keep our life simple and build from the information we took during our school days let us start with P, V, T. The simplest known example of an equation of state is the one which relates between the pressure, volume and temperature of a mole of ideal gas and that is the ideal gas law and that is known as $PV = RT$ where R is the universal gas constant. These equation of states are used to describe gases, fluids, fluid mixtures, solids and the interior of stars can also be used or explained using these equation of states.

Why? Why can they be used to explain the so many parameters of various kind of materials or states of matter? Can you change pressure and volume of a material? Yes, you can. Suppose you have a lattice which has periodicity shown by the open circles. Then you have a lattice with equal number of building blocks or atoms or molecules but their inter-atomic distances are shown by the filled circles. what will happen? The volume which this structure if I draw a 2D structure this concept will become even clearer. The volume which this will occupy or area in this case which a 2D lattice will occupy would be different and immediately what will you have? You will get a variable in terms of the area or volume and hence you will find that if V is changing P is kept constant R is a constant what is the impact which you will see for the movement from the condition of open circle to filled circle.

Obviously there must be the change in the temperature being felt by the material so that this relation remains intact and hence you will find that the temperature will change and that is why these equations are used and now you can immediately go back to the introduction which I gave today. If you go from one set of material to the other then you will see certain change in the temperature and we had seen in the previous lectures of the last week that you have relations such as exothermic endothermic. So if you move from one form to the other if the system has to take temperature or you have to have energy from the surroundings you take in terms of heat and then so that you can move from one form to the other and that is why you have such phase transitions because the relations have to be maintained. Please remember the information I gave earlier I am repeating because such relations can also be used to investigate very very interesting phenomena which are occurring in the interior of stars and then you get not many information come out of it and they are used to go to the next level of understanding about our universe. There are certain laws of thermodynamics which you have seen and what are those? You have seen that if P, V, T are well defined then what will you have? Using the definitions of thermodynamical equilibrium and equation of state which I have just discussed there are two ways for a system to be out of equilibrium.

What are those? P, V, T are well defined no problem but they do not lie on the equation of state or P or T vary from one point to the other. The example which I took earlier in the PV diagram if you had P_1, V_1 and P_2, V_2 if they were varying that means you were actually moving away from the equilibrium. So, considering this case of system A having P_1, V_1 and T_1 as the three thermodynamical parameters you are having a state which is system B with P_2, V_2 and T_2 as the thermodynamical parameters. When these two subsystems are brought in contact so P_1, V_1 and T_1 P_2, V_2, T_2 so they are two subsystems they are brought together what happens? This is the question which we are asking. They will form a single system which is out of equilibrium you can clearly see the temperature felt by open palm and closed fist would be different.

Because of this a spontaneous exchange will take place so that the combined system the combined system means the the fist and the palm system can achieve equilibrium. So that the total system which we are now considering have same pressure the volume is now V is $V_1 + V_2$ and temperature becomes T both the sides have the same temperature. From this we can say that if A B and C are different thermodynamical systems and A is in thermodynamical equilibrium with B and B is in thermodynamical equilibrium with C then A is also in thermodynamical equilibrium with C. So what have we seen? If you have two systems they were separate then they were brought together they become in equilibrium condition. Now you put another system for example I have this system attaching to the body then what should happen if B is in equilibrium with C A is in equilibrium with C.

Then A and B will also be in equilibrium that is what it means because if I have two systems which were coming together to obtain the same states that means P_1, V_1 and T_1 or P, V, T and if they were individually in equilibrium with another state then that states would also become in equilibrium with the overall system that is what the meaning is. The most common application of the zeroth law of thermodynamics is the thermometer. So you take a thermometer and then put it at the place where you want to sense the temperature and the thermometer would become in equilibrium with the surrounding and then you can read the temperature. Let us now move on to revise certain thermodynamical quantities which are used and will be used quite regularly. First of them is internal energy U .

What is that? Is the total energy that a system contains. It is the sum of all possible forms of energy contained in the body. This is another statement for defining internal energy and if it is a sum of all possible forms of energy it becomes functions of temperature, the chemical nature and it can also become a function of pressure or volume or it can become function of any of the thermodynamical parameters. So because it is a sum of all possible forms of energy contained in a body it can become a function of one of the thermodynamical parameters or it can become a function of more than one thermodynamical parameters. The next quantity is heat written as Q capital Q.

It is the thermal energy transferred between systems due to temperature difference. So for example if you remember the previous case system A, system B now if you have them coming together then if the two systems are at different temperatures then there would be some transfer of the energy and that would be in terms of internal energy change because they would be increasing the kinetic energy of molecules in a system or a substance. Heat is not a property of a system but a form of energy that increases the internal energy and the kinetic energy of a molecules in a system. Finally, you have the third that is the work W. So work performed by a system is the energy transferred by the system to its surrounding.

Work is a form of energy but it is energy in transit. So work is done then the material can go from one phase to the other. So work is not continuously being done it is a energy in transit. So these are the three quantities based on that let us discuss few more concept and that brings us to the concept of first law of thermodynamics. What is it? The internal energy of an isolated system is conserved under any thermodynamical change.

So you will find if it is an isolated system then even if you change the thermodynamics of the isolated system the internal energy will remain same. There are two kinds of energy that can be transferred between a thermodynamical system and its surroundings. Work and heat this is what we have seen. Work by mechanical contact or heat by thermal contact. Under a thermodynamical change what is happening? There is some change in the internal energy.

So there is some change. So you have ΔU . What can happen? Either you can do some work or get some work out and you can either supply heat or you can take heat. So there would be two things W and Q. So let us take the combination of $Q+W$ which will lead to ΔU . Now what will happen? The first law of thermodynamics is given by the statement that under an infinitesimally small thermodynamical change du is equal to $dQ + dW$.

Now what happens? If you have this $dQ + dW$ equals to du then you have the consequences which were given by various people and that led to the statements for second law of thermodynamics. The first one is the Clausius statement for second law which basically gives you a statement to the mathematical formulation in which it states no process is possible whose sole result is the transfer of heat from a colder to a hotter body. Some of you might think but what about fridges or refrigerators which we see? In a fridge an engineer has to do work to perform such heat transfer and so you are actually taking the heat out by an engine. The remark which is given earlier that is the Clausius statement leads to another formulation of a second law of thermodynamics that is given by Kelvin and Planck statement. It states no cyclic process is possible whose sole result is the complete conversion of heat into work.

So you cannot have a cyclic process where the whole of heat gets converted to work or vice versa. What have we written earlier? We had written ∂u is a combination of $Q+W$. So

you can give some heat, you can take some heat, you can get some work done or you will have to do some work. So this can be written as $du = TdS - PdV$ where dS is the change in entropy, P is the pressure and dV is the change in volume. Therefore what happens? u becomes a function of S and V .

Now entropy is the measure of disorder of a system. It is an extensive parameter of the thermodynamical system which means its value changes dependent upon the amount of matter that is present. Now if you go to the previous equation we had $TdS - PdV = du$. You had T V P and S . You had a pair of intensive parameters and you had a pair of extensive parameters.

These pairs are called as conjugate variables and their products has the dimension of energy. So $T S$ or $P V$ has the dimension of energy. So we can write du is change in internal energy can be $(\frac{du}{dS})_V \cdot dS + (\frac{du}{dV})_S dV$ where P is $(\frac{du}{dV})_S$ and T is equal to $(\frac{du}{dS})_V$. Given that conjugate variables are constrained to appear together because unless they appear together they will not have the dimensions of energy and if you want to have du which has the dimension of energy you cannot have other parameters on the right hand side which do not have the dimensions of energy. So dimensionality considerations forces you to have that these parameters which are conjugate variables appear together.

Because of these considerations there exists four possible choices for the pair of independent thermodynamical variables namely $S V$, $S P$, $T V$ or $T P$. Hence it became logical to conclude that there will exist a natural energy like quantity associated with each of these independent pair of choices. These natural energy like quantities are called thermodynamical potentials. So please remember the origin of the thermodynamical potentials lie in the requirement of having the same dimensions on both sides of the equations du is equal to $TdS - PdV$. If these thermodynamical parameters are there and they are going to appear in pairs then what can happen? If you have S and V as the pair into consideration then u is $TdS - PdV$ which we have defined as the internal energy if you take S and P as the pair which we will consider then you have H is equal to $u + PV$ and that is defined as enthalpy.

If you have $T V$ as the combination then you have F is equal to $u - TS$ and that is defined as Helmholtz free energy and finally if you have $T P$ as the combination then you have the Gibbs free energy that is defined as $u + PV - TS$ and these are the four thermodynamical potentials. Now if you have these equations which we have written there you have seen the requirement that they have to appear in pairs you have seen the requirements of thermodynamical potentials then if you see these parameters let us say $H S P$ or any other which we have just mentioned then you must have the condition which are similar for $u H F$ or G . Hence, let us see what happens if you consider that if you have du is equal to 0 the natural variables S and V will become fixed. Now if you have dH equal to 0 then what will happen we will have to see this example to understand further. Let us differentiate the

equation $H = u + PV$ then dH is equal to $du + d(PV)$ that will give you $TdS - PdV + PdV + VdP$ that is $dH = TdS + VdP$.

So how you can write dH that would become $(\frac{dH}{dT})_P dT + (\frac{dH}{dP})_T dP$ and you will define T and V as written here. Similarly, you can then get equations for Helmholtz free energy F or Gibbs free energy G . So you will get $dF = (\frac{dF}{dT})_V dT + (\frac{dF}{dV})_T dV$ and you can write the same equation for dG . Clear? So you have understood how you can then get the values for dF and dG . So you can write for du you can write for dH you can write for dF and you can write the values for dG .

The previous equations are again sorted to what is called as Maxwell's relations of thermodynamics and you have the Maxwell's equations in terms of T V S or P . So, $(\frac{\partial T}{\partial V})_S = -(\frac{\partial P}{\partial S})_V$. So you have the SPVT relations. So you have the four Maxwell equations.

These are very useful basically for two reasons. They relate the partial derivatives representing quantities which are difficult to measure experimentally to partial derivatives which can be easily measurable. For example, it is difficult to measure sometimes change in entropy, but it can become easy to measure the change in pressure and temperature. So if you are in a condition to measure the change in pressure and temperature at a given volume what you can then find out you will find that you are basically measuring the change in the energy which is associated with the corresponding conjugate pair. So, you can have internal energy, you can have enthalpy, you can have Helmholtz free energy or you can have the Gibbs free energy and by measuring the variation in V or T for example in terms of pressure the partial derivatives $(\frac{\partial V}{\partial T})_P$ you fail to understand the importance of this. So, what do I get? Actually, what you are getting is the change in the Gibbs free energy which is difficult to measure directly using any of these experimental techniques which you have.

But finding out change in volume or minute changes in temperature at a given pressure is a routine work in today's experimental labs and they can be measured easily and hence they become easily measurable in addition to that they give you additional information which was difficult to obtain otherwise. Therefore, what is happening if you take the whole condition as a whole the set of them describe the constraints imposed on the four thermodynamical parameters. What are those? T S V P why are we talking about the constraints because the fact which you should remember that only two of them are independent the other become dependent. Therefore, they play a similar role to that of an equation of state. So, you take two independent parameters and you get information about the dependent parameters.

Before I conclude now you will understand why the properties of materials change significantly as you change temperature volume or pressure because if you change temperature pressure volume or even entropy what are the parameters which are changing? You are changing the internal energy or enthalpy, the Helmholtz free energy or the Gibbs free energy and if the energy of the system is changing the behavior of the material will change and that is why as you move from one phase to the other you have different properties coming into picture. The importance of phase transformations and the classification of phase transformations would be discussed in the next lecture and based on the things which we discussed today that is the basics of thermodynamics the laws of thermodynamics and the origin of Maxwell's equations in thermodynamics and their importance for materials you will understand the nature of phase transformations and the importance of temperature and pressure variations during the occurrence of such phase transformations in solids. You can read these books for more information and I thank you for attending the first lecture of week 5. Thank you very much.