Physics of Functional Materials and Devices
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Lecture – 17, Week 4
Transformations kinetics and reaction rates

Welcome to the final lecture of week 4. In today's lecture, what we will do is we like to discuss about the various reactions or processes which can drive transformations. Transformation means changes from one form to the other. In the previous lecture, we talked about the energies associated with different types of materials leading to the formation of various types of materials. In today's lecture, let us discuss about the transformation or reactions. If there is a transformation, that means you change from one state to the other, then how do you classify those transformations? And if there is a transformation, if you have condition that you need energy, then what is it called? Or during transformation, the material actually gives out energy, then what is it called? You will see that those are the cases of endothermic or exothermic reactions.

Along with that, is the reaction homogeneous or heterogeneous? What do we mean and what is the basic difference between these two types of reactions would al So, be discussed today. And in the final part of the lecture today, we will talk about the reaction rate. Generally, how fast the reaction is moving? Is it first order? What type of factors that influence the reaction rates? What are the bottlenecks that would be discussed in the final part of today's lecture? If you talk to different people from coming from different backgrounds, let us say from physics or chemistry, from material science, from metallurgy, then they talk about transformations in different terms using different terminologies, but the underlying principle is very clear. The underlying principle is that, that one material would transform to the other state or phase only when the next phase, that is the new final phase, gives you a lower energy.

So, that is the driving force, that lowering of energy is the driving force. So, in physics, transformation basically refers to the process in which energy or matter is changed from one form to the other, So, that the energy of the new state is lower than the earlier case. In chemistry, a reaction or transformation is mostly described in terms of one or more substances or reactants that are converted from one to the other, called the products. So, **A, B** reacting to give **A, B**. Why should **A** and **B** react? You are having the case that **A** and **B** are reacting together to go to a state which minimizes the energy.

In material science, transformation can be expressed in terms of change in structure or composition or particle size, shape or they can al So, be in terms of lattice parameter changes. The structure changes occur as a result of rearrangement of atoms in materials. This is what we have understood till now. These changes can be expressed in terms of chemical reactions, phase transformations or diffusion. So, if you have two reactants giving a new product, then you talk in terms of chemical reactions.

If you have a new phase, for example, you go from a tetragonal phase to a cubic phase, then you have phase transformation. If you have movement of mass from one region to the other region of the material, then you talk in terms of diffusion. What are chemical reactions? These as we know are processes where there is interaction between atoms, molecules or ions or reactants leading to the formation of new product which will have chemical and physical properties different from the constituents. These would stabilize because of different energies that we discussed in the previous lecture. And you will have the case where the product which is formed can either release energy or absorb energy.

It can lead to a condition where there is change in temperature or color or shape of the particle, the size of the particle, but these would be different from the constituents or raw materials or reactants which were leading to the final product. So, the factors that influence the chemical reactions are temperature, pressure, the concentration of the reactants or you can have the surface area over which the reaction is taking place. In general, increase in temperature activates one or more number of reactant molecules and then they collide and initiate a reaction. They do not collide as per the word, they come near each other and then they are rippled. So, you have this attraction and repulsion and then there is a stabilization at a equilibrium position as we saw in the previous lecture and that leads to the stabilization of a new product.

Similarly, you can change pressure, surface area or concentration to get new products. Based on the internal energy during the chemical reactions, they are divided into two categories. Endothermic reactions or exothermic reactions. So, endothermic is what? You need some energy to break the bonds of the reactants, so that a new product can actually form. So, you need some energy that is endothermic.

This energy is acquired from the surrounding and mostly you need to heat the reactants so that this extra energy is supplied to them. And when a new material is formed, that means what? You have taken that energy and you have suddenly been able to stabilize a new state. For example, **A** reacting with **B** but giving **AB**. **AB** would be what? **AB** would be the case where they will have a lower energy. Lower energy means what? You will mark this condition by the drop in the temperature of the overall system.

These are typically the cases which you see in vaporization of water, photosynthesis, melting of ice or any other phase transitions in crystals also. Exothermic means what? You

need to take care of the case where the energy required to break the bonds of the reactants is lower than the energy released by the reaction. So, what will happen? You have excess energy. So, what will you do? You will release this energy and this energy is released to the surroundings in the form of heat and if that is happening, what will happen? You will have the rise in temperature of the overall system. And these are typically in combustion reactions, you will see in respirations or even various types of phase transitions.

Based on the uniformity of reactants or products in the reaction mixtures, they can be classified as homogeneous reactions or heterogeneous reactions. In homogeneous reactions, the process is the one where the reactants and the products are in the same chemical phase. Along with that, the reactants and the products are uniformly distributed throughout the reaction mixture. So, you have the case are in the same chemical phase. So, you have solid reacting with solid giving a solid or you have a liquid reacting with liquid giving a liquid.

In comparison, the heterogeneous reactions are the ones where the reactants and products are in the different chemical phase. Along with that, the reactants and the products are not uniformly distributed throughout the reaction mixture. So, gas or a gaseous phase reacting with a liquid phase giving a liquid or you can have a liquid solid giving liquid or a solid liquid giving a solid. So, these are heterogeneous reactions. In terms of how spontaneous they are, you can have certain classifications.

So, if you see, as we have seen, the driving force is that you need to minimize the energy. If you have a plot between Gibbs free energy and extent of reaction, you can have different regions. That means you have different regions of potential energy curve. If you are far away from minima, then you are at a case where the Gibbs free energy is less than zero. So, the reaction is moving towards the spontaneous change that can take it to the global minima or the lowest minimum energy state.

So, you will drive a spontaneous forward reaction. So, this is a spontaneous forward reaction. So, if delta G is zero, that means you are already at the equilibrium position. But if you are in the forward direction, then what will happen? You will find that if delta G is greater than zero, then the stable condition is not here. The stable condition is somewhere in the backward direction.

So, what will happen? You will have a condition where backward reaction is spontaneous. And as I said, the driving force of transformation or reaction to take place is the change in the Gibbs free energy. And you have driving force which is defined as minus the integration of initial to final Gibbs free energy with respect to T_g. And therefore, it is equal to minus G_f minus G_i. And the driving force of a spontaneous process is always positive.

The larger is the driving force, the more likely the transformation will take place. And what is the energy barrier for driving a chemical reaction? Can you think about it? Why reactions do not occur every time, whatever be the temperature, whatever be the pressure, whatever be the surface area, why the reactions are not always taking place? What is the energy barrier? So, consider an equilibrium reaction. You have gone from **A** to **B**, but the activation energy is the energy which is required that the reactants must have in order to form a product. So, what do I understand with that? So, reactant **A** and reactant **B**, they are different. Now if they have to react with each other, then you must ensure that they come together, interact, there is repulsive and attractive forces which act and finally, they form a stable **AB** combination.

For reactant A to react with B, you need to cross the energy barrier so that it can react with **B**. This is the energy barrier height and that is called the activation barrier. Once you give the heat, then reactant **A** can react with **B** to form a stable funnel product. You can also change the height of the barrier by changing the initial condition. For example, by giving additional energy to the reactant.

So, you have rather than starting from this point, what you can do is you can start the reactions from a slightly higher height. How you can do that? You heat these systems and you have actually given it higher energy. So, what will happen? The effective barrier height will come down and reactions would be faster. So, two necessary conditions, ΔG must be less than 0 or you should al So, ensure that the energy of a reaction is greater than the activation energy. And therefore, the activation energy clearly influences the rate of reaction.

What is this rate of reaction? The rate of reaction at a time t of a transformation is defined as $\frac{dF}{dt}$ where **F** transformation reaction, which is a function of time is defined as the number of atoms per unit volume in the final state at the time t to the total number of atoms per unit volume available for the transformation or reactions. So, let us say you said there are 100 atoms which can transform to **B**. But when you see that only transformation has been introduced in 80 of them. So, there is a fraction of total number of particles which would be reaching the final state and reacting with the next element or reactant. Therefore, what will happen? You will have the reaction rate k which would be a fraction of the total number of particles which reach the final state per unit time with respect to the total number of atoms which were available to take part in the reaction.

The unit of reaction rate is normally a function of time. So, if you allow the reaction to take place for longer period of time, you may have more reactions. If you reduce the time, the reactions would be much less. So, it is clear. The activation energy would control the way the reactions take place.

If the particles are not uniformly distributed, the reactions would be different. Therefore, distribution of particles in the energy states would define the rate reactions and finally the temperature would affect the reaction rates. If you see temperature in as the influential factor, then you can see it can be written in terms of the Arrhenius equation. So, you have the activation energy which is now going to be the main controlling factor in defining the rate reactions. You have the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

Where **k** is the reaction rate, **A** is the pre-exponential factor, $\mathbf{E_a}$ is the activation energy, **R** is the universal gas constant and **T** is the temperature.

We saw if the activation energy is comparatively low but the temperature is high, what will happen? Many atoms will get the kinetic energies to overcome this energy barrier and lead to the formation of product which will have a lower energy. If the activation energy is high compared with the thermal energies of the atoms, then what will happen? You will obviously have less number of particles crossing this barrier and hence you will have the reactions which would be much lower and transformation or reactions may actually be prohibited if the activation barrier heights are quite large and the thermal energies which you are providing are quite low. Now if you talk in terms of distribution of particles in various available energy states, how do they affect the reaction rates? The fraction of the particles with energies above a given energy is described by the Maxwell-Boltzmann distribution law which is given by:

$$N_i = \frac{N_0}{Z} G_i \, e^{-\frac{u_i}{K_B T}}$$

where **Z** is the partition function defined here. $\mathbf{u_i}$ is the energy of the particle, $\mathbf{N_i}$ is the number of particles which have energy $\mathbf{u_i}$, $\mathbf{N_0}$ is the total number of particles, $\mathbf{G_i}$ is the statistical weight of energy level $\mathbf{u_i}$, $\mathbf{K_B}$ is the Boltzmann constant and **T** is the absolute temperature of the system. From the Maxwell-Boltzmann law, the fraction of particles with energies equal or greater than a given energy can be calculated using the partition function.

And by simple mathematics, you can find that the fraction of molecules which have enough thermal energy to overcome the energy barrier **F*** would be equal to $\frac{N_i}{N_0}$ and that would turn out to be $\frac{e^{-\frac{u_i}{K_B T}}}{Z}$. **Z** is what? The partition function, please remember. So, if **u** activation $\gg$ $\mathbf{K_B T}$, the fraction is small and transformation would be much lower. But if the value of activation energy is less or much less than k beta T, the fraction is very high and transformation would be much higher. If you again go to the Arrhenius theory where temperature would al So, be playing a critical role, the n you know from the Arrhenius equation $k = Ae^{-\frac{E_a}{RT}}$ and we have seen earlier how this reaction is driven.

You should understand for endothermic reactions, heat is absorbed. That means T increases and rate of reaction al So, increases. In comparison, for exothermic reactions, the heat is released, T increases and it means the rate of reaction would decrease. From the transition state theory where al So, you are talking about the effect of temperature, k the reaction rate is k beta by h into T into e raised to the power of change in Gibbs free energy by RT. Now according to this transition state theory, the reaction rate is proportional to the probability of forming the activated complex which is dependent on the activation energy and temperature.

As the temperature increases, the probability of forming the activated complex increases and leading to the increase in the reaction rate. So, what we have seen today that transformations can occur through chemical reactions. They could occur due to phase transformations or diffusions. At constant temperature and pressure, transformations always occur spontaneously in the direction of decreasing Gibbs free energy. Driving force is a concept which should be understood is a positive quantity used for knowing the probability of occurring a transformation or reaction.

The activation energy is the minimum kinetic energy that reactants must have in order to form products. And the factors which influence the rate reactions are activation energy, temperature and molecular distribution of particles. The concepts of phase transformation and diffusion was only introduced in today's lecture. In coming weeks, we would be spending lot of time on these topics separately and hence we have not discussed these two topics in details in this lecture. You will have dedicated lectures coming on these topics very soon.

You can refer to these books for further understanding and I thank you once again for attending the fourth lecture of week 4. Thank you very much.