Diffusion in Multicomponent Solids
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Lecture-01
Introduction to the course and Thermodynamics Refresher

Welcome to the first class on diffusion in multi-component solids. My name is Kaustubh Kulkarni and over next 12 weeks we will go over in-depth treatment of various aspects of one of the most important phenomena that occurs in materials, that is, diffusion in solids, more particularly diffusion in multi-component solids. So, to start with, first let us ask the question- What do you mean by diffusion?

Student: Movement of atoms due to gradient in either concentration or chemical potential

Professor: Okay, so let us define diffusion here.

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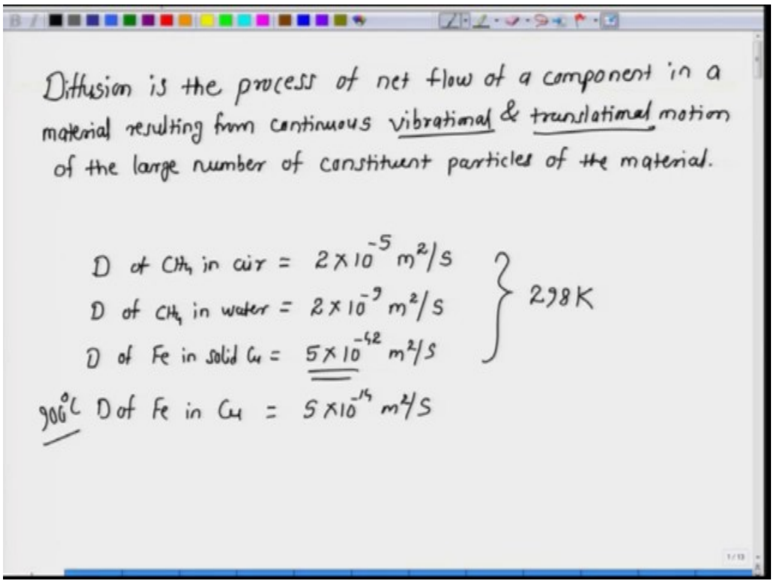

Diffusion is the process of net flow of a component in a material resulting from continuous vibrational & translational motion of the large number of constituent particles of the material.

$$\left.\begin{aligned} D \text{ of } CH_4 \text{ in air} &= 2\times10^{-5}\ m^2/s \\ D \text{ of } CH_4 \text{ in water} &= 2\times10^{-9}\ m^2/s \\ D \text{ of Fe in solid Cu} &= \underline{\underline{5\times10^{-42}}}\ m^2/s \end{aligned}\right\}\ 298K$$

$$\underline{900^\circ C}\quad D \text{ of Fe in Cu} = 5\times10^{-15}\ m^2/s$$

So that is more or less correct but in our context let us define diffusion more precisely. Diffusion is the process of net flow of a component in a material resulting from continuous vibrational and translational motion of the large number of constituent particles of the material. So, it is basically the transport phenomena occurring in materials and it is mainly based upon or mainly guided by the thermal fluctuations that occur in the particles of the material.

As you know, at any temperature greater than zero Kelvin the particles of the material are continuously under motion. There are different types of motions: vibrational, rotational, and translational. It is very easy to see in the liquid. All of you know about Brownian motion. So, that is basically because of the translational motion that occurs in the molecules of the liquid. In solids, the atoms or molecules really do not leave their positions. So they don't undergo the translational motions but they are continuously vibrating around their mean position. In solids there are fixed lattice sites and each atom or molecule is vibrating around its mean position. The energies of these vibrations are continuously changing because the thermal distribution is changing and one particular vibration may be so energetic that the atom can actually jump off its original site and go into the next lattice site. So in effect, this is called an atomic jump or atomic hopping.

In effect, because of this jump the atom has travelled a distance equal to the one atomic spacing. So, this has resulted into the net displacement of the atom and that is assisted by the thermal vibrations of the atom. That is why we call an atomic jump as the unit step of diffusion in solid. This diffusion is manifested very commonly in lot of intermixing phenomena that we usually or daily observe. One good example is if you drop a drop of ink in water you will see that the ink will slowly spread into the water and ultimately the whole water will take the colour of ink and that is basically because of the process of diffusion.

Of course, when you put the drop of water it is assisted also by the gravitational forces. The ink will initially try to go down but the sideways spreading of the ink is mainly because of the diffusion. You can also observe it in gases. For example, if you spray some perfume in one corner of the room, after sometime you can smell it in another corner. That is again because the molecules of the perfume are spreading by the process of diffusion in air.

Again, there may be air currents which will assist the spreading of that perfume but even in absence of these air currents, ultimately the perfume will reach from one corner of the room to the other because of diffusion through the air. But it is not so obvious in solids. And the main reason is that the diffusion process in solids is very-very slow. As an example let us compare the various diffusivities in different materials or different media.

For example, the diffusivity of methane in air is around 2×10^{-5} m^2/sec. The diffusivity of methane in water is around 10^{-9} m^2/sec. If you look at diffusivity, let us say of iron in solid copper, you find it is around 10^{-42} m^2/sec. All these values are at 298 Kelvin. So, you will notice that the diffusivity of iron in solid copper is ridiculously low, much lower compared to that in air or water, these general diffusivities in air or water.

Even if you consider at 900 °C, which is very close to the melting point of copper, diffusivity of iron in copper comes out to be around 10^{-14} m^2/sec. Even at 900 °C, diffusivity in solid copper is around 5 order of magnitude slower than diffusivity of methane in water and it is 9 order of magnitude slower than diffusivity of methane in air!!

Let us talk in terms of the diffusion distances which is more easy to see.

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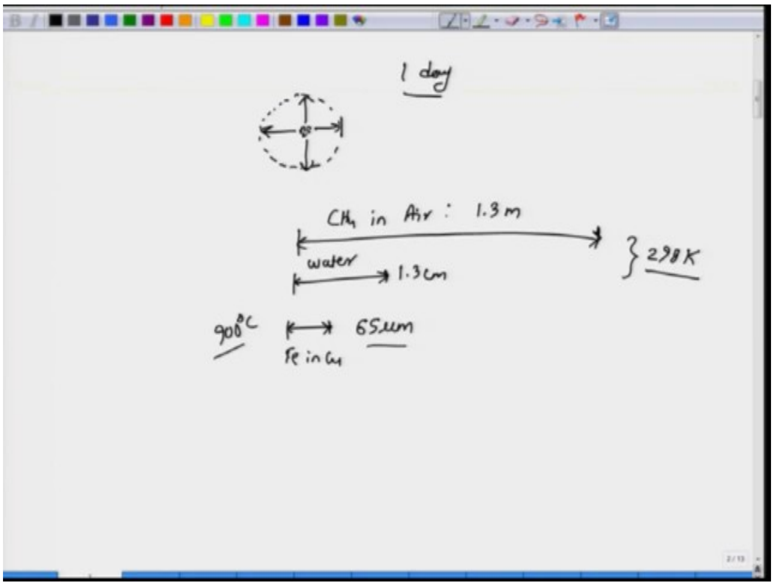

Let us say if we have an ensemble of particles accumulated at a point and we let all the particles to diffuse and then observe how much diffusion has progressed in certain time. Let us say in one day. As soon as we allow the particles to diffuse, the particles will diffuse randomly in all directions. If we consider diffusion of methane in air and if we track the front as a function of time, in one day this front would have progressed about 1.3 meter. Whereas if you consider methane in water this would have progressed only about 1.3 centimetre. These two examples are considered at temperature of 298 Kelvin. But if you consider iron in copper and that also at 900 °C which is much higher temperature, we will see that the diffusion front has progressed only around 65 micron with the diffusivity values that we listed earlier.

So the diffusion in solid is really very-very slow and this sluggishness is what makes it even more interesting and more critical in terms of its applications. Because diffusion is the process that controls most of the phase transformations in solids, like for example, precipitation. When you consider age hardening, the precipitation is important. So, the time required for the process is ultimately guided by the diffusion. Also, if you consider the homogenization treatments, again they are guided by diffusion. Sintering - these days people are talking about blended elemental powder metallurgy. In this, the powders are mixed in pure form and the in-situ alloying takes place during the sintering itself and that alloying takes place again mostly by solid state diffusion. And so if we want to understand and control these different processes, then it is important to understand diffusion in solids. More importantly, most of these materials which are used in practice they are based upon multi-component systems, which means these systems or these materials consist of three or more components.

It is very important to study diffusion particularly in multi-component solids. So, in this class we will talk about these different aspects of diffusion and every time I will also stress upon multi-component diffusion. So, we will treat binary diffusion as well as will extend the treatment to multi-component diffusion. When we study diffusion, there are couple of approaches through which we study these diffusion processes.

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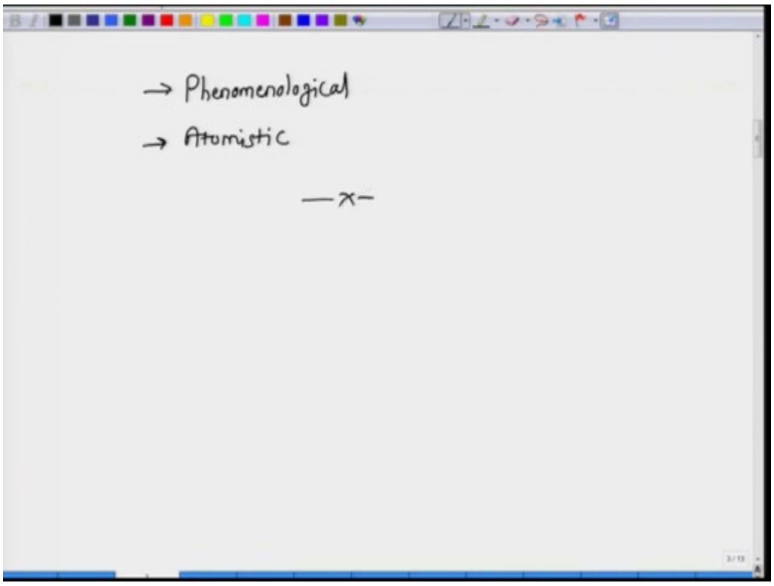

→ Phenomenological

→ Atomistic

—x—

The first one is referred to as phenomenological. As the name suggests it is phenomenological. What do you mean by phenomenological? Anybody?

Student: Based on some phenomena.

Professor: Yeah, right. As the name suggests, it is based upon observed phenomena, for example, Fick's law. It is based upon the observed phenomena that the flux is proportional to the concentration gradient and the constant of proportionality is diffusivity. The phenomenological approach is mainly based upon the macroscopic or microscopic observations of different phenomena and the diffusivity is an important parameter which helps us with this approach, which helps us to predict the evolution of concentration profiles in different systems.

The phenomenological approach is practically very important because the diffusivity database help us to actually model the different processes like homogenization or precipitation. The second approach is atomistic. This is more theoretical. As I mentioned earlier the diffusion is essentially guided by the thermal fluctuations of the atom. So, if we try to relate the atomic jump frequencies and thermodynamic factors with the diffusivity, that is done by the atomistic approach.

This is more theoretical but it helps us to establish physical significance of the diffusivities that we define in the phenomenological approach. We will study both of them in the first half.

We will talk mostly about the phenomenological approach and then in major part of the second half we will go through the atomistic view point of the diffusion.

So, we saw what is diffusion? Now, why diffusion occurs? What is the cause behind diffusion process?

Student: Chemical potential, Gradient.

Professor: Basically diffusion occurs because system naturally wants to move towards an equilibrium state. So, if the system is in non-equilibrium state it wants to move towards an equilibrium state. Diffusion occurs because the system wants to decrease its Gibbs free energy or it wants to increase its entropy. So, the diffusion is essentially accompanied by decrease in Gibbs free energy or increase in entropy.

Basically the diffusion is driven by these thermodynamic reasons, and it is very important to go over some of the thermodynamic concepts. So, in the first few lecture of this class, we will just have a refresher of the thermodynamics and I will try to link it to the diffusion wherever it comes.

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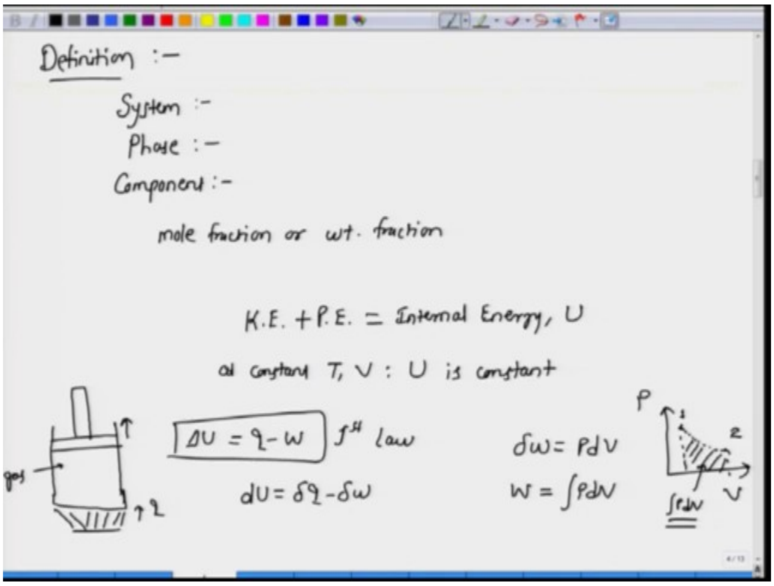

Definition :-

System :-

Phase :-

Component :-

mole fraction or wt. fraction

K.E. + P.E. = Internal Energy, U

at constant T, V : U is constant

$\boxed{\Delta U = q - W}$ 1st law

$dU = \delta q - \delta w$

$\delta w = PdV$

$W = \int PdV$

The thermodynamics basically starts with some of the definitions. You guys already know some of it. So, we define a system. What is a system?

Student: Matter under observation.

Professor: Right. So, any matter or set of materials under thermodynamic observation is the system. Then system may be composed of one or more phases. A phase is nothing but a part of the system which is physically distinct from the other parts of the system. So, essentially a phase is always distinguished by distinct physical boundary. So there will be a physical boundary between two different phases. And then what is a component?

We will talk about components a lot. So, component is essentially the elements or the chemical species that constitute the system. The composition of the system or of a phase is expressed in terms of the relative amounts of different components in the system. And some of the units are mole fraction or weight fraction, these give the relative amounts. So, when we talk about system, as I already said, any system is composed of large number of particles and these particles are continuously undergoing thermal motions, vibrations, rotational or the translational motions.

Because of these motions the system possesses some kind of kinetic energy. It is another property of these particles. Any two particles will attract each other if they are a little apart and if you try to squeeze them together they will try to repel each other. These attractive and repulsive forces between particles also give rise to some potential energy in the system. So, any system possesses kinetic energy and potential energy. Kinetic energy is because of the thermal motions of the atoms or particles and the potential energy is because of the relative positions of the particles within the system.

This total energy is referred to as internal energy - U and we know, at constant temperature and volume, internal energy of the system is constant. Now, the system can undergo change in internal energy if it exchanges energy with the surroundings and the energy exchange can be in two forms - one is heat, second is work. Let us consider a simple system of gas enclosed in a cylinder which is closed by a frictionless piston. We have gas inside the cylinder, the three walls of the cylinder are rigid and the fourth one that is the piston is movable. So it can easily slide up and down.

If we try to add heat to the system, what happens?

Student: Gas will expand and piston will move.

So it is easy to see if we add heat, the gas tends to expand. As the gas tends to expand, the pressure builds inside, the pressure inside becomes higher than the outside pressure and so the gas will push the piston outside and this will continue until when? Until the inside pressure becomes equal to the outside pressure. So, if you heat a little bit and take away the heat, the piston will move until the inside pressure becomes equal to the outside pressure because that is when the mechanical equilibrium is established.

And if the outside temperature is same as the inside temperature of the gas then the thermal equilibrium is established. The third type of equilibrium is the chemical equilibrium - when the chemical potentials are uniform. So when you have these three equilibria, the system is set to be in thermodynamic equilibrium. All the efforts of thermodynamics is to define the state of equilibrium and we need what is called as state variables to define the state of the system.

So, like temperature, volume, pressure - these are the state variables. Internal energy is also a state variable. Now, let us come back to this system. When we add little heat, q, the gas will expand, as the gas expands it is doing some work on the surroundings. So, with the addition of some heat - q, some of this heat has been utilized to perform work and the remaining is utilized to increase the internal energy of the system. This is the statement of the first law of thermodynamics.

$$\Delta U = q - w$$

If we write in terms of very small changes we write:

$$dU = \delta q - \delta w$$

dU is the small differential change in internal energy, δq is the small heat added, δw is the small work performed by the system. We write d for differential of U, but we write δ for q and w, the reason being -U is a state function but q and w are not. For example, δw is given by PdV. If we have to find work done during the process, we need to integrate.

Let us analyze the process on a P-V diagram. If we change the state from $1 \rightarrow 2$ along certain path, the work done will be given by area under this curve:

$$w = \int PdV$$

And so we see if you would have taken a different path, the work done would have been different to cause the same change of state. So, this is a path function. The work and heat are the path functions whereas internal energy is a state function. So, that is another way to state first law of thermodynamics that internal energy is a state function.

It is possible to perform only work without adding heat. Joule did that experiment, he performed different types of works in an adiabatically contained water, adiabatic system means heat cannot enter or leave the system. So, no heat exchange with the surroundings, but work can be done. So, you perform different types of works. He rotated a paddle wheel inside water then he passed electric current, electrical work, and he observed that to cause the same change in state of the water, he needs to do the same amount of work irrespective of what type of work has been performed.

Now, same state change can also be brought about by addition of heat. So, he concluded that heat and work they are basically interchangeable and then internal energy becomes the state function. So, this is the first law of thermodynamics. So, it helps us to understand how the internal energy will change based upon the heat and work effects. But still there are certain limitations.

So, what are these limitations of first law? So, basically it just states that:

$dU = \delta q - \delta w$

But it does not predict which way the reaction will proceed. For example, imagine you are driving a car. So, the car has a kinetic energy and suddenly you see somebody in front and you have to apply the brakes. What happens when you apply the brakes? The car stops. So, the kinetic energy of car has been converted into potential energy mostly of the brake shoes.

Now, can you convert potential energy of the brake shoe back to the kinetic energy so that as soon as you release the brake, the car will start moving? Is it possible? No, we know that the reverse process is not possible, but the first law does not have a problem with that as long as you satisfy:

$$dU = \delta q - \delta w$$

That is all it wants. But we know some of the processes can take place only in one direction and not in the other direction.

These are basically all the natural processes which are irreversible process. The direction cannot be predicted. Also what is that limit on the work to be done? That is not predicted by the first law. And what is the degree of irreversibility? So, if you start certain reaction, it starts proceeding in certain direction, at what point it will stop? Will it progress to the end or will it stop in between? The first law does not have answer to that. So, we have to talk about second law of thermodynamics. We will talk about it in the next class.