Diffusion in Multicomponent Solids
Professor Kaustubh Kulkarni
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur Bangalore
Lecture 03
Application of Second Law and Illustration of Intermixing as Irreversible process

So, welcome back. In last class we went over the first law and second law of thermodynamics. In this class, we would like to go over the application of second law in order to analyze the irreversible processes and specifically we would see how the intermixing or interdiffusion becomes an irreversible process because it causes increase in entropy.

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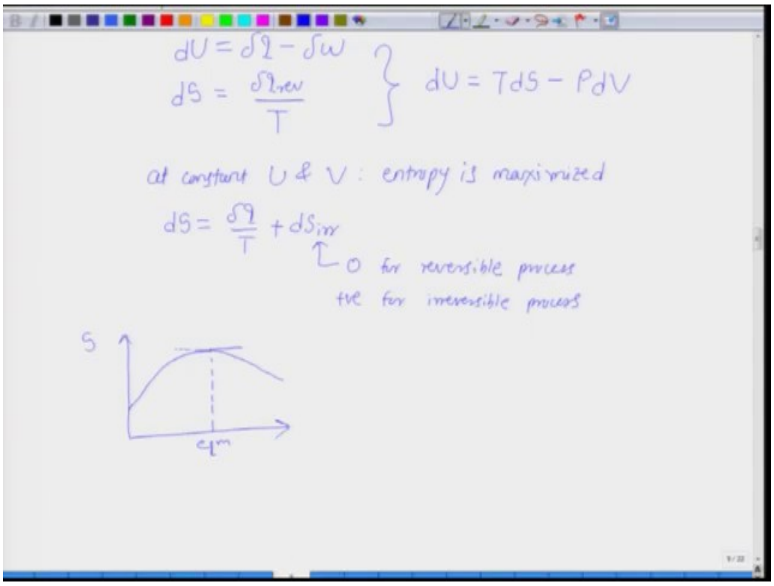

$$\left.\begin{array}{l} dU=\delta q-\delta w \\ dS=\dfrac{\delta q_{rev}}{T} \end{array}\right\} dU=TdS-PdV$$

at constant U & V : entropy is maximized

$$dS=\frac{\delta q}{T}+dS_{irr}$$

0 for reversible process
+ve for irreversible process

So, just a quick refresher. The first law defines the state function called internal energy in terms of heat effects and work effects. And the second law defined another state function called entropy which is basically $\frac{\delta q_{reversible}}{T}$, heat absorbed at constant temperature during a reversible process divided by the temperature. So, the combined statement of first and second law leads to the equation of state, which tells:

$$dU = TdS - PdV$$

So, the second law helped us to define the criteria for equilibrium in terms of entropy or in terms of internal energy. In terms of entropy we say, at constant U and V, entropy is maximized. At constant internal energy and volume, the equilibrium state corresponds to the maximum entropy. So obviously, any process would occur if it causes an increase in entropy or during a reversible process the entropy remains constant. We can also write during a small change of state:

$$dS=\frac{\delta q}{T}+d\,S_{irreversible}$$

in which case δq is the heat absorbed during the process and $d\,S_{irreversible}$ is some quantity which is either 0 for a reversible process or has a positive value for an irreversible process.

So, what this basically tells me is that if during an irreversible process the heat absorbed is lesser compared to a reversible process. Infact, the maximum heat is absorbed during a reversible process and correspondingly the maximum work is done during a reversible process, which also tells me if we note the definition of entropy carefully, that:

$$dS=\frac{\delta\, q_{reversible}}{T}$$

which means, we can analyze the entropy changes considering the heat effects only during the reversible process.

But, entropy is a state function. The entropy change for a given process is always same whether the process is reversible or irreversible, because S does not depend upon the path by which the process is carried out. And because of that, we can replace any irreversible process with equivalent sequence of reversible processes and analyze the entropy change for the reversible processes. So we can know the entropy during an irreversible process. This basically also helps us to define the degree of irreversibility of the process.

Let us consider an example. What are different irreversible processes? Diffusion is one irreversible process. Most of the natural occurring processes are in fact irreversible processes. So, there will be some entropy production. So, to what extent any process will continue? Once the process starts, to what extent it will continue? Till there is an increase in entropy. If we track the entropy as the process occurs, the process starts because there is an increase in entropy. As the process occurs there is an increase in entropy and at some point the entropy reaches maximum. At this point, the process will stop because that is the equilibrium state. Because if the process continues beyond this point, it will cause a decrease in entropy which is not allowed by the second law. So, depending upon the degree of irreversibility, the magnitude of this $d\,S_{irreversible}$ will change. So, for example, if the process is reversible then

$dS_{irreversible} = 0$

So, there is no production of entropy. If the process is irreversible, then $dS_{irreversible}$ has some positive value and we say that entropy is produced because of the irreversibility of the process. Similarly, another extreme is when there is no heat effect and correspondingly there is no work done and so entire change in entropy appears as the production of entropy - dS is equal to $dS_{irreversible}$. This is an extreme case of irreversibility. Any other example of extreme irreversibility or extremely irreversible process?

Student: Paste out of a toothpaste

Professor: So, the expansion of an ideal gas against vacuum is an extremely irreversible process, because that expansion is against 0 pressure. So, there is no work done, no heat effects and so in this case dS is equal to $dS_{irreversible}$.

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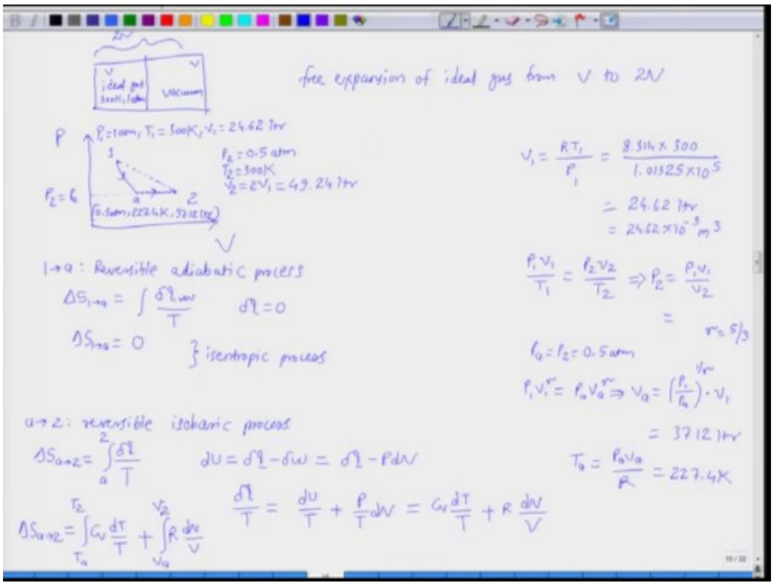

free expansion of ideal gas from V to 2V

$P_1 = 1atm, T_1 = 300K, V_1 = 24.62$ ltr

$P_2 = 0.5$ atm

$T_2 = 300K$

$V_2 = 2V_1 = 49.24$ ltr

$1 \to a$: Reversible adiabatic process

$\Delta S_{1\to a} = \int \frac{\delta q_{rev}}{T}$ $\quad \delta q = 0$

$\Delta S_{1\to a} = 0$ } isentropic process

$a \to 2$: reversible isobaric process

$\Delta S_{a\to 2} = \int_a^2 \frac{\delta q}{T}$ $\quad dU = \delta q - \delta w = \delta q - PdV$

$\frac{\delta q}{T} = \frac{dU}{T} + \frac{P}{T}dV = C_v\frac{dT}{T} + R\frac{dV}{V}$

$\Delta S_{a\to 2} = \int_{T_a}^{T_2} C_v\frac{dT}{T} + \int_{V_a}^{V_2} R\frac{dV}{V}$

$V_1 = \frac{RT_1}{P_1} = \frac{8.314 \times 300}{1.01325 \times 10^5}$

$= 24.62$ ltr

$= 24.62 \times 10^{-3} m^3$

$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Rightarrow P_2 = \frac{P_1V_1}{V_2}$

$=$

$\gamma = 5/3$

$P_a = P_2 = 0.5$ atm

$P_1V_1^\gamma = P_aV_a^\gamma \Rightarrow V_a = \left(\frac{P_1}{P_a}\right)^{1/\gamma} \cdot V_1$

$= 37.12$ ltr

$T_a = \frac{P_aV_a}{R} = 227.4K$

Let us try to analyze that. The problem is, if an ideal gas which is say at 1 atmospheric pressure and 300 Kelvin, expands against vacuum to double its volume, what is the entropy produced? Consider a container whose total volume is 2V. And let us say this container is divided into 2 compartments with a thin wall. Each compartment has a volume V. In one of the compartments, I have an ideal gas which is at 300 Kelvin and 1 atmospheric pressure, the second compartment is vacuum.

At some instant I allow the wall to move freely without friction then what should happen? Because of the pressure difference, the gas will tend to expand and the expansion will continue until the gas occupies the volume of entire container 2V. The gas will freely expand against vacuum from V to 2V. So, this is the free expansion of ideal gas from V to 2V. We have to analyze what is the entropy change during this process.

Let us plot this process on a P-V diagram. So, state 1 changes to state 2 by an irreversible process, state 1 is basically 1 atmosphere and 300 Kelvin, state 2 we know the volume has been doubled. So, V_2 is equal to $2V_1$. Now, since there is a free expansion, there is no work done, there is no external heat. So, the internal energy of ideal gas does not change. Internal energy of an ideal gas is a function of only temperature. Since, there is no change in internal energy, there is no change in temperature.

T_2 remains 300 kelvin. So, how do we evaluate the entropy change for this process? This is an irreversible process that is why we denote this by a dotted line. So, we have to replace this with a sequence of reversible processes which would bring about the same change of state. So, you can select any combination of reversible processes. Here, let us say the first process is from $1 \rightarrow a$. So this is basically a reversible adiabatic process and the process continues until the pressure reaches the value P_2.

So, P_2 is equal to P_a, let us call this state a, and then the second step is the reversible isobaric process from $a \rightarrow 2$. So, $1 \rightarrow a$ is a reversible adiabatic process and $a \rightarrow 2$ is a reversible isobaric process. So, let us try to figure out that P, T and V conditions for each of these states $1, a$ and 2. We know P_1 and T_1, so V_1 is obviously $\frac{RT_1}{P_1}$ if we are assuming 1 mole of ideal gas. So,

$$V_1 = \frac{8.314 \times 300}{1.01325 \times 10^5} = 24.62\, ltr$$

which is same as $24.62 \times 10^{-3} m^3$.

And V_2 is $2V_1$. So, it is 49.24 liters. Now, as we go from state $1 \rightarrow 2$, we can write:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Since,

$$T_1 = T_2$$

we can evaluate P_2 as

$$P_2 = \frac{P_1 V_1}{V_2}$$

and if we substitute we get P_2 is equal 0.5 atmosphere. Now, we need to know the conditions at a, we know that $a \to 2$ is an isobaric process. So, basically P_a is equal to P_2 which is 0.5 atmosphere and when $1 \to a$ is an reversible adiabatic path, the equation for which we know:

$$P_1 V_1^{\gamma} = P_a V_a^{\gamma}$$

So, we have:

$$V_a = \left(\frac{P_1}{P_a}\right)^{1/\gamma} V_1$$

$$\gamma = \frac{C_P}{C_V}$$

C_P is heat capacity at constant pressure and C_V is heat capacity at constant volume. If we assume monoatomic ideal gas, then $C_P = 2.5R$ and $C_V = 1.5R$

$$\gamma = \frac{5}{3}$$

With that V_a comes out to be 37.12 liters. And using again ideal gas law, we can evaluate T_a:

$$T_a = \frac{P_a V_a}{R} = 227.4\,K$$

So, now we have evaluated each of the states. We can now try to analyze the entropy changes. Let us first consider the process $1 \to a$, which is reversible adiabatic process. So, we can write the entropy change for $1 \to a$:

$$\Delta S_{1 \to a} = \int \frac{\delta q_{reversible}}{T}$$

And since this is an adiabatic process, we know:

$$\delta q_{reversible} = 0$$

So,

$\Delta S_{1\rightarrow a}=0$

So, for any reversible adiabatic process, the entropy change is 0. And that is why all the reversible adiabatic processes are also referred to as isentropic processes.

So, the entropy change from $1\rightarrow 2$ is only because of this process $a\rightarrow 2$. Let us try to calculate that.

$$\Delta S_{a\rightarrow 2}=\int_{a}^{2}\frac{\delta q_{reversible}}{T}$$

Now, if I apply first law for this process:

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

This is a reversible process. So,

$$\frac{\delta q}{T}=\frac{dU}{T}+\left(\frac{P}{T}\right)dV$$

We know:

$dU=C_V dT$

and

$P=\frac{RT}{V}$

Using the above two equations:

$\frac{\delta q}{T}=\frac{C_V dT}{T}+\left(\frac{R}{V}\right)dV$

So:

$$\Delta S_{a\rightarrow 2}=\int_{T_a}^{T_2}\frac{C_V dT}{T}+\int_{V_a}^{V_2}\left(\frac{R}{V}\right)dV$$

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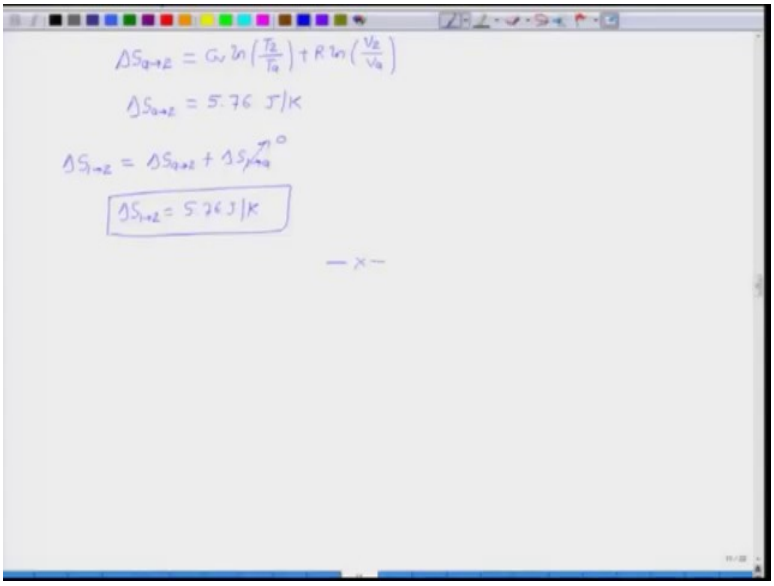

$$\Delta S_{a\to 2} = C_v \ln\left(\frac{T_2}{T_a}\right) + R\ln\left(\frac{V_2}{V_a}\right)$$

$$\Delta S_{a\to 2} = 5.76 \ J/K$$

$$\Delta S_{1\to 2} = \Delta S_{a\to 2} + \cancelto{0}{\Delta S_{1\to a}}$$

$$\boxed{\Delta S_{1\to 2} = 5.76 \ J/K}$$

— x —

So, we have basically;

$$\Delta S_{a\to 2} = C_V \ln\left(\frac{T_2}{T_a}\right) + R\ln\left(\frac{V_2}{V_a}\right)$$

We know all the values of T_a, T_2, V_a, V_2. On substitution these values:

$\Delta S_{a\to 2} = 5.76\, Joule/Kelvin$

So, the entropy change for the process $1 \to 2$ is the summation of that for $1 \to a$ and that for $a \to 2$. We know for $1 \to a$ it is 0 and so:

$\Delta S_{1\to 2} = 5.76\, Joule/Kelvin$

This is basically the entropy change associated with free expansion of ideal gas to double its volume. Now we would like to analyze the process of intermixing in this context, so I will change this problem a little bit.

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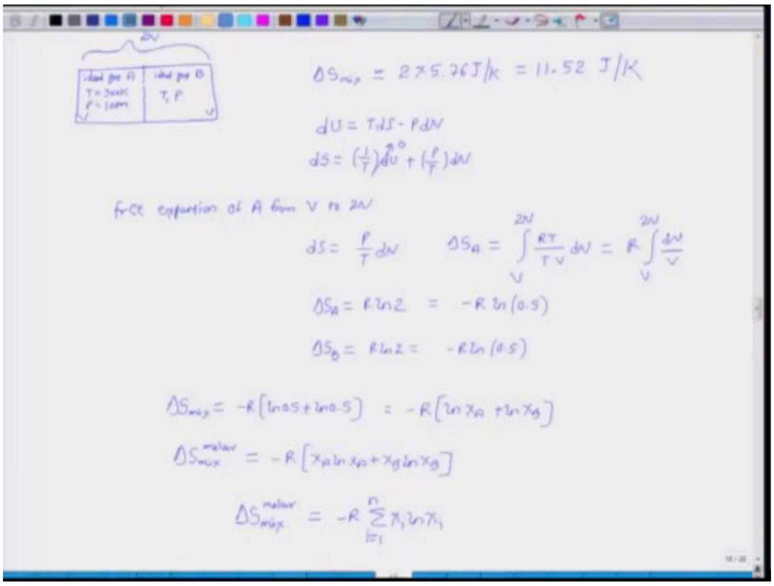

$$\Delta S_{mix} = 2 \times 5.76 \, J/K = 11.52 \, J/K$$

$$dU = TdS - PdV$$

$$dS = \left(\frac{1}{T}\right)\cancel{dU}^{0} + \left(\frac{P}{T}\right)dV$$

free expansion of A from V to 2V

$$dS = \frac{P}{T}dV \qquad \Delta S_A = \int_V^{2V} \frac{RT}{TV}\,dV = R\int_V^{2V}\frac{dV}{V}$$

$$\Delta S_A = R\ln 2 = -R\ln(0.5)$$

$$\Delta S_B = R\ln 2 = -R\ln(0.5)$$

$$\Delta S_{mix} = -R[\ln 0.5 + \ln 0.5] = -R[\ln X_A + \ln X_B]$$

$$\Delta S_{mix}^{molar} = -R[X_A \ln X_A + X_B \ln X_B]$$

$$\Delta S_{mix}^{molar} = -R\sum_{i=1}^{n} X_i \ln X_i$$

Consider again the same container with a thin wall in between, the total volume of the container is $2V$ and the wall divides the container into two compartments of equal volume each of V. Now, instead of vacuum in 1 compartment, I have two different gases in two compartments. Let us say the first compartment has an ideal gas A and the second compartment has another ideal gas B. Both are let us assume monatomic ideal gases. Both are at same temperature, let us say T is equal to 300 Kelvin and P is equal to 1 atmosphere, the same temperature and pressure in the other compartment. So, there is a little bit of change in the problem. Now I have two gases in two compartments. And now at some instant suppose I remove this thin wall then what should happen? We know by intuity that A and B will start intermixing with each other or they will start diffusing into each other and as the time progresses the inter diffusion will progress and the equilibrium state will be achieved when there is a complete intermixing.

If you look at the individual gases A and B, what is the initial condition? Consider gas A, the initial condition is it is occupying volume V and the final condition after intermixing is it is occupying volume 2V. So, before removing the wall the ideal gas A had only volume V to occupy. After removing the wall now, ideal gas has volume 2V to occupy. So, the ideal gas A will expand freely from volume V to 2V.

This is similar to the problem that we solved, the free expansion of ideal gas. But there is one more process here, the ideal guess B will also expand from V to 2V and so the total entropy change because of intermixing will be 2 times. We have seen the change in entropy because of free expansion of ideal gas to double its volume was 5.76 joules per Kelvin. So, that comes out to be around 11.52 joules per Kelvin.

You can also analyze this process in a slightly different way, we know the equation of state in terms of U or S, so we know:

$$dU=TdS-PdV$$

So, if we write in terms of S, we write:

$$dS=\left(\frac{1}{T}\right)dU+\left(\frac{P}{T}\right)dV$$

Now, if you consider each of the gas, so let us say free expansion of ideal gas and we know that the free expansion is associated with 0 work and so there is no change in internal energy. So this term is basically 0. Hence,

$$dS=\left(\frac{P}{T}\right)dV$$

If we substitute for P:

$$P=\frac{RT}{V}$$

$$\Delta S_A=\int_V^{2V}\left(\frac{RT}{TV}\right)dV=\int_V^{2V}\left(\frac{R}{V}\right)dV=Rln2=-Rln(0.5)$$

We can apply the same procedure for free expansion of B, we find out:

$$\Delta S_B=Rln2=-Rln(0.5)$$

So, the total entropy change for intermixing would be:

$$\Delta S_{mix}=-R(\ln 0.5+\ln 0.5)$$

And if we notice the mole fractions of A and B after intermixing, there are total 2 moles 1 mole of each A and B total 2 moles, so the mole fraction of each is 0.5. So, we can write it in terms of mole fraction :

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

This is the entropy change for 2 moles of the gas. The mixture contains 2 moles of the ideal gas A and B, so if we divide by 2 that will give me the molar entropy of mixing.

$$\Delta S_{mix}^{molar} = -R(0.5\ln 0.5 + 0.5\ln 0.5)$$

We can write it as:

$$\Delta S_{mix}^{molar} = -R(X_A \ln X_A + X_B \ln X_B)$$

This equation looks familiar, I hope you guys have studied this before. So, we have the equation for entropy of mixing for ideal gases. This is applicable for mixing of any number of ideal gases. If we have let us say n number of gases:

$$\Delta S_{mix}^{molar} = -R\sum_{i=1}^{n} X_i \ln X_i$$

And obviously, we can see this is a positive quantity. An intermixing of ideal gases is accompanied by increase in entropy and that is why the intermixing becomes an irreversible process. So, we considered this for ideal gases, mixing of ideal gases. What would change if I consider mixing of real gases? Obviously, the entropy of mixing will not be same as we calculated for ideal gases, why? First of all in ideal gas, we know that there are no interactions between the particles, but in real gases there are interactions between the particles.

So, any two particles will attract each other if separated by some distance and if you try to squeeze them together they will repel each other and because of these attractive and repulsive forces, there are interactions. So, if you try to expand real gas, it will also require work to be done against this inter particle forces. So, there is a work and heat effect involved. We analyzed entropy so far in terms of the heat effects at constant temperature. Now, let us try to see what is the physical significance of entropy? Can anybody tell me what does entropy physically mean?

Student: Physically entropy means randomness.

Professor: So entropy is basically randomness in the system. More the order in the system, lesser will be its entropy.

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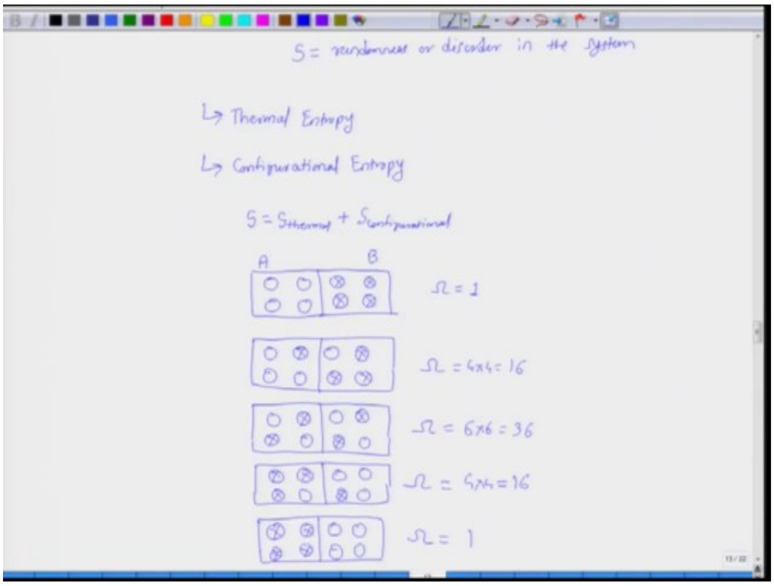

S = randomness or disorder in the system

↳ Thermal Entropy

↳ Configurational Entropy

$S = S_{thermal} + S_{configurational}$

So, the physical significance of entropy is randomness or disorder in the system. Now, this randomness or disorder is on account of two factors. The first factor is called thermal entropy and the thermal entropy arises because of randomness in the distribution of available energy among the constituent particles. You know that the constituent particles are continuously undergoing some motions - rotational, vibrational and translational. And with time the energy of individual particle is changing, but as long as the temperature and volume is constant the total internal energy is constant. But, the way this total energy is distributed among these particles is continuously changing. Now that means, at any given instant there are large number of ways in which the available internal energy can be distributed among the constituent particles and this gives rise to what is called as thermal entropy.

The second part is the configurational entropy and this is because of the different number of ways in which the constituent particles can be arranged in space. This can be easily seen in solids. In solids basically the atomic positions are fixed. So, if you have only a pure element, let us say there are no vacancies, then there is only one way in which all the atoms of A can be arranged on the given number of lattice sites. We are assuming that all the atoms of A are the same and indistinguishable. But suppose if I add a few atoms of B or if I replace few atoms of A with another type of atoms B. Then now, I have again a large number of ways in which this few atoms of B can be distributed among the total number of lattice sites. This is called the configurational entropy. The total entropy of the system is the sum of thermal entropy and configurational entropy.

Now with this, we can also see the intermixing process in, for example, solids. Suppose if I keep two solids in contact with each other, let us say solid A and solid B and let us consider only four atoms in each block. So, atoms A and atoms of B are denoted by this cross. If I put them in contact with each other, what should happen? We know that A and B will start diffusing into each other. So over the time, more and more atoms will interchange. So, let us say there is at first only one atom interchange. One atom of B comes into A and one atom of A goes into B.

Initially before this intermixing started, in how many number of ways these atoms can be arranged? There is only one way because all the A atoms are indistinguishable, all the B atoms are indistinguishable amongst themselves. So, there is only one number of way in which these atoms can be arranged. Now, after the interchange, how many configurations are available? There are four number of ways in which B can be arranged on side of A and one atom of A can be arranged in four different ways on the sides of B. So there will be total 4 times 4 equal to 16 number of ways.

If one more atom interchange, so now there are two atoms of B in A and two atoms of A in B. So, what are the different number of configurations? So on each side, there are 6 different configurations and if you combine it with the other side, there will be 6 times 6 is equal to 36 different ways. Now, if 3 atoms interchange. Again, each configuration is possible four times. So, 4 times 4, 16 different ways. When all of the atoms interchange, we have pure B on left, pure A on right, so there is only one way in which this can be arranged.

So, if you see as the interdiffusion starts we go from first to second configuration, the entropy is increasing. As you go from second to third, there is a still increase in entropy. But as you go from third to fourth, there is a decrease in entropy. So, the interdiffusion will proceed until the entropy is maximized. In this case, you see that the composition is uniform throughout. If any further interdiffusion or intermixing occurs, the entropy is decreasing.

The interdiffusion will stop when the equilibrium state is reached and which here is the uniform composition throughout the mixture. Again this is valid for ideal mixing. By ideal mixing we mean there are no interactions between the atoms or more correctly the interactions AA, BB and AB are all same. So, there is no preference of the sites. But in real solutions, these interactions are different and so there will be some short range order and the final equilibrium state may be different.

More accurately, instead of composition we talk about chemical potentials. So, the interdiffusion will proceed until the chemical potentials of all the species are equalized throughout the mixture. So, the chemical potential is the fundamental driving force for this process of interdiffusion or intermixing. Any question? So we will stop here. Thank you.