# Diffusion in Multicomponent Solids
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### Lecture No 02
## The Second law of Thermodynamics

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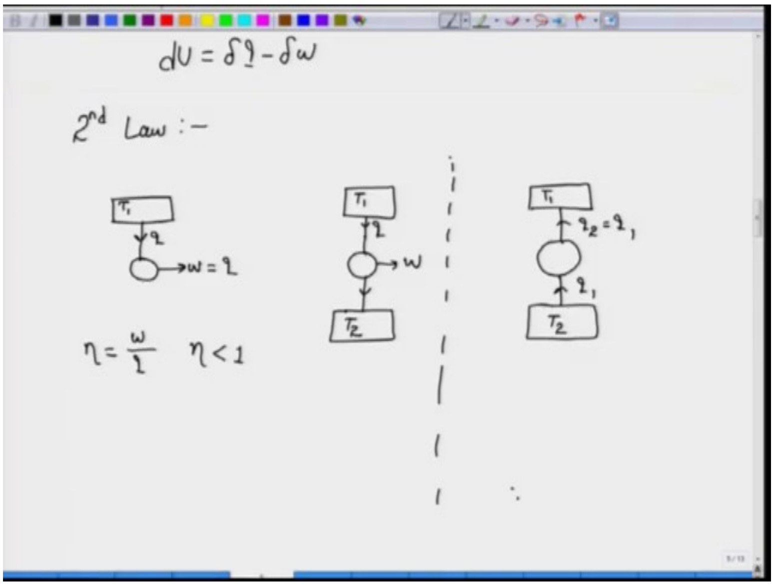

Welcome back. So, in last class we talked about First law of Thermodynamics and its limitations. The first law of thermodynamics basically states, that $dU = \delta q - \delta w$ and we saw it has certain limitations that it cannot predict the direction of a process, it cannot predict the degree of irreversibility of the process and it does not put any limit on the work to be done. These limitations are overcome by the second law of thermodynamics.

There are various ways, to state the second law of thermodynamics, one of the ways is it states that, it is not possible to construct a cyclically operating device which will accept some heat from a high temperature reservoir and convert all of it into work. Such a device is not possible that is one of the way to state second law.

So, what basically this device is doing, is accepting heat from a high temperature reservoir at T1 and then converting all of it into work. So, in other way, we can state that if we define efficiency of this heat engine as work done divided by heat absorbed so, the second law states that, the efficiency has to be always less than 1. Because $w$ has to be less than $q$.

Now all of the heat accepted cannot be converted into work so some of the heat has to be rejected because it is a cyclic process, it has to be a cyclic process. If the heat engine has to operate continuously it has to be a cyclic process which means the system has to come back to its original state. So, to come back to its original state the remaining heat has to be rejected. So, essentially any heat engine that operates has to interact with two thermal reservoirs, one from which it accepts heat, then it perform some work $w$ and the remaining heat is rejected to a low temperature reservoir.

Another way to state the second law is - it is not possible to construct a device which operating in cycle absorbs heat from a low temperature reservoir and transfers it to a high temperature reservoir. Essentially it is not possible to conduct heat from low temperature to higher temperature without any external influence. Such a device is not possible.

This is second way to state the second law of thermodynamics. So essentially, the second law has put a limit on the work to be done, right, the efficiency cannot be 1 or greater. It has to be less than 1. And it also, establishes the direction. Heat cannot be conducted from low temperature to higher temperature without any external influence.

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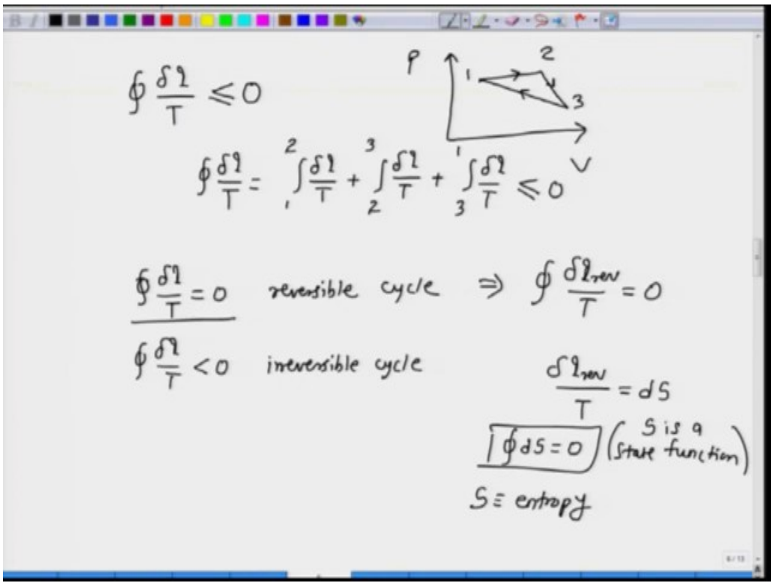

$$\oint \frac{\delta q}{T} \leq 0$$

$$\oint \frac{\delta q}{T} = \int_1^2 \frac{\delta q}{T} + \int_2^3 \frac{\delta q}{T} + \int_3^1 \frac{\delta q}{T} \leq 0$$

$\oint \frac{\delta q}{T} = 0$ reversible cycle $\Rightarrow \oint \frac{\delta q_{rev}}{T} = 0$

$\oint \frac{\delta q}{T} < 0$ irreversible cycle

$$\frac{\delta q_{rev}}{T} = dS$$

$\boxed{\oint dS = 0}$ (S is a state function)

$S \equiv$ entropy

So, the important consequence of the second law of thermodynamics is that:

$$\oint \frac{\delta q}{T} < 0$$

Cyclic integral means the integral taken over all the process in a cycle. So, this important inequality is called Clausius inequality. This is an important consequence of second law of thermodynamics. If we define a cycle let us say on a P-V diagram, 1 → 2, 2 → 3 and 3 → 1. If we, apply this inequality to the cycle $1-2-3$ here what it says is:

$$\oint \frac{\delta q}{T} = \int_1^2 \frac{\delta q}{T} + \int_2^3 \frac{\delta q}{T} + \int_3^1 \frac{\delta q}{T} \leq 0$$

This has to be less than or equal to 0.Now, the equality is valid if the cycle is reversible. Reversible cycle means, each of the process in the cycle is reversible. So, whole cycle is conducted along an equilibrium surface. In that case, the equality is valid. So, $\oint \frac{\delta q}{T} = 0$ if the cycle is reversible and the inequality is valid if the cycle is irreversible. The cycle is irreversible if any of the process is irreversible and this is very-very important inequality.

So, now we can state this as:

$$\oint \frac{\delta\, q_{reversible}}{T} = 0$$

$\delta q$ reversible is basically the heat absorbed during a reversible process or heat effect during a reversible process. Now, if we define $\frac{\delta\, q_{reversible}}{T}$ as a variable $dS$, we can write in:

$$\oint dS = 0$$

and we know, this is a property of a state function. So, $\oint dS = 0$ essentially means that the variable $S$ is a state function and this variable $S$ is called as entropy.

So, essentially you can also state the second law of thermodynamics as the entropy is a state function. Now, this gives a very important consequence if we analyze this inequality further now that we know the definition of entropy.

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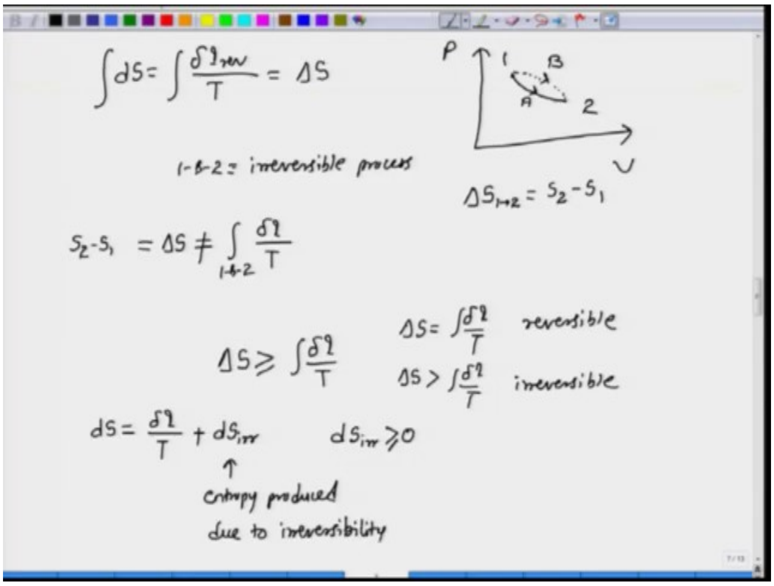

$$\int dS = \int \frac{\delta q_{rev}}{T} = \Delta S$$

1-B-2 = irreversible process

$\Delta S_{1\to 2} = S_2 - S_1$

$$S_2 - S_1 = \Delta S \neq \int_{1\text{-}B\text{-}2} \frac{\delta q}{T}$$

$\Delta S = \int \frac{\delta q}{T}$ reversible

$\Delta S > \int \frac{\delta q}{T}$ irreversible

$$\Delta S \geq \int \frac{\delta q}{T}$$

$dS = \frac{\delta q}{T} + dS_{irr}$ $\qquad dS_{irr} \geq 0$

↑

entropy produced due to irreversibility

Remember, when we define entropy we are considering entropy in terms of heat effects and we are considering the reversible processes. So,

$$dS=\frac{\delta q}{T}$$

If we carry out certain change of state from 1 → 2, the change in entropy 1 → 2 will be $S_2 - S_1$.

And in terms of heat effect, we define it as $\int_1^2 \frac{\delta q}{T}$. So, if we analyze the heat effect of this process 1 → 2 and if it is reversible then we can define $\int \frac{\delta q}{T} = \Delta S$.

Let us carry out the same state change by another path which is irreversible. Let us call the initial process as $1 \rightarrow A \rightarrow 2$, now $1 \rightarrow B \rightarrow 2$ is an irreversible process. Then, we cannot say $\Delta S = \int \frac{\delta q}{T}$ because this is not a reversible path. So, the heat effects will be different.

However, entropy is a state function so $\Delta S = S_2 - S_1$ because entropy being a state function the difference $\Delta S$ will depend only upon the initial and final state. It is not a path function.

So, what happens to the heat effects? So, it happens that, $\Delta S \geq \int \frac{\delta q}{T}$. The equality is valid if the process is reversible and inequality is valid if the process is irreversible.

If we talk about the small differentials, we can write $dS$ for any process is equal to $\frac{\delta q}{T}$ plus some positive quantity because $dS > \frac{\delta q}{T}$. So, $dS$ has to be equal to $\frac{\delta q}{T}$ plus some positive quantity which we denote as $d\,S_{irreversible}$. So, $d\,S_{irreversible}$ is a positive quantity greater than or equal to 0.

So, again if the process is reversible then $d\,S_{irreversible}$ is 0 and we get back the original definition.

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

If the process is irreversible then $d\,S_{irreversible}$ has to be a positive quantity. It means entropy is produced in an irreversible process. So, this is the entropy produced due to the irreversibility of the process.

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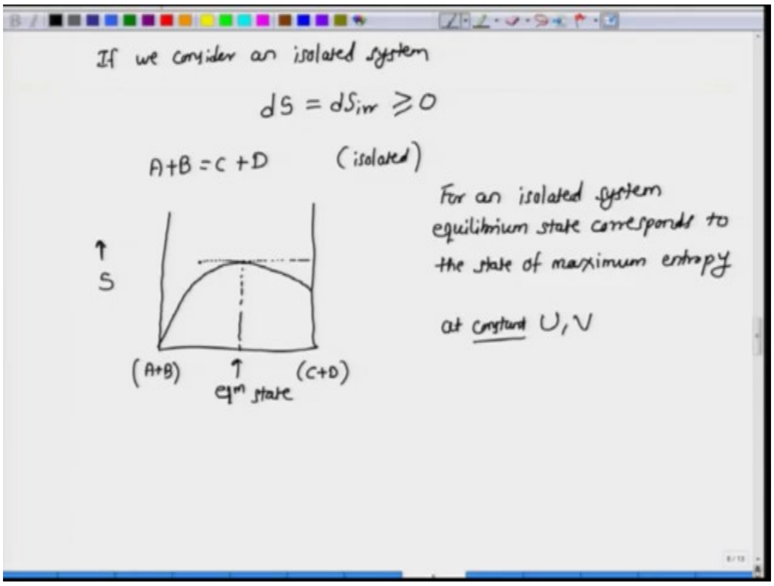
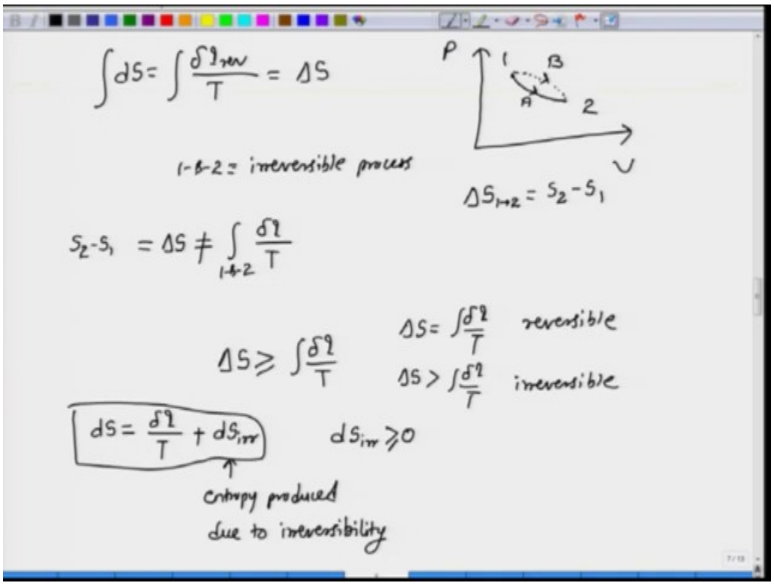


If we consider an isolated system

$dS = dS_{irr} \geq 0$

A+B = C + D (isolated)

For an isolated system equilibrium state corresponds to the state of maximum entropy at constant U, V



$\int dS = \int \frac{\delta q_{rev}}{T} = \Delta S$

1-B-2 = irreversible process

$\Delta S_{1\to2} = S_2 - S_1$

$S_2 - S_1 = \Delta S \neq \int_{1\text{-}B\text{-}2} \frac{\delta q}{T}$

$\Delta S \geq \int \frac{\delta q}{T}$

$\Delta S = \int \frac{\delta q}{T}$ reversible

$\Delta S > \int \frac{\delta q}{T}$ irreversible

$\boxed{dS = \frac{\delta q}{T} + dS_{irr}}$ $dS_{irr} \geq 0$

Entropy produced due to irreversibility

Now, let us we consider an isolated system. An isolated system means it does not interact with surrounding in anyway neither in the form of heat nor in the form of work. Which means, $\frac{\delta q}{T}$ is essentially 0. So, $dS$ has to be equal to $d\,S_{irreversible}$, $dS_{irreversible}$ is always greater than or equal to 0.

It means the entropy of an isolated system can only increase or remain constant. The entropy will increase if the process is an irreversible process. The entropy will remain constant if the process is a reversible process and this is very important because it helps us to establish the criteria for equilibrium. And what is that criteria? If the entropy can only increase, it can never decrease, so the equilibrium state should correspond to what?

Student is answering: Maximum value of entropy.

Professor: Maximum value of entropy because the equilibrium state is where the system has no desire to change from that state unless acted upon by an external influence. Even if a small perturbance is introduced in the system, the system does not want to change.

So let us see, for example, if we consider a process a reaction $A+B=C+D$ and we want to understand to what extent it will proceed. On the x-axis we plot the composition of $C+D$, the left hand y-axis is 100 percent $A+B$, right hand y-axis is 100 percent $C+D$ and we will see how the entropy changes.

And this is carried out in an isolated system. If the reaction is carried out in an isolated system, what happens? Initially the reaction will proceed. As the reaction proceeds the entropy will increase. At some point it will reach maximum and then the entropy will start decreasing. This will be the nature of the curve. So, what happens? Basically there is a maximum on the entropy curve somewhere and this is the equilibrium state.

So, as $A+B$on the left hand side is reacting to form $C+D$ the entropy is increasing. That is possible if it is an irreversible reaction so the reaction can proceed. When it reaches this point any further reaction would cause a decrease in entropy. Now, that is not allowed by second law because this is an isolated system. So, the decrease in entropy of the system is not allowed. So, the reaction will stop and no further reaction will be possible.

Similarly, if we come from right hand side, we start from $C+D$ as it reacts to form a little bit of $A+B$ the entropy is increasing. So, if we start from pure $C+D$ it will react, will form $A+B$ and the reaction will continue until you reach this maximum in entropy. So, this is how we get the criteria for equilibrium.

So, the criteria for equilibrium in terms of entropy is for an isolated system equilibrium state corresponds to the state of maximum entropy. As we say, isolated system which means?

Student is answering: No transfer of energy and heat.

Professor: Right. So basically we are holding internal energy of the system constant and also the volume of the system constant. So, $U$ and $V$ are constant. We can also say that at constant internal energy and volume, the equilibrium state corresponds to the state of maximum entropy and this is the criteria for equilibrium.

This is very important and we will refer back to the irreversibility when we talk about diffusion with respect to the irreversible thermodynamics. We will try to analyze diffusion process with the theory of irreversible thermodynamics. There this equation will be very important because diffusion is accompanied by production of entropy.

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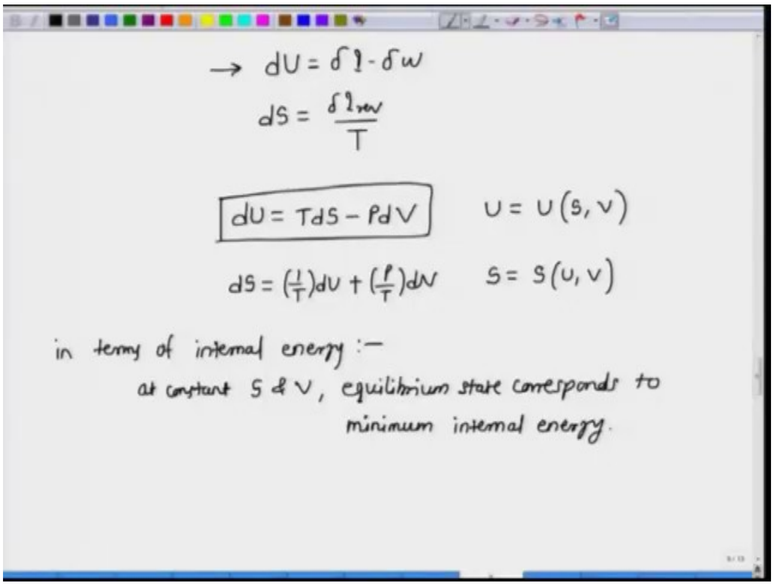

$$\rightarrow dU = \delta q - \delta w$$

$$dS = \frac{\delta q_{rev}}{T}$$

$$\boxed{dU = TdS - PdV} \qquad U = U(S, V)$$

$$dS = \left(\frac{1}{T}\right)dU + \left(\frac{P}{T}\right)dV \qquad S = S(U, V)$$

in terms of internal energy :-

at constant S & V, equilibrium state corresponds to minimum internal energy.

So, now we have two laws the first law states:

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

The second law states that:

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

If we consider a reversible process and substitute second law in the first law and $\delta w = PdV$, we write:

$$dU = TdS - PdV$$

So, this is the combined statement of first and second law of thermodynamics.

This essentially tells me $U$ is a function of $S$ and $V$. You can also rearrange this. You can write:

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

Or in other words $S$ is a function of $U$ and $V$. So, we have already seen when we talked about entropy that if we want to use entropy as a criterion for equilibrium we hold $U$ and $V$ constant.

So, when we use entropy as our state function to define the criteria of equilibrium we use internal energy and volume as the independent variables. Now, based upon this combined equation you can also define criteria of equilibrium in terms of internal energy.

So, in terms of internal energy, the criteria of equilibrium can be defined as follows. At constant entropy and volume, equilibrium state corresponds to minimum value of internal energy. In other words, if we hold entropy and volume of the system constant then the internal energy of the system can only decrease, it can never increase. Then it is obvious that the equilibrium state will correspond to minimum value of internal energy because, from there the system will have no desire to change in either direction. So, the second law has helped us to overcome the limitations of first law. It has put a limit on the work done, it has defined the direction of the process and then it has also defined the degree of irreversibility or to what extent the reaction can occur as long as the entropy can increase in an isolated system with constant $U$ and $V$ or as long as the internal energy can decrease in a system with constant $S$ and $V$.

We have now two state variables which we can use to define the equilibrium, but there is a little bit of problem. If, we use $S$, we need to use $U$ and $V$ as independent variables. If we use internal energy we need to use $S$ and $V$ as independent variables. And these are not really easy to control.

Imagine if, you want to use internal energy for example and I ask you hold the entropy and volume of the system constant. Is it easy to do? No. So, we need to define another state variable which can be easily used or using which we can define the criteria of equilibrium in terms of easily controllable independent variables.

For example, temperature and pressure - they are easy to control. So, can we define some variable which can define criteria of equilibrium using $T$ and $P$ as independent variables? So, that brings out the question of how do we define the next variables and that we will talk about in the next class.