Thermodynamics: Classical to Statistical

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Lecture - 04

Calculation of entropy for various processes

In the last class we discussed about ‘S’ is a state function and we proved that ‘S’ (entropy) is a state function. We also proved ‘q’ is a path function. Then we discussed about change in entropy, dS (for isolated system) is greater than 0 for spontaneous change and equals to 0 at equilibrium. By definition, all reversible processes are in equilibrium. So dS system equals to 0 for reversible process and greater than 0 for irreversible process (spontaneous process). But, all systems are not like isolated system. So what would be the entropy change for not isolated systems?

$$dS_{system} = dS_{produced} + dS_{exchange}$$

Entropy change of system (dS_{sys}) consists of two components, one is called $dS_{produced}$ and another one is $dS_{exchange}$. So, what is $dS_{produced}$ then? $dS_{produced}$ is the entropy change by the process itself, and $dS_{exchange}$ is the entropy change due to heat exchange between the system and surroundings. So, $dS_{exchange}$ will be 0, as there is no heat exchange between the system and surroundings. And for isolated process dS_{system} is nothing but $dS_{produced}$. Because, there is no heat exchange between the system and surroundings. We can write,

$$dS_{system} = dS_{produced} + dS_{exchange}$$

Now, for a reversible process, we can write,

$$\delta q = \delta q_{rev}$$

We just discussed the $dS_{produced}$ for reversible process is 0. So,

$$dS_{system} = dS_{exchange} = \delta q_{rev}/T$$

Now for any irreversible processes $dS_{produced} > 0$ (just now we discussed) and $dS_{exchange}$ is nothing but $\delta q_{irrev}/T$. So,

$$dS_{system} = dS_{produced} + dS_{exchange} > \delta q_{irrev}/T$$

For reversicle process,

$$dS_{system} = \delta q_{rev}/T$$

For irreversicle process,

$$dS_{system} > \delta q_{irrev}/T$$

Now, if you combine them we get,

$$dS_{system} \geq \delta q_{rev}/T$$

Equal sign represents reversible process and greater than sign refers to irreversible process. This whole thing we already studied this is known as Clausius Inequality. So just now we discussed Clausius inequality. One thing we should remember is we must always devise a reversible process to calculate entropy change. For example, we have a system which contains two bulbs like Figure 1.

Figure 1

We have bromine gas here and this is vacuum there is no any gas here and this is our initial state. When we open the stop cock the gas will spread. So we get the final state like this. This is bromine gas. So, this is our volume V_1 this is nothing but V_i and this is final volume $_{V2}$ nothing but V_f. So, V_f is consist of the volume for the sum of the volume of bulb1 and bulb2, and V_i is the initial volume which is the volume of this bulb. So, this is initial state and this is final state. Remember if we remove the stop cock gas will spread spontaneously. So, this is an irreversible process. But how do we calculate the entropy change for this process. So, we know and suppose there is no temperature change. As well as Br_2 behaves ideally. These are these two assumptions we are making here. So, now we know,

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

dU =0, as no temperature change and ideal gas.

$$\delta q_{rev} = -\delta w_{rev} = (nRT/V)dV$$

So,

$$dS = \delta q_{rev}/T = (nR/V)dV$$

If you integrate this from S1 to S2 and the corresponding V1 to V2, we get,

$$\Delta S = S_2 - S_1 = nR\ln(V_f/V_i)$$

Now what we did here? Although the process is irreversible one but we considered process is taking place reversibly. Why? Because S is a state function. So we are moving from initial state, we are going from initial state to final state. So basically, what we are doing here? We are devising another path which is taking place reversibly. And we are calculating entropy change here. So, this is how we can calculate entropy change. So far what we discussed,

$$dS_{system} = dS_{produced} + dS_{exchange}$$

For finite change,

$$\Delta S_{system} = \Delta S_{produced} + \Delta S_{exchange}$$

$$(\Delta S_{system})_{isolated} \geq 0$$

Now, we will consider different cases, like for isothermal reversible expansion and what would be the entropy change for this process and for ideal gas.

$$\Delta U = 0$$

$$\delta q_{rev} = -\,\delta w_{rev} = (nRT/V)dV$$

$$\Delta S_{system} = nR\ln(V_2/V_1)$$

$$\Delta S_{surrondings} = -\,\delta q_{rev} = -nR\ln(V_2/V_1)$$

$$\boldsymbol{\Delta S_{total} = \Delta S_{universe} = \Delta S_{system} + \Delta S_{surrondings} = 0}$$

Now, what about isothermal irreversible processes? Let us see. For irreversible isothermal expansion, what would be the entropy change? We can have two cases. One is the isothermal one, again and if we consider ideal gas,

$$\Delta U = 0$$

$$\delta q_{irrev} = -\,\delta w_{irrev}$$

So depending on the work done, we will have entropy terms.

Case I:

$$P_{ext} = 0$$

$$\delta w_{irrev} = -\,P_{ext}dV = 0$$

$$\text{So, } \delta q_{irrev} = 0$$

So, it says no heat is delivered to the system by the surroundings. So, when external pressure is 0, no heat is delivered to the system by the surroundings.

So there is no entropy change of the surroundings. So, $\Delta S_{surroundings} = 0$. Now what about ΔS_{system}?

$$\Delta S_{system} = nR\ln(V_2/V_1)$$

So,

$$\boldsymbol{\Delta S_{total} = \Delta S_{system} = nR\ln(V_2/V_1) > 0 \text{ for expansion prpocess.}}$$

Case II: when P_{ext} is not equal to 0.

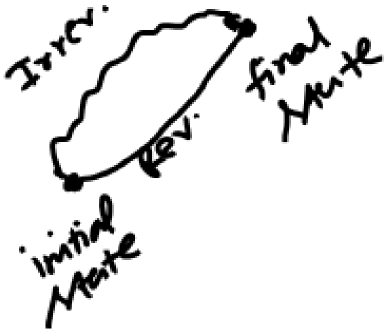

Figure 2

Then so, we have here think about like this. So we have here initial state and we are going to final state. So this is your irreversible process. But we are devising a path like process is taking place in reversible manner here.

$$dU = \delta q_{rev} + \delta w_{rev}$$

$$dU = \delta q_{irrev} + \delta w_{irrev}$$

$$TdS_{system} + \delta w_{rev} = \delta q_{irrev} + \delta w_{irrev}$$

$$dS_{total} > 0$$

We can carry out the process we are not discussing here and then we can end up with dS_{total} is greater than 0.

We have to apply here clausius inequality. And then already you have arrived at this expression. So, what we got so far, for reversible isothermal expansion,

$$\mathbf{\Delta S_{total} = \Delta S_{universe} = 0}$$

And for irreversible process or irreversible isothermal expansion, we get,

$$\mathbf{\Delta S_{total} = \Delta S_{universe} > 0}$$

$$\mathbf{\Delta S_{universe}\ (= \Delta S_{total}) \geq 0}$$

Equal sign refers to reversible process and greater than sign refers to irreversible process. Now, we will consider different cases and we will see how we can calculate ΔS_{system}. So we will calculate entropy change for ideal fixed mass closed system gas processes. First we will consider for an ideal gas at constant volume process. Gas is ideal gas and the process is a constant volume process, no P-V work. In that case del w is 0. So dU is nothing but δq, and if we consider this is reversible process we can write like this,

$$dU = \delta q_{rev}$$

$$C_V\, dT = TdS$$

$$dS = C_V(dT/T)$$

If we integrate this dS and temperature goes from T_1 to T_2.

$$\Delta S = C_V \ln(T_2/T_1)\text{, we consider } n=1$$

For n moles,

$$\Delta S = nC_V \ln(T_2/T_1)$$

Now this is at constant volume process, what about at constant pressure process?

Next we will consider for an ideal gas at constant pressure.

$$dS = (\delta q_{rev})_P/T = nC_P(dT/T)$$

$$\Delta S = nC_P \ln(T_2/T_1)$$

Case III: Third case, for an ideal gas and adiabatic process. This is the simplest one we can think of. Because,

$$\boldsymbol{\Delta q = 0 \Rightarrow dS = 0 \Rightarrow \Delta S = 0}$$

Next, we will consider entropy change in terms of volume and temperature.

$$\delta q_{rev} = T\,dS = \delta U - \delta w_{rev}$$

$$\Rightarrow T\,dS = nC_v\,dT + P\,dV$$

$$\Rightarrow T\,dS = nC_v\,dT + \frac{nRT}{V}\,dV \quad \text{for ideal gas}$$

$$\Rightarrow dS = nC_v \frac{dT}{T} + \frac{nR}{V}\,dV$$

$$\Rightarrow \int_{S_1}^{S_2} dS = nC_v \int_{T_1}^{T_2} \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Rightarrow S_2(T_2, V_2) - S_1(T_1, V_1) = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$

$$\Rightarrow \boxed{\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}}$$

So, this is entropy change in terms of volume change and temperature change.

Similarly, one can carry out entropy change in terms of pressure and temperature.

$$\mathbf{\Delta S = nC_P\ln(T_2/T_1) - nR\ln(P_2/P_1)}$$

Similarly, one can carry out entropy change in terms of pressure and volume.

$$\mathbf{\Delta S = nC_P\ln(V_2/V_1) - nC_V\ln(P_2/P_1).}$$