Thermodynamics: Classical to Statistical
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Lecture - 03
Introduction to Entropy

In the last class we discussed about heat capacity, heat capacity at constant volume and constant pressure.

Now,

$$(\delta H/\delta T)_P = C_P$$

If we take dT on both side and if we do the integration, by taking the limit of H from H_1 to H_2 and the same for temperatutre is T_1 to T_2 and if C_P is independent of temperature. Then we get,

$$\Delta H = H_2(T_2) - H_1(T_1) = H_2 - H_1 = C_P dT$$

So, next we will briefly discuss what is Kirchoff's equation or Kirchoff's law.

$$\Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \Delta C_p(T)\, dT$$

This is Kirchoff's law, the derivation we are not going to discuss now. We all studied this thing. Where, you know ΔCp represents the difference of the heat capacities of the individual products and reactants at temperature T. So, also this is Kirchoff's law.

Now, we will move to limitations of first law of thermodynamics. There are some thermodynamic phenomena which cannot be explained by first law of thermodynamics.

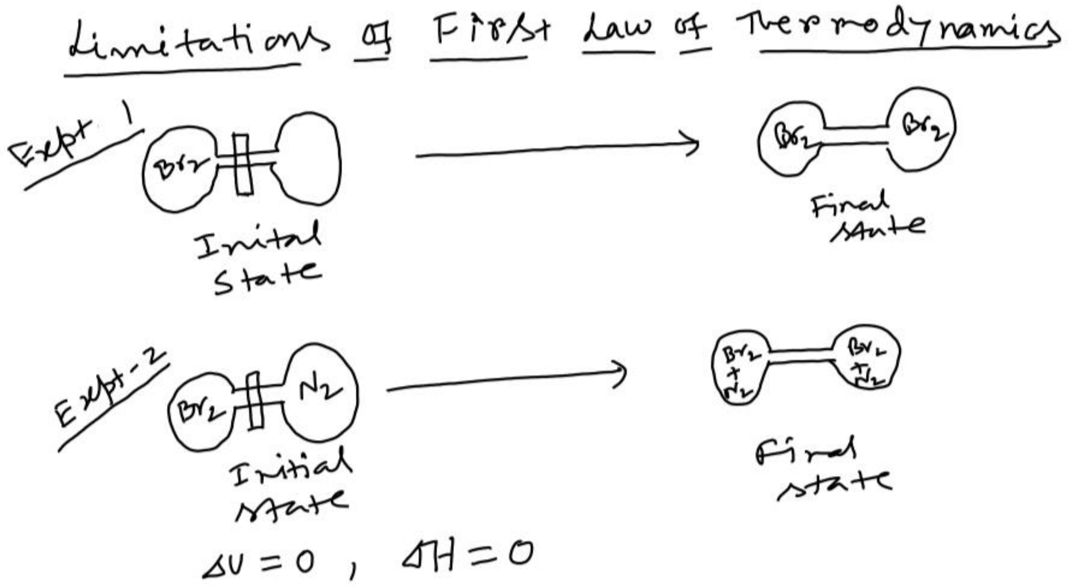

Figure 1

Suppose, we have one bulb (Figure 1) here which is filled with bromine gas and there is a stopcock over there. This is initial state. If we remove the stopcock, what we get? We get bromine gas molecules will occupy both the bulbs. So this is our final state. This is experiment 1. Consider one more experiment like this. so you have bromine gas in one container and Nitrogen gas in another container and if you remove the stopcock, they will mix with each other. So in both the bulbs you get mixture of bromine and nitrogen. This is initial state and this is final state. This is experiment 2. For both these experiments ΔU is 0, and ΔH is 0. So, from first law of thermodynamics we get the concept of internal energy and enthalpy. So, these two processes cannot be explained from first law of thermodynamics. So what is happening here. So if we examine the above processes from a molecular point of view, we see that each process involves an increasing disorder or randomness of the system. If we see the experiments carefully again, initially we had bromine gas here in one bulb, another bulb was

was empty and if we remove the stopcock, this is the stopcock, bromine gas will spread. So the randomness means each bromine molecule in both the bulbs are now available to move around. Similarly here for bromine and nitrogen case, for experiment 2, if remove the stopcock the bromine gas will have access to other bulb. Similarly for nitrogen gas molecules they will have access to occupy the other bulb. So, randomness and disorderness increases. So, why it is important? For the processes where energy is not a prime factor then we need to see the randomness or the disorderness of the system. Now in order to quantify the disorderness or randomness, we need to have a function or we need to have a function or a state function rather because a state function has advantage over any other function because property of a state function depends upon state of the system, so we need to have a state function. So we will discuss this thing later also and actually it gives the concept of entropy. We define entropy by S. So, entropy is nothing but disorderness or randomness of a system. If you remember correctly, we have so far discussed or we have rather proved that U (internal energy) is a state function, w or work done is a path function, what about q? so heat q is a path function we have not proved it yet. So, today we will prove it that q is a path function. Consider a reversible process. From first law of thermodynamics,

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

$$C_V(T)dT = \delta q_{rev} - PdV$$

$$\delta q_{rev} = C_V(T)dT + (nRT/V)dV \text{ (For ideal gas, } P = nRT/V)$$

This is the equation we have derived so far.

Now,

$$C_V(T)dT = d[\int C_V(T)dT + \text{contant}]$$

This is perfect differential. Rather this is dU and what about the other term? We cannot write (nRT/V)dV like this because T (absolute temperature) depends on V. So who is troubling us? Troubling us is T. If we divide this equation by T then our problem will be solved.

$$\delta q_{rev}/T = (C_V(T)/T)dT + (nR/V)dV$$

Each term in the right hand sides are perfect differential, which says that $\delta q_{rev}/T$ is perfect differential. So what we have obtained so far? We have obtained that δq_{rev} is not a perfect differential, which says that q is not a state function. But, $\delta q_{rev}/T$ is a perfect differential. So $\delta q_{rev}/T$ is a state function and we know $\delta q_{rev}/T$ is nothing but dS ($dS = \delta q_{rev}/T$). That we have studied. So in a single shot we proved that q is not a state function, q is a path function as well as we proved that entropy is a state function. So we have proved that entropy is a state function. We can prove entropy is a state function in another manner in a PV diagram.

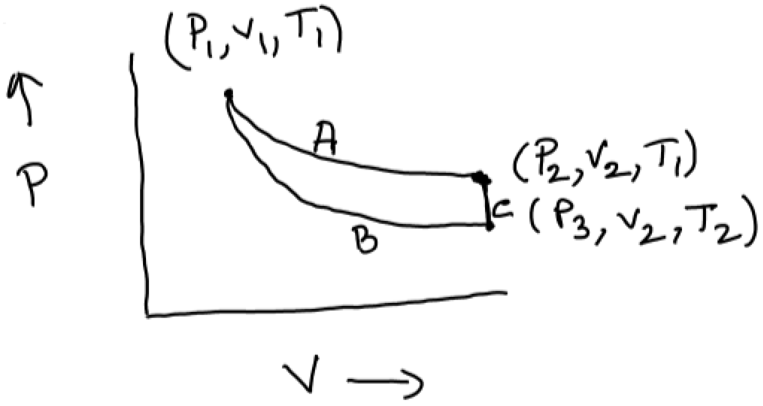

Figure 2

So we consider a PV diagram like Figure 2. (P_1, V_1, T_1) is our initial state and (P_2, V_2, T_1) is our final state. So we can reach from the initial state (P_1, V_1, T_1) to the final state (P_2, V_2, T_1) through the path A, or we can first go to a point (P_3, V_2, T_2) and then we go from here. So this is path B and path C. So path A is reversible isothermal expansion. In reversible isothermal process, temperature is constant, volume increases from V_1 to V_2. So this expansion process. What about path B?

Path B is reversible adiabatic expansion. So path B is an adiabatic process and this is expansion process because again volume increases from V_1 to V_2. And, what about path C? So path is nothing but reversible heating at constant volume. There is no volume change but the pressure increases from P_3 to P_2. So if you want keep the volume constant but you want to increase the pressure, you need to increase the temperature. So the process is reversible heating at constant volume. So what we get so far? From this diagram and the information we have so far,

$\delta q_{rev,B} = 0$, for path B, as adiabatic process.

For path C: $\delta w_{rev} = 0$, as no PV work.

$$dU_C = \delta q_{rev,C} = C_V(T)dT$$

We need to prove, $\Delta S_A = \Delta S_B + \Delta S_C$

For path A: $dS_A = \delta_{qrev,A}/T$

$$dU_A = 0$$

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

$$dS_A = (nR/V)dV$$

$$\Delta S_A = nR\ln(V_2/V_1)$$

For path B: $\Delta S_B = 0$, as $\delta q_{rev,B} = 0$

For path C: $dS_C = \delta_{qrev,C}/T = (C_V(T)/T)dT$

Now, for adiabatic process $\delta q = 0$. So it says, $dU = \delta W_{rev}$. So it gives us,

$Cv(T)\, dT = -(nRT/V)dV$ and temperature changes from T_1 to T_2 and volume from V_1 to V_2. By integrating this, we get,

$$C_V(T_2 - T_1) = nRT\ln(V_1/V_2)$$

So, for path C: $\Delta S_C = C_V\ln(T_2/T_1) = nR\ln(V_2/V_1) = \Delta S_A$

S0, , $\mathbf{\Delta S_A = \Delta S_B + \Delta S_C}$, as $\Delta S_B = 0$

So it says that ‘S’ is a state function because we arrived the final point P_2, V_2, T_1 from initial point P_1, V_1, T_1 in two different manner, one is via path A and another is combination of path B and C, and in both cases we get same entropy change. It states ‘S’ is a state function.

Next we will move to the second law of thermodynamics. There are several statements but we will consider one, we will discuss one statements today. This one statement is the entropy of an isolated system increases as a result of a spontaneous process. We will consider how we will prove it.

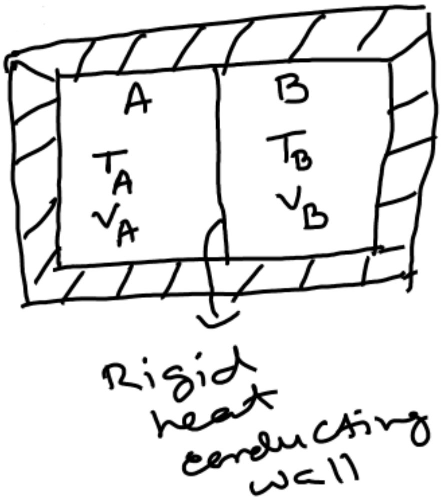

Figure 3

So, what we consider? We consider one big system like Figure 4, in that container we have a wall, this is rigid heat conducting wall, which has two compartments, we say this is compartment A and this is compartment B and these two compartments are separated by a rigid heat conducting wall and temperature of this compartment is T_A and volume of this compartment is V_A and if we say temperature of this compartment is T_B and volume of this compartment is V_B and the entire system is isolated from the surroundings. Now, compartment A and compartment B they are in equilibrium with themselves means compartment A is in equilibrium with itself and compartment B is in equilibrium with itself, but they are not in equilibrium with each other. So we know when there is a temperature change spontaneously from or heat goes spontaneously from higher temperature to lower temperature. Since these two compartments are separated by rigid heat conducting walls, the heat can be transferred from one compartment to another compartment, but volume cannot be changed. Since the whole system isisolated,

$$U_A + U_B = \text{constant}$$

Because of rigid wall,

$$VA = \text{constant and } VB = \text{consatnt}$$

Now, what is entropy change?

$$dS_A = \delta_{qrev,A}/T_A$$

$$dS_B = \delta_{qrev,B}$$

Since, $\delta w = 0$,

$$\delta_{qrev,A} = dU_A \text{ and } \delta_{qrev,B} = dU_B$$

So,

$$dS_A = dU_A/T_A$$

$$dS_B = dU_B/T_B$$

Total entropy change,

$$dS = dS_A + dS_B = dU_A/T_A + dU_B/T_B$$

$$\text{Again, } U_A + U_B = \text{constant} \Rightarrow dU_A = -dU_B$$

$$\text{So, } dS = (1/T_B - 1/T_A)dU_B$$

Case I: $T_B > T_A$ then $dU_B < 0$, So, $\mathbf{dS > 0}$

Case I: $T_B = T_A$ then **dS = 0.**

So what we observed here? We observed if there is a temperature difference between the compartments then entropy increases and the whole thing is isolated from the surrounding, there is no contribution of the surroundings to the system. So in entropy change is positive means that process is spontaneous one, the heat passes through the wall from one compartment to the other compartment spontaneously if there is a temperature difference between the compartments. If there is no temperature difference between compartments dS is 0, there is no net entropy change for this process.

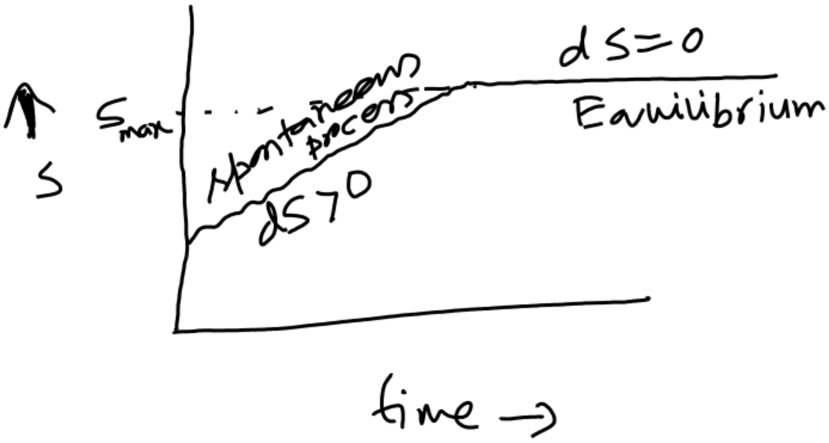

Figure 4

So if we plot schematically as how entropy changes with time (Figure 4), we get here spontaneous change, spontaneous increase in entropy and once it reaches equilibrium then there is no entropy change. And this is dS > 0, so this is your spontaneous. This is equilibrium. So at equilibrium there is no entropy change of the system here because we consider isolated system here. So dS = 0 and system reaches equilibrium for this isolated system and dS keep on increasing till it reaches equilibrium and this is the point we can say it is maximum entropy. So once it reaches maximum entropy then it reaches equilibrium.