Advanced Thermodynamics and Molecular Simulations
Prof. Prateek Kumar Jha
Department of Chemical Engineering
Indian Institute of Science – Roorkee

Lecture 08
Thermodynamic Functions for Multi-Component Systems; Chemical Potential; Why Do We Minimize Thermodynamic Functions?

So hello all of you. So in the last lecture we have discussed the idea of thermodynamic functions, we discussed the idea of Legendre transformation, how we can get the energy functions that we know internal energy, enthalpy, Helmholtz and Gibbs free energy. So in today's lecture we will extend these ideas to multi component systems and we will also discuss why do; we say that we should always have the minimum energy of a system the minimum Gibbs energy or Helmholtz energy or whatever description that; you may recall. So why what is the theoretical basis for that particular logic. So just to quickly recap.

(Refer Slide Time: 01:09)

So we have discussed these 4 functions internal energy U, enthalpy H, Helmholtz free energy F and Gibbs free energy G which are defined in this particular way-

$$H \equiv U + pV$$
$$F \equiv U - TS$$
$$G \equiv U + pV - TS$$

And we can also write this in differential form as-

$$dU = TdS - pdV; U(S,V)$$
$$dH = TdS + pdV; H(S,p)$$

$$dF = -SdT - pdV; F(T,V)$$
$$dG = -SdT + Vdp; G(T,p)$$

So let us first discuss what exactly will change if I have a multi component system. So for doing that let us first discuss like what exactly happens when we add a molecule to the system. So going back to our example when we were distributing quanta of energy into different molecules in the system we always assume that the numbers of molecules are constant but let us say for example if I have a system containing some molecules 'n' and let us say for example if I want to add a new molecule in the system, the system is going from n molecules to 'n+1' molecule. So when that molecule moves in let us call it a foreign molecule that moves in the system that molecule must be carrying some energy where from it is coming from.
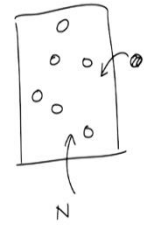
(Refer Slide Time: 03:03)

So let us say for example in a bulk system. Let us say for example we mix 2 liquids then molecules in one liquid will move to the other liquid. So that molecule that is coming from one liquid to the other that must be coming with some energy then once it comes here then it forms new pairs or new forces with the other molecules already present in the system. So let us say for example the new foreign molecule is liked by the molecules present in the system already in that case we say that the mixing is favoured, if it is not light then the mixing is not favoured. So all of this must be coming in terms of some energetic condition that in one case it should be favoured in one case it does not that must be driven by some energetic condition and that is where the idea of chemical potential comes handy.

So what a chemical potential essentially is the change in the energy and we discuss like which energy we are talking about in a minute but this is a change in the energy of the system by

adding a molecule. Now as such the idea of chemical potential is also valid when you have the 1 component system. Let us say for example if I add a water molecule to a glass of water so that water molecule must be carrying some energy as it comes in, however provided that the properties of that water molecule is the same as all the other water molecules in the container that change is simply adding to the volume of a system. We will discuss in the next lecture the idea of intensive and extensive variables and there you will see that if I simply mix 2 pure liquids we basically do not change the intensive variables and we come to that as we go there. However if I add a molecule of a different species then that is already present or molecule of a species that is already present but adding that molecule changes its concentration.

Let's say if you have a binary system of a and B and you have let us say 10 A molecules and 20 B molecules by adding a new B you are changing the ratio of A to B molecules. So by addition of a molecule you are changing the composition of the system. So whenever that happens this energy becomes nontrivial and that is where the idea of chemical potential becomes more relevant. So in general we define μ_j as the change in energy by adding a molecule of species 'j' provided that we have multiple species present in the system or multiple components present in the system. So then going back to our earlier definitions of energy let us say if I look at my dU, dU was-

$$dU = TdS - pdV$$

so we already have accounted for the temperature entropy and pressure and volume and clearly this energy that I am talking about that is the change driven by addition of a molecule is clearly not accounted for in whatever we have written so far there must be something else coming in this picture and that something is simply the definition of the chemical potential. So we say that μ_j is the change in the energy by adding a molecule of species 'j' so let us say in total we are adding some dN_j molecule where N_j is the number of molecules of species 'j' in system. So, dN_j is the change that that is happening this multiplied by μ_j that is the energy by adding one molecule in the system. So this summed over all the species becomes the definition of change in internal energy for a multi component system i.e.

$$dU = TdS - pdV + \sum \mu_j dN_j$$

Now when we talk about for example enthalpy, again you will have the same change what will change between internal energy and the enthalpy is that the other natural variables will change.

Let us say for example if I write dH = TdS + Vdp for a one component systems that remains unchanged the only difference between U and H in this case if I exclude the chemical potential part is that the volume as a natural variable in U is replaced by pressure as a natural variable in H but the effect of addition of the molecule that I have added remains the same. So this will be simply-

$$dH = TdS + Vdp + \sum \mu_j dN_j$$

that is to say that I can write now all of my expressions of the one component system by extending to the multi component system as-

$$dU = TdS - pdV + \sum_j \mu_j dN_j$$

$$dH = TdS + Vdp + \sum_j \mu_j dN_j$$

$$dF = -SdT - pdV + \sum_j \mu_j dN_j$$

$$dG = -SdT + Vdp + \sum_j \mu_j dN_j$$

(Refer Slide Time: 09:51)

So now you recall that I was telling you that chemical potential is a change in energy and it did not say which energy is that so which energy is that depends on what are the other controlling variables. Let's say for example if I am controlling temperature and pressure in that case I will use Gibbs energy, if I am controlling temperature and volume I will use the Helmholtz free energy, if I am controlling entropy and volume I will use the internal energy and so on. So that

particular contribution coming from the addition of the molecule of species 'j' that remains the same in all these cases. Now what also happens is that earlier U was a function of S and V alone but now U is also a function of the number of molecules in the system because we have added a new term dN_j multiplied by μ_j, N_j becomes the independent variable or the controlling variable so we should have ability to control the number of molecules or we should have ability to perform experiment for different number of molecules of species 'j'.

So I will use a curly bracket { } here to indicate that this is for all species in the system. So this curly bracket indicates that we are actually doing U, S, V, N_1, N_2, N_c and c for the c components that we have in the system. So if you have 2 components you will have N_1 and N_2 if you have three you will have N_1, N_2, N_3 and so on. So whenever I use a curly bracket it means I am writing a shortcut for all possible values of 'j'. So now we can write functions as-

$$dU = TdS - pdV + \sum_j \mu_j dN_j; U(S, V, N_1, N_2, N_c)$$

$$dH = TdS + Vdp + \sum_j \mu_j dN_j; H(S.p, \{N_j\})$$

$$dF = -SdT - pdV + \sum_j \mu_j dN_j; F(T, V, \{N_j\})$$

$$dG = -SdT + Vdp + \sum_j \mu_j dN_j; G(T, p, \{N_j\}$$

So if this idea is clear now we are coming to the basic point of thermodynamics that is like although we have defined the thermodynamic functions and we have mathematically found a relation between all these functions that we have written, we have not so far said that what should be this value of energy ultimately where the system should go towards and what thermodynamics says that we need to minimize this energies and when I say minimization it means different things in different contexts. So, I am coming to the point of why do we minimize the thermodynamic functions and which thermodynamic functions we should minimize under which particular condition.

(Refer Slide Time: 14:12)

So, let us get on this by using some examples. So let us say for example I am looking at a system that is isolated and what do we call an isolated system- the one where the system and the surrounding does not exchange mass or energy, there cannot be mass exchange and there cannot be any energy exchange, so what this means is that when I go to the first law and we talk about energy of system + surrounding or to the second law when we talk about entropy of system + surrounding, the surrounding itself is not playing any role in the isolated system case because there is no exchange whatsoever between the mass and energy. So we do not even have to worry about the entropy change in the surrounding or the energy change in the surrounding the system itself is sufficient for the description of the system.

So in this particular case we have certain number of molecules in the system and we start with some energy and we have said the energy is sum over the number of molecules having some energy ϵ_i multiplied by the energy ϵ_i where i represents the energy levels that can be present in the system-

$$U = \sum n_i \epsilon_i$$

So you can have ground state ϵ_0 first state ϵ_1 second state ϵ_2; energies have to be discretized there can be a maximum possible energy and there can be a minimum possible energy and we have discussed that this N_j or N_i is given by the Boltzmann distribution at equilibrium.

So with this particular idea now we can say that where is the tendency of system what the system wants to do? So we have said in the very beginning when we are doing the coin toss

example that the system favours a most probable distribution or when we discuss the exchange of quanta we said that it should favour a most probable distribution and what is that correspond to it corresponds to the highest entropy that means the entropy has a tendency to maximize and that is also a statement of second law of thermodynamics. The only change here is that there is no surrounding whatsoever. So in this case essentially what should happen is that S should be maximized and that means that ΔS should be higher than zero.

Now we know that U is a function of S and V so therefore I can also write S as a function of U and V and U in this case is constant. So I have ability to control U and I have anywhere doing a constant volume system there is no additional work being done on the system. So volume also we can control so it is-

$$dU = TdS - pdV + \sum_j \mu_j dN_j$$

I can also write this expression by moving dS to the other side and dU to the right hand side. So what you will have is-

$$dS = \frac{dU}{T} + \frac{pdV}{T} - \sum_j \frac{\mu_j dN_j}{T}$$

whatever we had here was for one component system for a multi component system you will have U, V, N_j and it is this entropy that we have to maximize.

So the problem really is maximization of the entropy and the way we have written we have simply replaced internal energy by the entropy as the function of interest because mathematically I can write the expression that for dU in terms of dS as well and we have a clear sense that the entropy should be maximized we should go towards the most probable distribution.

Now let's imagine that the system is not isolated let us now take a case when the system is a closed system and what is a closed system?

(Refer Slide Time: 19:43)

Why do we minimize thermodynamic functions?

A closed system is where the system can now; cannot exchange mass so mass exchange is not allowed but it can exchange energy with the surrounding. So this means I can no longer ignore the surroundings because surroundings are exchanging energy in the system whether it is adding or taking away is not very important it is exchanging energy in some particular way so therefore those must be considered. So, now the first law tells me that my ΔU of the system + ΔU of the surrounding should be equal to 0, note that it was also true in the previous case except that the ΔU of system was not affected by the surrounding at all because surrounding has no effect on the system; but in this particular case what this means is that the energy of the system U can actually change because the ΔU of surrounding may be non-zero or the energy of the surrounding can change. Once they exchange energy then U is no longer constant. So in the earlier case when we said that I write S as a function of U and V I had the ability to control U because U was not changing in the system. In this case the U in the system can change because surrounding can add energy on the system or take energy from there, this is a very important point that comes in existence as soon as we are doing a closed system.

Now the second law tells me that ΔS of system + ΔS of surrounding should be higher than 0 and then the argument of Clausius is that ΔS of surrounding is the heat added to the surrounding divided by the temperature. So what this boils down to is-

$$\Delta S_{syst} + \frac{q_{surr}}{T} > 0$$

Now I will invoke the first law again what the first law tells me is that the change in the internal energy is given by the heat that is added and the work that is done on the system. So the ΔU system is also given by the q and the work that is done on the system the same thing I can write

for the surrounding as well. So now we have assumed that the system or we can assume that the system is having a constant volume let us say if it is a closed container. So in that case there is no work being done because work we have defined as pressure multiplied by volume change. So if I assume constant volume then we can say that ΔU of surrounding $= q$ of surrounding because the W is zero. So therefore-

$$\Delta S_{syst} - \frac{\Delta U_{syst}}{T} > 0$$

and what this means is that-

$$T\Delta S_{syst} - \Delta U_{syst} > 0$$
$$\Delta U_{sys} - T\Delta S_{sys} < 0$$

(Refer Slide Time: 23:35)

So, although the entropy was being maximized when we had an isolated system, in the closed system entropy is still being maximized but that entropy is for system plus surrounding. So what we have managed to write is the same expression of second law of thermodynamics in terms of the energy change and the entropy change for system alone And what this means is that instead of S being maximized we can define a function U - TS that should be minimized the change in U - TS that is given by ΔU - TΔS which by the way is only true when the temperature is constant. So let us say we are able to maintain constant temperature then the change in U - TS is ΔU - TΔS. Now that change should be less than 0 unlike ΔS in the previous example so this means U - TS should be minimized and what is U - TS?

The U - TS is we have defined as the Helmholtz free energy. So now what we have concluded is that for a closed system at constant volume and we have assumed constant temperature as well, and at constant temperature the Helmholtz free energy should be minimized and this is no big news in other words because this free energy was a natural function of temperature and volume what this means we should have ability to control temperature and volume. So if I can do the experiment at constant temperature that means I can control temperature. Similarly if I can do experiment at constant volume I can control the volume.

So what essentially it means is if I am doing an experiment at constant T and V or more correctly saying if I can control temperature and volume then the Helmholtz free energy should be minimized and the minimum value will correspond to the equilibrium condition. So equilibrium this is the thermodynamic equilibrium at controlled temperature and volume is given by minimum of F that tells the tendency of the process. This is the confusion that people often have those coming from the undergrad thermodynamics background we are told that Gibbs energy should be minimized and we always take blindly that the Gibbs energy has to be minimized this is not true we need to look at what exactly is being controlled in the experiment we are doing.

If the temperature and volume is being controlled whenever we say constant T and constant V what it means I can do the experiment at different temperatures and different volume. So I have ability to control temperature and volume and in those cases the thermodynamic equilibrium is given by the minimum of the Helmholtz free energy.

So it really depends on the system under consideration when we were doing isolated system in that case it was equilibrium was given by the entropy maximum actually entropy maximum is always the condition but it is the entropy of system + surrounding, only in the case of isolated system surrounding did not have any effect and therefore we said that we should simply maximize the entropy of the system.

(Refer Slide Time: 28:48)

Why do we minimize thermodynamic functions?

So if this is clear to us let us now do a third example and look at what we have if we have an open system. So open system is one in which we can not only exchange mass but we can also exchange energy with the surrounding, and again the approach that we follow remains the same as what we had followed earlier again we assume for the argument sake that volume is constant. So now how do we proceed so we again write the first law expression as-

$$\Delta U_{syst} + \Delta U_{surr} = 0$$

$$\Delta U_{syst} = -\Delta U_{surr}$$

$$\Delta U_{syst} = -q_{surr} + \sum_j \mu_j dN_j$$

keep in mind that whatever change that we have in the system for the number of molecules will be negative of the change in the surrounding because molecules if they come from surrounding system the number of molecules in surrounding is decreasing and number of molecule in system is increasing.

Again we had the same argument for the entropy change ΔS system + ΔS surrounding must be higher than zero and ΔS surrounding again is q surrounding by T however the q surrounding has changed now. So now we have-

$$\Delta S_{sys} + \Delta S_{surr} > 0$$

$$\Delta S_{sys} + \frac{\sum_j \mu_j dN_j - \Delta U_{syst}}{T} > 0$$

$$\Delta U_{sys} - T\Delta S_{sys} - \sum \mu_j \Delta N_j > 0$$

So what we have tried to establish is the meaning of the energy that we need to minimize will change depending on the system under consideration. So we should not really blindly take this energy or that energy we should try to see what is the variable that is being controlled in the problem, are we doing experiments at controlled volume or at controlled pressure, are we doing experiments at controlled entropy or controlled temperature, are we doing experiments at constant number of moles or constant chemical potential the last one we will discuss later?

So this is how we can build the appropriate thermodynamic function for that problem and this is what we have to minimize not Helmholtz or Gibbs or internal energy for every particular problem because that will only have a meaning when we have certain variables being controlled. Let us say Gibbs energy only have a meaning when temperature and pressure are the controlling variable. Helmholtz energy only has a meaning when temperature and volume are being controlled. If we are doing for a case where temperature and pressure is being controlled we should not be using the Helmholtz free energy we should be using the Gibbs free energy. So this is how we will choose a thermodynamic function and this is actually completes the idea of energy that we began with ultimately energy is defined as a thermodynamic function in our argument and that thermodynamic function has to be minimized.

Now which thermodynamic functions we use depend on the problem under consideration? So before we conclude the lecture there is one point I want to mention here that even though we wrote this chemical potential μ_j and it may appear to you as something that is constant. It is actually not a constant always. So let us say for example if I add a foreign molecule in the system and I add one molecule then I add the next then I add the next then I add a next and I keep on doing it the chemical potential will not remain the same because after some time if it is being favoured you should either have more affinity for that molecule or if it is not being favoured you should have lesser affinity and this should reflect in a change in chemical potential.

So the way you think about it let us say for example if I start with pure water and I add one spoon of sugar. So for some first spoon I can easily mix it and it dissolves when I add the second spoon it may also dissolve but after third fourth or fifth spoon it will become increasingly more and more difficult for the sugar to dissolve in water and after certain point the sugar will precipitate and this happen because the chemical potential changes as the composition changes.

So keep in mind that the chemical potential is not a constant it is a function of composition. Similarly chemical potential is also a function of temperature and pressure. If for example we are adding sugar in hot water it should be easier to mix in comparison to the cold water. The same dependence may also be with the pressure. So that particular argument actually drives whether you will have a mixing of 2 systems or whether you will have a demixing or a phase separation and will come to that in later part of this course.

So with that I want to conclude here, thank you.