Chemical and Biological Thermodynamics: Principles to Applications
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Lecture - 18
Chemical potential of a substance in mixture

We have earlier discussed chemical potential of a perfect gas; we have also discussed chemical potential for a real gas. We have derived relevant expressions. Now, let us move on from pure substances to substance in a mixture. Suppose, if we have a mixture then how do we define the chemical potential of a component in a mixture. Let us discuss that today.

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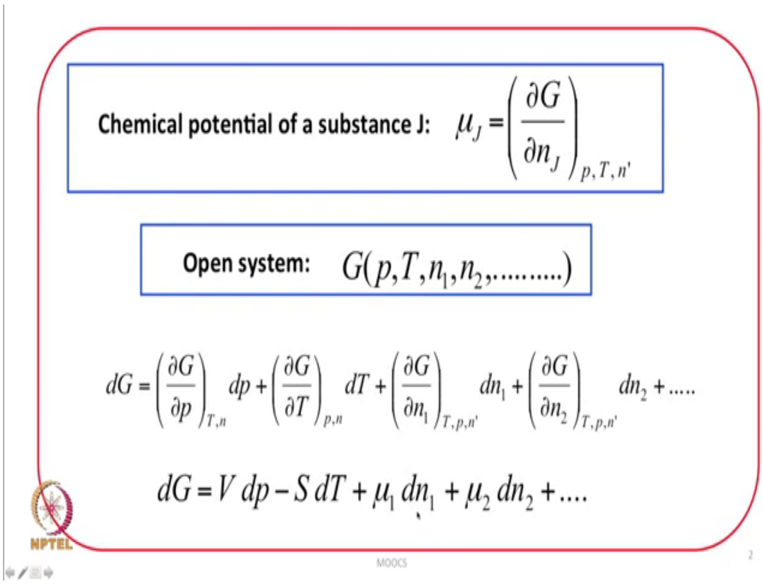

Chemical potential of a substance J: $\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{p,T,n'}$

Open system: $G(p,T,n_1,n_2,.........)$

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n} dT + \left(\frac{\partial G}{\partial n_1}\right)_{T,p,n'} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,p,n'} dn_2 + ...$$

$$dG = V\,dp - S\,dT + \mu_1\,dn_1 + \mu_2\,dn_2 + ...$$

The chemical potential of a substance J is defined as the change in Gibbs energy when 1 mole of that substance is added keeping pressure, temperature and composition of everything else constant. The meaning of each symbol in this expression is mu is used symbol for chemical potential and J is the substance J, G is Gibbs energy and n J is the number of moles of J, p, T have their usual meanings, when n prime means the composition of everything other than the component J is held constant. So, therefore, chemical potential of a substance J is the change in Gibbs energy when 1 mole of that substance is added to that mixture under the conditions of constant pressure, constant temperature and the composition of everything else also constant other than the substance J itself. Now, since we are talking in terms of the changes in compositions that means we are now talking about the open system, we are allowing the composition to change. So, therefore, as is mentioned over here, in an open system, the Gibbs energy will depend upon pressure, temperature, number of moles of component one, number of moles of component two etcetera, etcetera.

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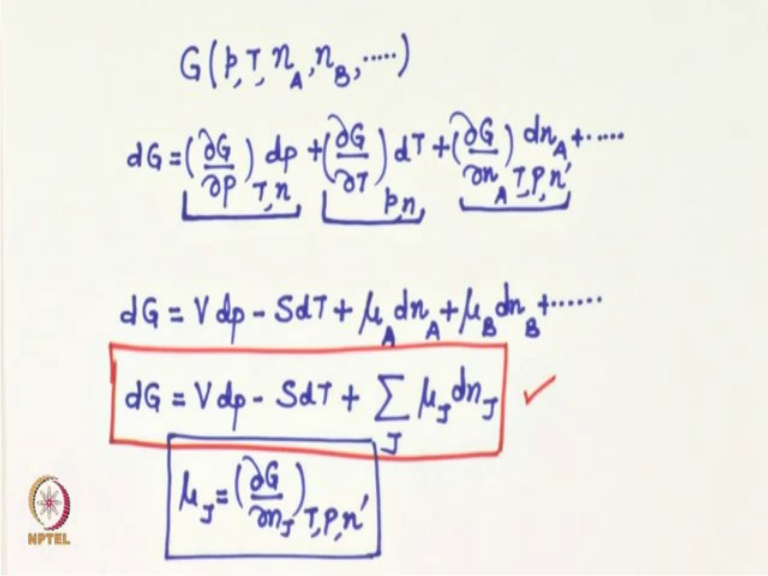

$$G(p, T, n_A, n_B, \ldots\ldots)$$

$$dG = \underline{\left(\frac{\partial G}{\partial p}\right)_{T,n}} dp + \underline{\left(\frac{\partial G}{\partial T}\right)_{p,n}} dT + \underline{\left(\frac{\partial G}{\partial n_A}\right)_{T,p,n'}} dn_A + \ldots\ldots$$

$$dG = V\,dp - S\,dT + \mu_A\,dn_A + \mu_B\,dn_B + \ldots\ldots$$

$$\boxed{dG = V\,dp - S\,dT + \sum_J \mu_J\,dn_J} \checkmark$$

$$\boxed{\mu_J = \left(\frac{\partial G}{\partial n_J}\right)_{T,p,n'}}$$

So, therefore, let us discuss. If G depends upon pressure, temperature, number of moles of A, number of moles of B so on instead of A, B, I am free to write 1, 2 also. And now if there is a small change then dG will be written as dou G by dou P at constant temperature and composition dp plus partial derivative of G with respect to T at constant pressure composition, this will be dT plus partial derivative of G with respect to n A temperature, pressure and prime constant, it will be d n A plus further in terms of n B etcetera, etcetera.

And we have earlier discussed that when the composition is constant what is the meaning of dG by dP at constant temperature. We have also discussed what is the meaning of dG by dT at constant pressure, this is volume, this is minus S. We have discussed several times earlier that means, dG will be equal to v d p minus S d T plus this quantity we have just discussed as chemical potential chemical potential of A d n A plus chemical potential of B d n B plus so on. I can further write this as dG is equal to V d p minus S d T plus let me now write all this in the form of summation J mu J d n J. And I recover my definition of chemical potential again from this equation if the temperature pressure is fixed and composition of everything else is fixed then from this expression I get mu J is equal to dou G by dou n J at constant temperature, pressure and n prime.

When you fix the temperature, this term disappears; when you fix the pressure, this term disappears; when you fix the composition of everything else then everything all those terms will disappear except the one corresponding to the species J. Let us look at the slide. Now, this is what I just discussed that dG when you expand this will take up this form we have just discussed. And we also discussed that this derivative at constant composition is volume, this derivative at constant composition and constant pressure is minus S, and this is the expect this is the form of or alternate form of this equation.

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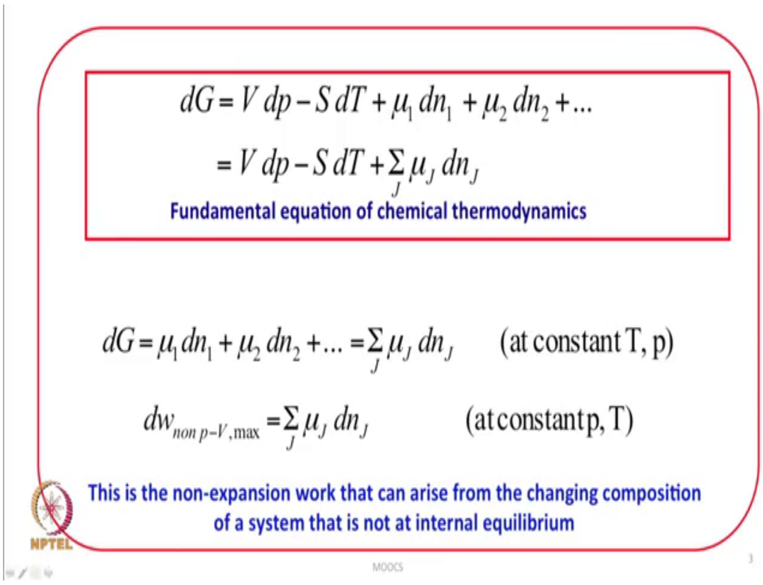

$$dG = V\,dp - S\,dT + \mu_1\,dn_1 + \mu_2\,dn_2 + \ldots$$
$$= V\,dp - S\,dT + \sum_J \mu_J\,dn_J$$

Fundamental equation of chemical thermodynamics

$$dG = \mu_1\,dn_1 + \mu_2\,dn_2 + \ldots = \sum_J \mu_J\,dn_J \qquad \text{(at constant T, p)}$$

$$dw_{non\ p-V,\max} = \sum_J \mu_J\,dn_J \qquad \text{(at constant p, T)}$$

This is the non-expansion work that can arise from the changing composition of a system that is not at internal equilibrium

We have just derived this equation dG is equal to V dp minus S dT plus summation J mu J d n J. And this equation is also known as the fundamental equation of chemical thermodynamics, because it gives information on changes in Gibbs energy, when the pressure changes, when the temperature changes, when the composition changes. And it also allows you to get information on the changes in Gibbs energy at constant pressure, at constant temperature, and when the composition only changes. A information that you need there is on chemical potential.

If I fix the temperature and pressure then V dp minus S dT term will go if I fix the temperature and pressure. Only the remaining term will remain that is dG in that case will be equal to if you expand this we get mu 1 d n 1 plus mu 2 d n 2 so on so on which is equal to this summation J mu J d n J at constant temperature and pressure. And I again now connect this dG to our previous discussion that the change in Gibbs energy at constant temperature and pressure is equal to the maximum non pressure volume work that we can extract from the system.

So, that is why let us take a look at the slide at constant pressure and temperature, the maximum non pressure volume work can be obtained from the knowledge of chemical potential and the changes in composition. What it tells is that when the composition in a system changes that change in composition can be used to extract non-pressure, volume, work. One such example is electrochemical cells where the reactions take place at both the electrodes at cathode and at anode, and the new products are formed. The composition of the mixture changes, and this change in composition is doing work and in this particular case that is the electrical work, so that is why this comment. This is the non-expansion work that can arise from the changing composition of a system that is not an internal equilibrium. The example that I just took of an electrochemical cell is also not at internal equilibrium, because the reactions are taking place at the respective electrodes at cathode and at anode.

Now, we will take look at the wider significance of chemical potential. So, far we have discussed the chemical potential in terms of this partial derivative that is dou G by dou n J at constant T, P, n prime. It is possible to define chemical potential in terms of changes in other thermodynamic properties. For example, the other thermodynamic properties are Helmholtz free energy, enthalpy internal energy. Is it possible to express chemical potential in terms of the changes in Helmholtz free energy, in terms of the changes in enthalpy or in terms of the changes in internal energy, because if we can establish such relations then we can appreciate the wider significance of chemical potential.

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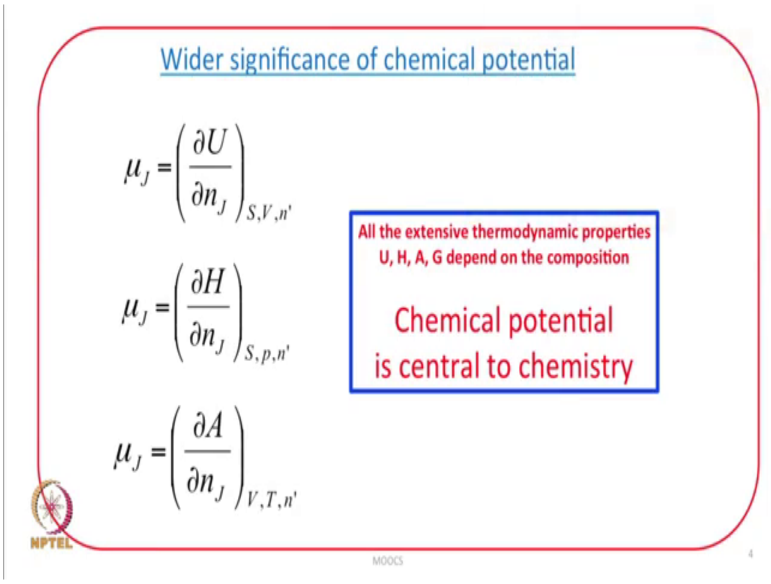

Wider significance of chemical potential

$$\mu_J = \left(\frac{\partial U}{\partial n_J}\right)_{S,V,n'}$$

$$\mu_J = \left(\frac{\partial H}{\partial n_J}\right)_{S,p,n'}$$

$$\mu_J = \left(\frac{\partial A}{\partial n_J}\right)_{V,T,n'}$$

All the extensive thermodynamic properties U, H, A, G depend on the composition

Chemical potential is central to chemistry

Let us take look at the slide the chemical potential can be expressed as the partial derivative of internal energy with respect to n J under constant entropy, volume and n prime conditions. It is very easy to derive that, but before doing that. Let us keep this equation in mind because I will be using this equation again and again, dG is equal to V dp minus S dT plus summation J mu J d n J, this equation I will be using.

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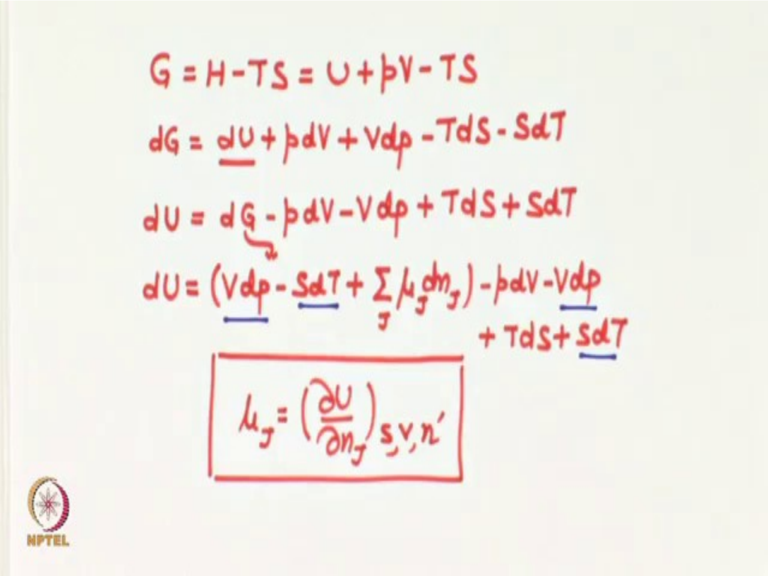

$$G = H - TS = U + pV - TS$$

$$dG = \underline{dU} + pdV + Vdp - TdS - SdT$$

$$dU = dG - pdV - Vdp + TdS + SdT$$

$$dU = (\underline{Vdp} - \underline{SdT} + \sum_J \mu_J dn_J) - pdV - \underline{Vdp} + TdS + \underline{SdT}$$

$$\boxed{\mu_J = \left(\frac{\partial U}{\partial n_J}\right)_{S,V,n'}}$$

I will start with G, G is equal to H minus T S, which is equal to U plus p V minus T S, H is equal to U plus p V. Now, I will let the reaction proceed by a small amount or the free energy change by a small amount, as a result of the change in composition, this will be dU plus p dV plus V dp minus T dS minus S dT. And dU that is what I am interested in expressing chemical potential in terms of dU this is equal to dG minus p dV minus V dp plus T dS plus S dT. Now, I use the expression for dG that I told you to remember earlier dG is equal to V dp minus S dT plus summation J mu J d n J, this is dG. And I will write everything else now minus p dV minus V dp plus T dS plus S dT, the various quantities which are going to cancel is V dp with V dp, minus S dT with plus S dT, these are going to cancel.

So, therefore, from this expression, I can write chemical potential of species J will be equal to dou U by dou n J at constant entropy, volume and composition of other components, at constant entropy, volume and n prime, this is what we wanted to prove. So, you see we have been able to establish a relation between the chemical potential and changes in internal energy. So, these intensive properties you see are getting connected to chemical potential through the changes in composition. In other words, it also tells that these intensive properties do depend upon the composition of the system.

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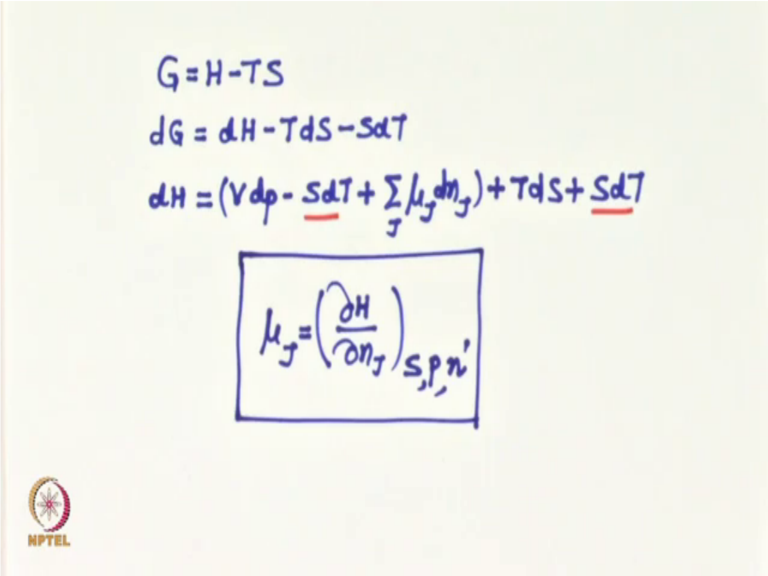

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$$dH = (Vdp - \underline{SdT} + \sum_J \mu_J dn_J) + TdS + \underline{SdT}$$

$$\boxed{\mu_J = \left(\frac{\partial H}{\partial n_J}\right)_{S,p,n'}}$$

Let us move further and establish another relation. We show that the chemical potential in a mixture of a species J can also be expressed in terms of enthalpy. Let us use that. And here once again I will start with g every time I will start with G, because I am going to use the expression for dG. And since I am interested in establishing relation with enthalpy, I always use G is equal to H minus T S. So, dG is equal to dG minus T dS minus S dT or dH is equal to dG. dG again I am going to use the same information V dp minus S dT plus summation J mu J d n J, this is for dG plus T dS plus S dT.

And you see here this term gets cancelled. And this allows me to write expression for chemical potential in terms of enthalpy, entropy constant, pressure constant and composition of other constituents constant. Now, we establish the relationship between chemical potential and the change in enthalpy. Similarly, we can also derive another expression. Here you see the chemical potential can also be connected with the changes in Helmholtz energy which is quickly we can derive that.

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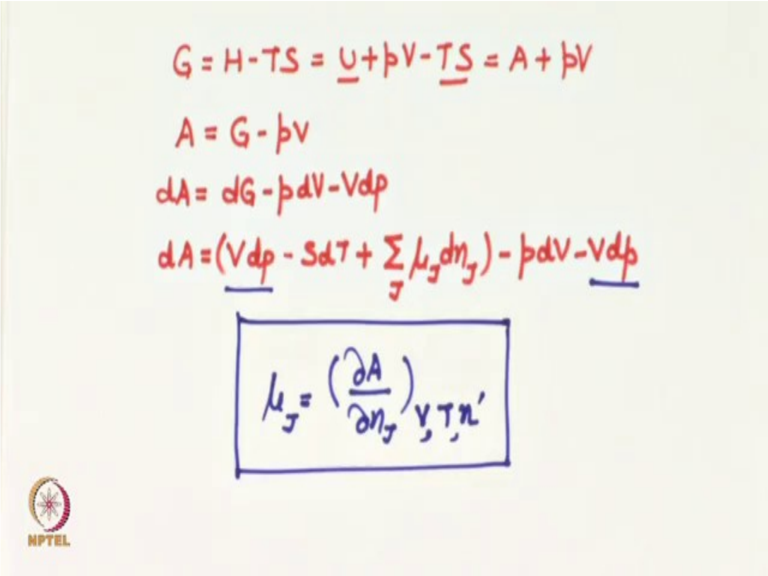

$$G = H - TS = \underline{U} + pV - \underline{TS} = A + pV$$

$$A = G - pV$$

$$dA = dG - pdV - Vdp$$

$$dA = (\underline{Vdp} - SdT + \sum_J \mu_J dn_J) - pdV - \underline{Vdp}$$

$$\boxed{\mu_J = \left(\frac{\partial A}{\partial n_J}\right)_{V,T,n'}}$$

Once again start with G is equal to H minus T S and in order to establish a connection between G and A, I will use H is equal to U plus p V minus T S, U minus T S is equal to A, which is equal to A plus p V. Or A is equal to G minus pressure into volume. dA is equal to dG minus p dV minus V dp. Let us substitute for dG, dG same thing that let us remember what we discussed earlier, dG is V dp minus S dT plus summation J mu J d n J, this is for dG minus p dV minus V dp. So, what is getting cancelled over here is equal to V dp and V dp. And from this, I can write the chemical potential is equal to change in Helmholtz free energy, when one mole of substance J is added the constants are constant volume, constant temperature and n prime. This is the next connection between the chemical potential and the change in Helmholtz free energy.

So, what we have done is shown that all the extensive thermodynamic properties such as internal energy, enthalpy, Helmholtz free energy, and Gibbs energy depend on the composition. And this is the reason chemical potential is considered to be central to chemistry. The advanced discussion in chemistry when we mostly talk about the equilibrium processes is done in terms of chemical potential. And the reason is quite obvious here is that all the extensive properties we have shown that they depend on the composition. Even the equilibrium that we are going to discuss further we will be discussing in terms of the chemical potential.

However, please remember that the most widely used definition of chemical potential is still in terms of the Gibbs energy. Whenever we are asked can you define chemical potential, the usual answer is the change in Gibbs energy when one mole of that substance is added at constant temperature, pressure and composition of everything else is constant. Even though this is the most widely used definition; the other definitions of chemical potential we have also discussed. And it is possible to express the chemical potential in terms of the changes in other thermodynamic properties.

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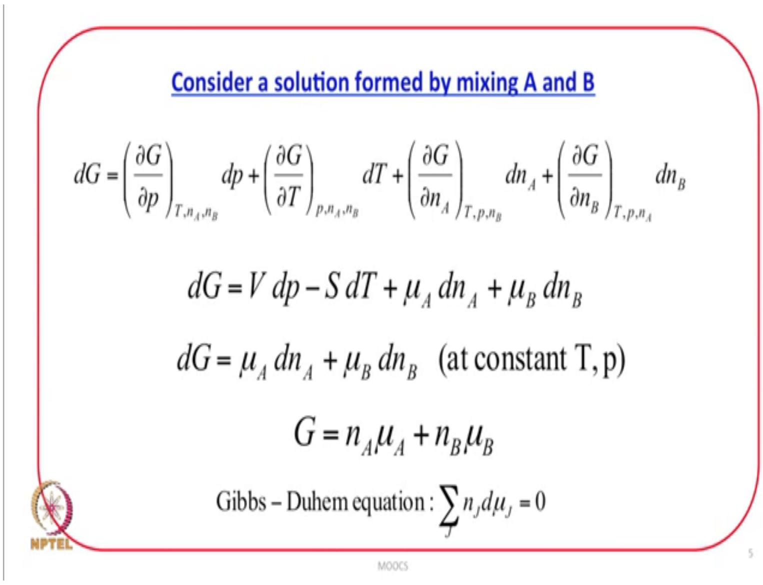

Consider a solution formed by mixing A and B

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n_A,n_B} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n_A,n_B} dT + \left(\frac{\partial G}{\partial n_A}\right)_{T,p,n_B} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{T,p,n_A} dn_B$$

$$dG = V\,dp - S\,dT + \mu_A\,dn_A + \mu_B\,dn_B$$

$$dG = \mu_A\,dn_A + \mu_B\,dn_B \quad \text{(at constant T, p)}$$

$$G = n_A\mu_A + n_B\mu_B$$

$$\text{Gibbs – Duhem equation}: \sum_J n_J d\mu_J = 0$$

Now, let us consider a solution which is formed by mixing A and B. If it is a binary mixture, the free energy will depend on pressure, it will depend on temperature, it will depend on n A, it will depend on n B.

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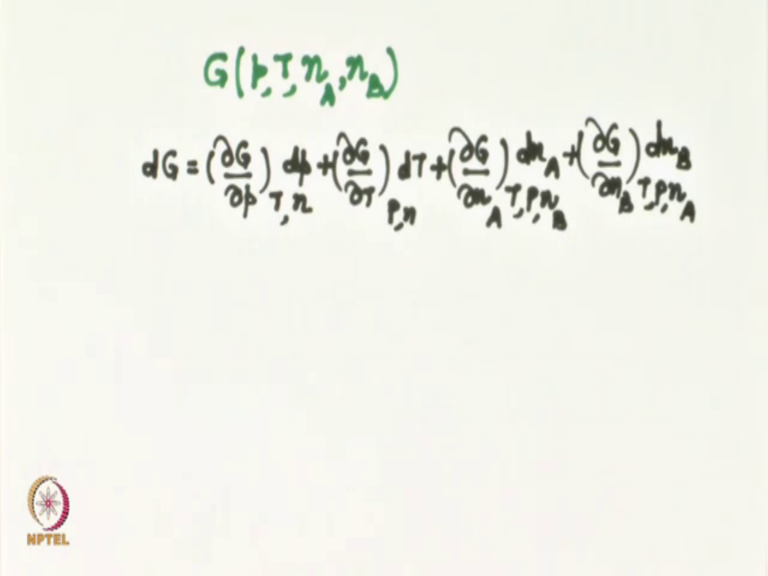

$$G(p, T, n_A, n_B)$$

$$dG = \left(\frac{\partial G}{\partial p}\right)_{T,n} dp + \left(\frac{\partial G}{\partial T}\right)_{p,n} dT + \left(\frac{\partial G}{\partial n_A}\right)_{T,p,n_B} dn_A + \left(\frac{\partial G}{\partial n_B}\right)_{T,p,n_A} dn_B$$

Now, I can write dG is equal to dou G by dou p at constant temperature n dp plus dou G by dou T at constant pressure n dT plus dou G dou n A temperature, pressure, n B constant d n A plus dou G dou n B temperature pressure n A d n B. It is in the same way as we have discussed earlier. You can rewrite this expression in terms of dG is equal to V d p minus S d T plus mu A d n A plus mu B d n B. And we have discussed that why this is equal to V, why this is equal to minus S and these are the definitions of chemical potential mu A and mu B.

If I fix the temperature and pressure then dG is equal to mu A d n A plus mu B d n B. And from this equation, this strongly suggests that if I integrate and try to find out the total value of the Gibbs function, since chemical potential is constant the expression that will turn out to be G is equal to mu A times n A plus mu B times n B, because you are treating the chemical potentials to be constant over here. So, please remember that if I have the information on chemical potentials of A and chemical potentials of B, number of moles of A and number of moles of B, I can calculate the value of Gibbs free energy

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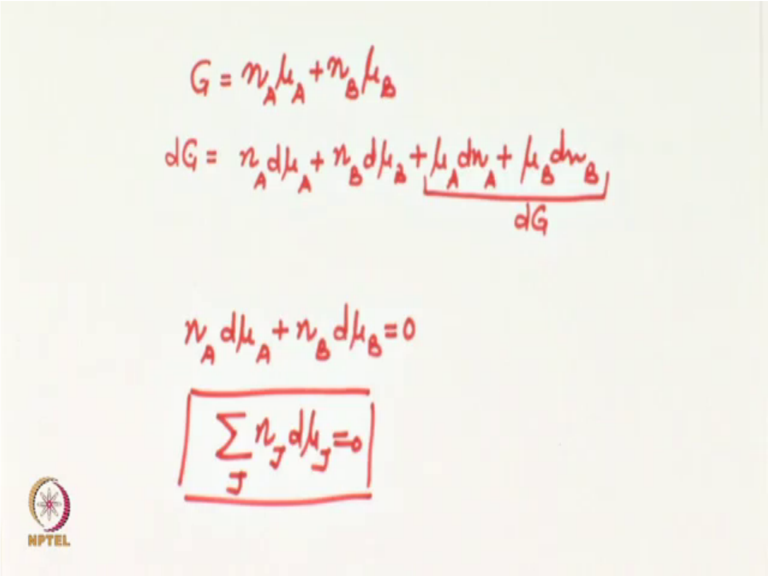

$$G = n_A\mu_A + n_B\mu_B$$

$$dG = n_A d\mu_A + n_B d\mu_B + \underbrace{\mu_A dn_A + \mu_B dn_B}_{dG}$$

$$n_A d\mu_A + n_B d\mu_B = 0$$

$$\boxed{\sum_J n_J d\mu_J = 0}$$

So, if I have the information on dG, we are writing as n A times mu A plus n B times mu B. Therefore, dG I can write n A d mu A plus n B d mu B plus mu A d n A plus mu B d n B, I can write this. And we have just shown that mu A d n A plus mu B d n B at constant temperature and pressure is same as dG, we have just shown that. The dG is equal to mu A d n A plus mu B d n B. This discussion suggests that n A times d mu A plus n B times d mu B is equal to 0. In a more generalized form, we can write this as summation J n J d mu J is equal to 0 and that is what we call Gibbs-Duhem equation.

Look at the slide, the according to Gibbs-Duhem equation, summation n J d mu J is equal to 0; that means, if chemical potential of one species decreases, the chemical potential of the other species must increase to keep this summation the decrease or increase weighted by their number of moles equal to 0. Gibbs-Duhem equation is an important equation which establishes relation between the changes in chemical potential and number of moles.

So, I hope that the meaning of chemical potential in a mixture is very clear. We must distinguish between the definitions of chemical potential of a pure substance and chemical potential of a substance when it is in a mixture. Today, we have discussed that the chemical potential is central to chemistry. And later on as the discussion progresses, we will definitely demonstrate that how this chemical potential is central to chemistry and answers many questions.

Thank you very much.