Introduction to Chemical Thermodynamics and Kinetics

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Lecture – 15
Spontaneity and equilibrium – part 3

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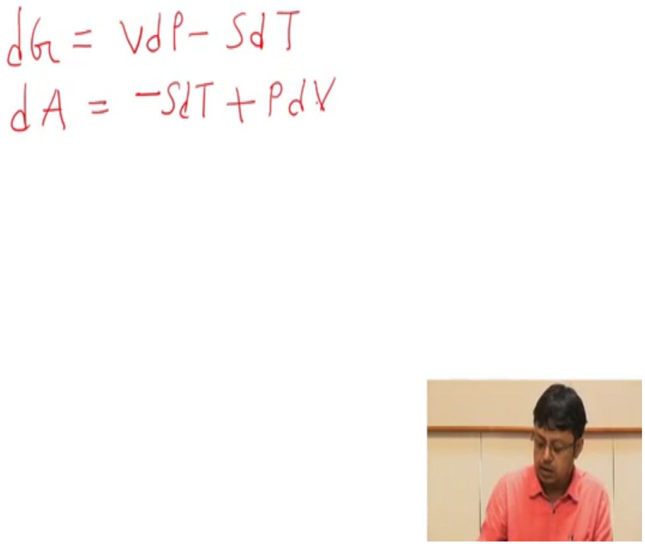

$$dG = VdP - SdT$$
$$dA = -SdT + PdV$$

So, what we just discussed is that the 2 most important relations are dG is VdP minus SdT and dA is minus SdT plus 3 dV and then.

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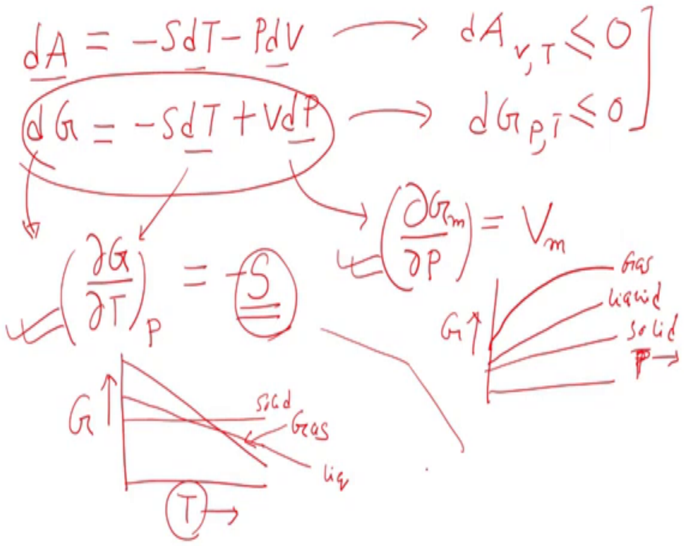

$$dA = -SdT - PdV \longrightarrow dA_{V,T} \leq 0$$
$$dG = -SdT + VdP \longrightarrow dG_{P,T} \leq 0$$
$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$
$$\left(\frac{\partial G_m}{\partial P}\right) = V_m$$

So, according to our just discussion which we just had we said that the 2 most important quantities are dA and dG and the conditions for spontaneity and equilibrium for these 2 thermodynamic functions are given by dA is minus SdT minus pdv and dG is minus SdT plus V dP.

So, you can easily figure out that for dA the conditions to be kept constant are temperature and volume, then dT and dV will be 0 and then dA equal to 0 at constant temperature volume or dA at constant or dG at constant pressure and temperature similarly can be less than equal to 0.

So, these are the natural choice for the conditions for equilibrium and spontaneity which will be frequently using now let us focus on the Gibb's free energy change only. So, start with this equation and we can first ask this question what is the derivative of the Gibb's free energy with respect to say temperature and pressure because just like we formulated the Maxwell relations we can in the similar spirit write del G del say first we are taking the gradation of this Gibbs free energy with temperature.

So, then we will just use del G del T at constant pressure that will be nothing, but equal to S now we are using only the equilibrium sign here because we are only considering the variation keeping the system at equilibrium. So, this will be equal sign. Now, what will be the curve for this if I plot G versus T. How the curves look like now remember S is entropy and entropy is a positive quantity which means del G del T P is always a negative quantity or del G del T P it decreases as we increase the temperature because del G del T P is the slope. So, Gibbs free energy decreases with increasing temperature.

Now, the decrease will be more for a gas it will be much less for liquids and solid. So, if this is gas, let me draw it once again suppose this is for gas and then the liquid will decay a little bit and the solid will decay even less. So, this is the curve for liquid and this is the curve for solid now you see that this decay is linear in the sense that as long as the slope is constant which is the entropy of the solid or the liquid or the gas then the slope will of course, be linear; however, we will see that if there is a phase transition if we keep on increasing the temperature and suppose there is a all of a sudden a phase transition, then will have breaks in these curves.

So, the curve will look like something like this and like this which we will discuss when we talk about phase transition similarly you can ask a similar question like what will be the variation of the Gibbs free energy with pressure and you can easily figure out from this equation that it is nothing, but v now usually people do not plot v people divide both side by the Avogadro number or the sorry the number of moles.

So, then what you will get is this will be nothing, but your more volume and this will be the molar Gibbs free energy now if we plot the change in Gibbs free energy as a function of temperature sorry pressure how it will look like. Now it is actually dependent on the molar volume. So, if I increase the pressure how the volume will change. So, for gas the change in volume will be something like that we will discuss why the curve looks like this and for liquids and solids the volume will be like this the change will be like this.

So, this is for gas, this is for liquid for solid the curve will be more or less flat because the change is very minimal because the molar volumes of solid or volume of the of a solid does not change too much if I apply the pressure now you can easily figure out from these equations that we can get a feeling of how Gibbs free energy is changing with respect to pressure and temperature, but let us first discuss before discussing why their curves are like this let us first discuss another important quantity which is not the Gibbs free energy, but the Gibbs free energy divided by temperature how that quantity change.

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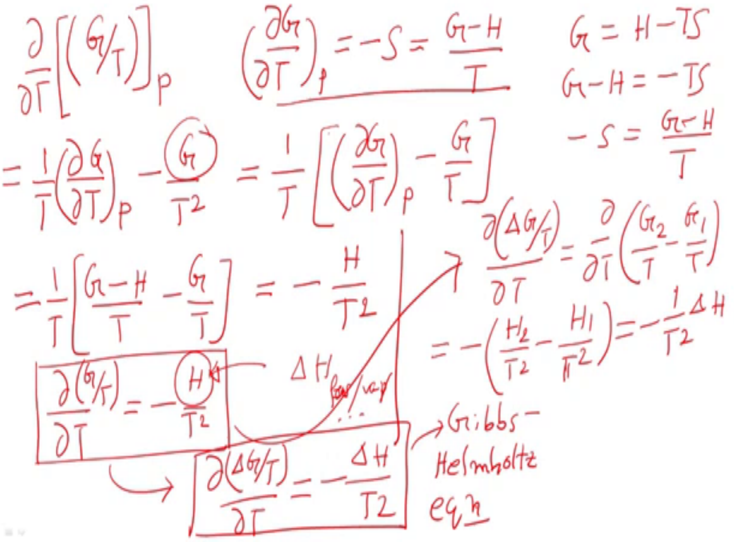

$$\frac{\partial}{\partial T}\left[\left(G/T\right)\right]_p \qquad \underline{\left(\frac{\partial G}{\partial T}\right)_p = -S = \frac{G-H}{T}} \qquad G = H - TS$$

$$G - H = -TS$$

$$-S = \frac{G-H}{T}$$

$$= \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = \frac{1}{T}\left[\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T}\right]$$

$$= \frac{1}{T}\left[\frac{G-H}{T} - \frac{G}{T}\right] = -\frac{H}{T2}$$

$$\boxed{\frac{\partial (G/T)}{\partial T} = -\frac{H}{T^2}}$$

$\Delta H_{fus/vap}$

$$\frac{\partial(\Delta G/T)}{\partial T} = \frac{\partial}{\partial T}\left(\frac{G_2}{T} - \frac{G_1}{T}\right)$$

$$= -\left(\frac{H_2}{T2} - \frac{H_1}{T^2}\right) = -\frac{1}{T2}\Delta H$$

$$\boxed{\frac{\partial(\Delta G/T)}{\partial T} = -\frac{\Delta H}{T2}}$$

Gibbs-Helmholtz eqn

Now, let us consider how this quantity Gibbs free energy divided by T changes with temperature for that we can calculate this quantity how what is the derivative of G by T at the partial derivative of G by T with respect to temperature keeping the pressure constant.

So, let us use the chain rule of differentiation. So, if we take first the differential with respect to differential of G. So, the first term will be one over T del G del T P and the second term will be the differential of one over t. So, that will be G over T square now we know that already we showed it del G del T P is nothing, but minus s, but if you use minus S, here we will not get a very useful relationship because the G is sitting here.

So, we can write the minus S again in terms of G now from definition G is H minus TS. So, G minus H is minus TS. So, minus S is G minus H divided by T. So, it is G minus H divided by T now if you put this in this equation what we get is one over T we can take one over T common and then, I will have del G del T P minus G over T because we have taken one over T common here and then we get for del G del T P which is minus S will just write G minus H by T minus G by T and you took one over T common then this G by T factor will cancel out.

And we will be left to it minus H by T squared. So, this equation that del del T of G by T is minus H by T square is a very very important relationship because here we see that we can directly measure you can directly measure the change in Gibbs free energy divided by temperature with respect to temperature and connect it to the enthalpy now whenever we have a phase change, we can actually use this equation because during the phase change we can have that usually the pressure and temperature are kept constant. So, you can have; for example, if we are considering a vaporization of water, then that is asserted heats change will be nothing, but since it is at constant pressure q P will be equivalent to H and then will be considering only H of the fusion.

Now, instead of H of the fusion what we need now is delta H of say fusion or vaporization or sublimation whichever process it is. So, how do you write it in terms of delta H now we can start from the same equation and we can write that well, I can actually use say if we ask this question what will be del del T of delta G by T we can have it rewrite it bring very nice way that we can write what is delta G delta G is nothing, but G 2 minus G 1. So, you can just write it as G 2 divided by T.

Student: 0.

Minus G 1 divided by T and we can use the same expression and then what we will discover this is nothing, but del minus H 2 divided by T square minus H one divided by T square. So, which is nothing, but minus one of over T square into delta H. So, we can get another useful relation which is del of delta G by T del T is minus del H by T square. So, either form is known as Gibbs Helmholtz question.

So, this will be very important when we discuss phase transition. Now let us discuss why the curves of G versus P or G versus T looked like the way we drew; now remember for a finite change which is delta G we can always write remember that GS as state function dG between state 1 and 2 and then if we consider say a constant temperature process.

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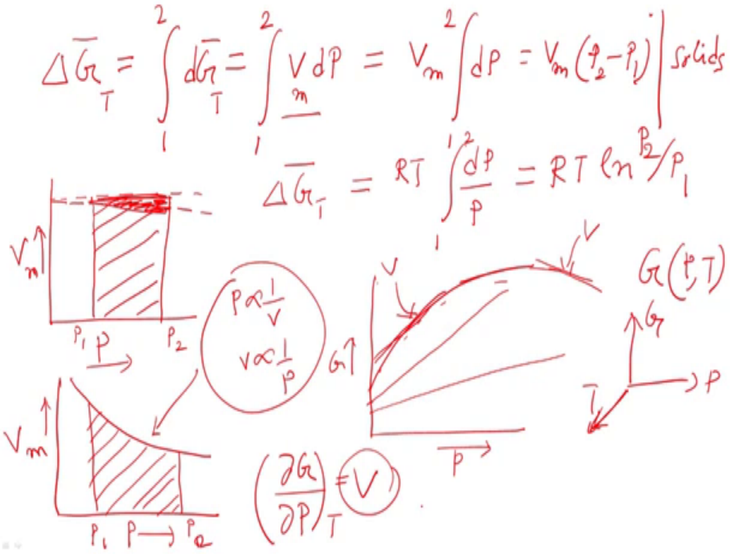

$$\Delta \bar{G}_T = \int_1^2 d\bar{G}_T = \int_1^2 V_m\, dP = V_m \int_1^2 dP = V_m(P_2 - P_1) \Big| \text{Solids}$$

$$\Delta \bar{G}_T = RT \int_1^2 \frac{dP}{P} = RT \ln P_2/P_1$$

$$P \propto \frac{1}{V} \qquad V \propto \frac{1}{P}$$

$$\left(\frac{\partial G}{\partial P}\right)_T = \boxed{V}$$

So, there it will be nothing, but V dP because dG was VdP minus SdT. So, we will have volume 1 to 2 and again, if we are considering say molar volume we can use either the sign m or we can use G bar whichever is fine, but just dividing both side by the number of moles and then you get a equation for the molar volume. Now, if the molar volume is constant which will be the situation for say solids, then, I will have a very simplified integration which is nothing, but molar volume times the final pressure minus initial pressure. So, this will be true only for solids and if you know plot how the delta G looks like so, the molar volume will be more or less constant and if I multiply it by P 2 minus P 1.

So, the delta G will be nothing, but the area under this curve; however, in reality if we apply more and more pressure the molar volume will actually decrease and there will be some error introduced in this because we are basically including this area which you should not have included. Now similarly if it is a gas, then we can actually use the ideal gas equation where we have to write this volume in terms of pressure using NRT by v, but it is molar volume. So, it is will be RT by V and since the temperature is constant you can take it out of the integral.

So, I will have here one going to state 2 then the expression will be RT ln P 2 by P 1 and how the curve will look like. So, its a logarithmic plot and you know how the PV diagram looks like, but instead of pv we are drawing here as VP diagram keep that in mind and then we have like this because according to Boyles law P is proportional to v or we could write actually we proportional to P.

So, this is the curve and if we take to one lower limit which is P 1 and one upper limit which is P 2 then the Gibbs free energy will be nothing, but area under the curve, but the change in Gibbs free energy will be nothing, but area under this curve and then you can always argue that when we vary the temperature only to the other quantity which is just discussed for a gas remember that it was we had an equation like del if we just go back and check this thing your del G del P the variation of Gibbs free energy with respect to say with respect to pressure at constant temperature was v now think about it how the curve will look like for a gas we draw a curve like this now this is coming because here we are plotting G versus P as you increase the P. Now the V is also changing the slope of the curve is V here.

So, as I am changing the pressure initially I had a very high slope why because at low pressure the volume was more at higher pressure the volume was less. So, that is why the slope is changing slope of the curve; however, for solids and liquids the change in the volume with respect to pressure is not that much overall remember that V is a positive quantity that is where you have a positive slope, but the slope itself is changing.

So, that is why I had a curve like this and for solids it does not almost does not change; however, for gas it changes a lot because gases are more compressible than solids and liquids and that is why this curve looks like this where this act slope at any point is given by the volume, but the volume itself actually decreases as we change the increase the pressure. So, the slope itself is decreases as we are increasing the pressure.

So, you could actually plot the variation of Gibbs free energy as a function of pressure and temperature together and get something like a surface plot which we also plot it for pressure volume temperature when they are all traveling together and you can get a surface just like we did for a pressure volume temperature for ideal gas and similarly could generate a surface or you could plot the G versus P and T together and this is a very interesting surface you can have a look at it. It is given in the book by Peter Atkins which is referred for this course now we will conclude our discussion on for this part here and before that let us summarize what we discussed in this entire section which we where we discussed about spontaneity and equilibrium.

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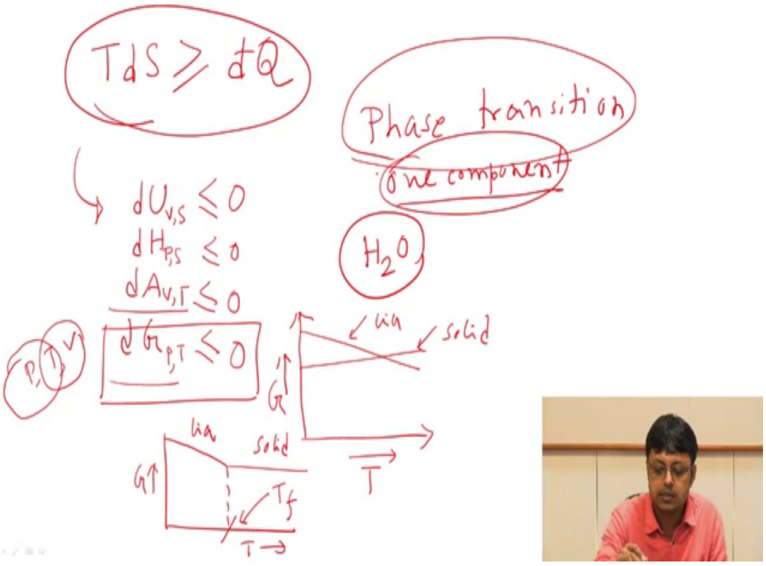

So, we started from a very fundamental equation that TdS must be greater than or equal to d cross q starting from the argument that d S is equivalent to d cos q reversible when the reversible heat change is either the same of the heat change of the process if the process is reversible or it will be more than the heat change of the process which is a d cross q if the process is not reversible and then starting from this fundamental equation we built up many other equations in terms of d U d H dA and d G and we showed that each of this equation will give rise to a condition for spontaneity or equilibrium.

But the spontaneity is given by the lessons and the equilibrium is given by the equal design, but the conditions are very very different for du it was constant following temperature and sorry it was constant volume and entropy because d u was TdS minus pdv for d H it was constant pressure and entropy because it was TdS plus VdP and for dA, we had constant volume and temperature and dG you had constant pressure and temperature and since.

Pressure volume temperature are 3 more of fundamental parameters which we can keep constant or change as our will. So, we often either change the temperature and the volume or the pressure and the temperature. So, the natural quantity to look at is either dA or dG and we argued that in most of the cases we keep the pressure constant which means this is the most useful relationship which we will be using.

Now in the next lecture we will discuss we just build up from our discussion on this particular aspect and then we will be talking about phase transition and then first we will talk about only one component in the sense that only one pure substance is present for example, say water and we will discuss how the free energy or the Gibbs free energy at constant pressure is changing if we change the temperature for example, and we know that water if we just hit ice it will first melt into water and then over a large range of 0 degree centigrade to hundred degree centigrade.

It will be a liquid water and then it will wall and form water vapor. So, that is the gaseous phase and we will talk about it how does it look like in an energy diagram in an equivalent energy diagram and how what happens when the how the curve looks like when we have phase transition meaning when at some point when we are having say ice to water transition how the curves look like of course, I mean in those curves will have a discontinuity as is obvious when you are discussing that the change in Gibbs free energy.

As a function of temperature or certain changing this branch as a function of pressure we discussed that this is the pressure curve and we could discuss the temperature curve also like this and then remember that we said that there the curves will look like this and suppose this is for a curve of liquid and this is suppose curve for a solid.

And then if you have a liquid to solid transition then the curve will first change like this and then eventually it will change much more slowly. So, the curve will be something like this it will first come like this and then it will change slowly something like that will happen. So, we will discuss what how to represent this thing and where this temperature will be called as say this is basically liquid to solid. So, this curve will be something like a TS. This temperature is the freezing temperature should call as TF.

So, you will draw such curves and we will try to understand how the free energy of the system which is the Gibbs free energy is changing with temperature as well as with pressure and then we will talk about the phase transition for one component system and after that we will consider we will discuss about chemical equilibrium and then we will consider discuss some part of electro chemistry and there we will conclude our part on or the lectures on thermodynamics portion and then we will discuss start to discussion on the chemical kinetics.

Thank you.