Introduction to Chemical Thermodynamics and Kinetics

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Lecture – 25
Chemical Equilibrium – Part 5

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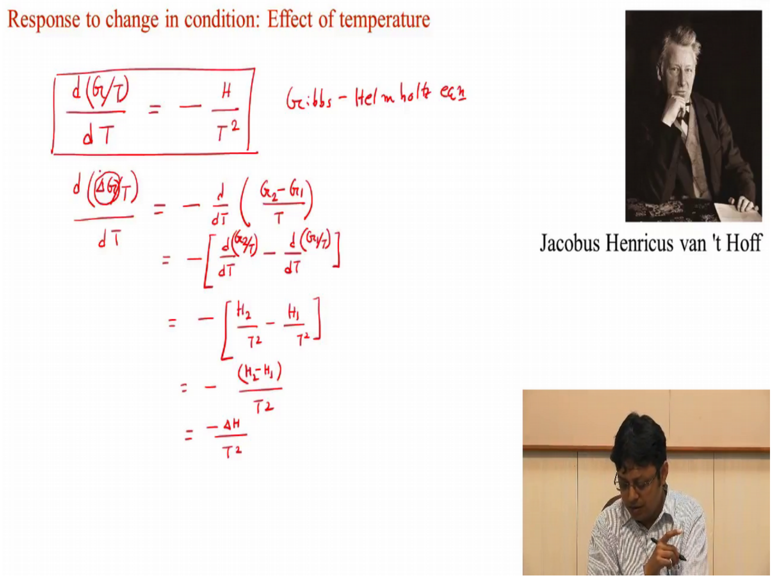

Response to change in condition: Effect of temperature

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

Gibbs - Helmholtz eqn

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

$$= -\left[\frac{d(G_2/T)}{dT} - \frac{d(G_1/T)}{dT}\right]$$

$$= -\left[\frac{H_2}{T^2} - \frac{H_1}{T^2}\right]$$

$$= -\frac{(H_2-H_1)}{T^2}$$

$$= \frac{-\Delta H}{T^2}$$

Jacobus Henricus van 't Hoff

Now, we are going to discuss the effect of temperature on the equilibrium constant. Remember that the equilibrium constant was defined as the standard Gibbs free energy change at constant sum at sum defined pressure which was 1 bar.

So, it means that the equilibrium constant will now change with respect to temperature because there is no specification with respect to temperature. So, we can actually define the equilibrium constant in different I mean like there are different ways of thinking about how the equilibrium constant is changing with respect to temperature. But would like to connect it to the heat or the enthalpy of the reaction because; usually you see you try to follow the heat released in the reaction in the chemical reaction.

But here we are talking about the delta G naught the delta H, but the question is how will you connect it? And that connection was meant by a van t Hoff and van t Hoff did lot of work on thermodynamics as well as chemical kinetics and he started many different systems and he was the first to received the noble prize in chemistry.

And also he and Oswald together started the first journal or basically periodical on physical chemistry. Around 1887 they started together this beautiful journal called Jaxa for physical chemistry you can actually read about it more on some web resource. Nw we will we will just going to discuss the front of treatment how the equilibrium constant is going to affect that temperature.

Now, what we are going to do is already known to you; we talked about this how G tends to or say the reaction free energy or the free energy has a variation with the temperature that if you remember that there was a Gibbs Helmholtz equation which we discussed sometime back.

And that basically tells that if we had this thing the G of T dT that will be nothing, but minus H by to T square. And similarly we also wrote it in the differential form in the sense that if this is correct then you can say that fine what is the value of this quantity?

So, that will be nothing, but minus we can write it term by term. So, T dT of delta G is nothing, but G 2 minus G 1. So, suppose the system is undergoing a finite change from state 1 to state 2 divided by T. And now we can actually very cleverly write Gibbs Helmholtz equation in this form. So, it is nothing, but d dT of G 2 by T minus dT T of G 1 by T.

So, according to this definition again it this is the Gibbs Helmholtz equation or Gibbs Helmholtz relation. And then we see that we have minus H 2 by RT square minus H 1 by RT square, which is nothing, but minus H 2 minus H 1 divided by T square there on be any R which is nothing, but minus delta H by T square.

And that exactly what we are going to use and then what we say here is that we can actually write the Vant Hoff equation. Now remember that we also could write it in terms of I mean how do how you this is basically the Gibbs helmholz relation, but the question is how do you connect it to the to the equilibrium constant? Now it is very obvious because we have a delta G here; so, we will connect it to the definition of a equilibrium constant and you already know that delta G 0 is minus RT ln k or k equilibrium.

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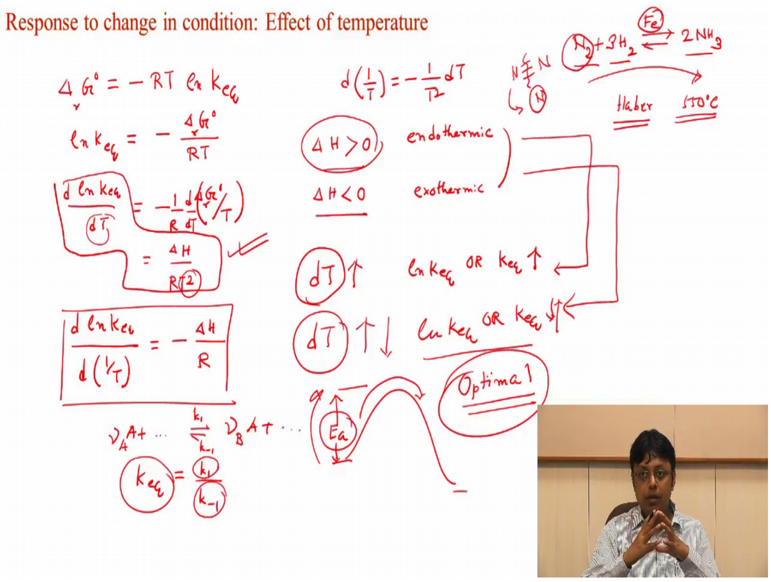
Response to change in condition: Effect of temperature

So, we can write that ln k equilibrium is nothing, but minus delta G reaction free energy and the standard state divided by RT. So, we can write it instead of taking the equilibrium constant versus temperature, we can actually write it d ln k equilibrium dT and then we will have minus delta G R 0 1 over R you can take common and basically d dT of this quantity.

Now, that we are going to now we are going to use the Vant Hoff equation. And we already know that it is minus delta H by T square now this minus and this minus cancels. So, I will have 1 over RT squared or we can just write it as a delta H by RT square. So, alternatively you could also write the Gibbs Helmholtz equation in a slightly different fashion. Now instead of writing it as like this you could write it as say this 1 over T term you could actually bring it forward and then you could write it in terms of d ln k equilibrium d 1 over T how it varies ?

Now, you can easily figure out what is this quantity. So, d of 1 over T is nothing, but minus the derivative of the 1 over t so, 1 over T square with a minus sign and times the differential of T. So, that will be dT by what minus 1 over t. So, what we could write right from this equation this particular equation this will be 1 over T square.

So, that 1 over T square term we are just bringing on the other side I mean like this if you just bring it on the other side it will be basically multiplied by T square or you can divide it by 1 over T square and include a minus sign and then this you will get. So, either this equation or this equation where d ln k dT is del H by RT square is known as a Vant Hoffs equations for a variation of the equilibrium constant with temperature.

Now, when you have the delta H for the reaction is say positive which means it is an endothermic reaction. Remember that delta H is the heat change associated with the reaction and the heat change positive we say in the in by our convention when the surrounding supplies energy to the system.

So, these are the endothermic reactions that we have discussed; if that is negative that is positive then this log of d ln k dT a basically the slope of ln k versus T curve will be positive because delta H is positive in this case.

Otherwise, if we have an exothermic reaction where heat is released and then if you plot ln k equilibrium versus temperature then you will see a negative slope.

So, the then you can actually predict the how the whether this reaction is endothermic or exothermic by looking at the equilibrium constant or whether the equilibrium constant is are changing with temperature or not. Now what is the essence of that is that positive slope means actually we are having when the ln equilibrium when you are increasing the temperature if the dT is high.

And then we are seeing ln equilibrium ln k equilibrium sorry or equivalently you can say k equilibrium that actually is also increasing for endothermic reactions. Which means that for endothermic reactions if we supply heat from outside; how do you change the dT? The dT means actually it is the temperature of the system you are raising, but that I can only do by supplying heat from outside.

So, if I supply heat from outside; so, and increase the temperature then the k equilibrium of the reaction is also increasing which means I will have more product divided by the product versus reactant ratio will be more which means the forward reaction is getting more and more favored. Because if you remember whatever is the reaction what whichever way you write it nu A plus whatever is going to nu B plus whatever reactions; ultimately the equilibrium constant is can be written as the forward versus reverse reaction which means if that is going higher this means actually the forward by reverse is getting higher.

So, the forward is increasing and the reverse is decreasing or in some way which means you are getting more product than the reactant; you are shifting the equilibrium towards nu new site in a very positive way. This exactly the same opposite thing will happen. So, we will see that for this case; if I increase it this ln k equilibrium when exothermic reaction are equivalently the equilibrium constant that decreases for an exothermic reaction; Which means if I had reduce the temperature for an exothermic reaction, then I could actually increase the equilibrium constant.

In the or the product ratio, but usually you might have a kinetic barrier meaning that the reactants are may need a very very a very much initial temperature some amount of heat in order to form the product. So, which means actually they always have a kinetic barrier in the sense that they need to surmount some amount of energy or then use to actually spend some amount of energy to cross a barrier. And that crossing of the barrier we will discuss in detail when we discuss the kinetics part, this is known as the activation energy and that energy has to be supplied first.

So, it is not always that do not think that if I go to a 0 Kelvin temperature then the reaction will be the fastest it is not like that. So, you need a minimum temperature and then only you can see that fine I will have a maximum amount of the product.

So, always that is the reason we keep this temperature at an optimal temperature; if we reduce this too much then actually you cannot get anything. For example, you have started it like for this premise reaction which we will also discuss when we considered the catalysis part is going to say ammonia nitrogen and hydrogen which is extremely important reaction for our survival. Now this reaction is actually exothermic it produces lot of heat.

So, if you have a quencher of it or basically if you reduce the temperature; then there reaction will shift towards this side the forward side and we will have more and more ammonia; however, you will realize that you need some amount of energy in order to proceed this reaction because the reaction actually involves the step, where actually this nitrogen molecules need to be the bond between the nitrogen atoms in the nitrogen molecule needs to be broken to generate these nitrogen atom which will react with the hydrogen atoms to give you some product.

And this reaction happens always were in presence of some iron catalyst and we will discuss in detail how the surface catalysis works. And then when it happens then we see that this breakage of the bonds requires some energy. So, that is basically the activation barrier of this reaction because it needs to break the bond and then only it can go to the product site.

So, that is why Haber when he did this we a famous reaction he kept the temperature I think around 550 degree centigrade and that he called as the optimal temperature. So, you need a optimal temperature to be maintained throughout so, that you get the maximum product pressure. It is not like that for every exothermic reaction you have to since actually heat is released you can actually quench the heat of course, you can increase the yield.

But inherently the system also needs some heat; otherwise the reaction will not start at all. So, now we conclude our part on this chemical equilibrium.

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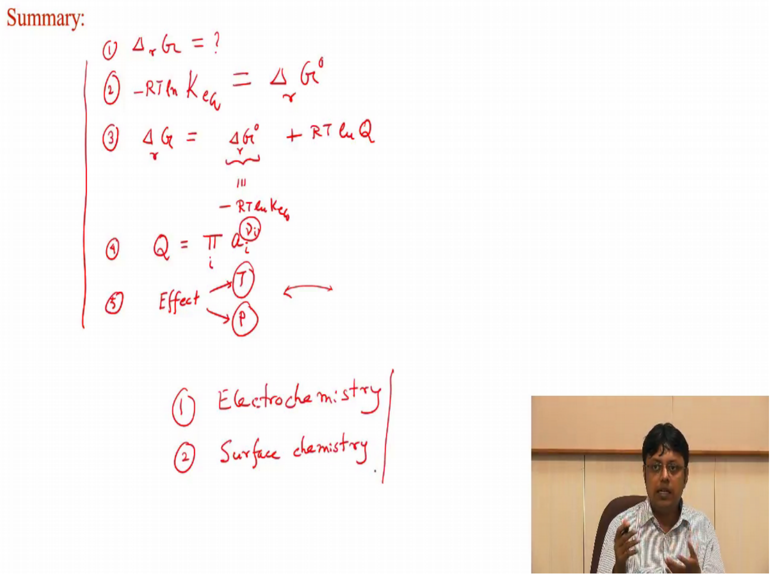

Summary:

① $\Delta_r G = ?$

② $-RT\ln K_{eq} = \Delta_r G^0$

③ $\Delta_r G = \underbrace{\Delta_r G^0}_{\equiv\, -RT\ln K_{eq}} + RT\ln Q$

④ $Q = \prod_i a_i^{\nu_i}$

⑤ Effect $\to$ Ⓣ, $\to$ Ⓟ $\leftrightarrow$

① Electrochemistry

② Surface chemistry.

So, to summarize what we discuss is that we first discussed the concept of the how to write the equilibrium constant?

So, we showed that the k equilibrium or minus RT ln k equilibrium can be connected to the reaction Gibbs free energy at standard state. Prior to that we actually defined what is the reaction Gibbs free energy? What is delta 0? How we can write it as a difference between the chemical potentials. And then we kind of expanded it for a general case and we showed that these delta G reaction free energy can be written as a part which is delta; the standard part which is actually connected to this k equilibrium which is nothing, but minus RT ln k equilibrium and plus RT ln Q where Q is the quotient for any k at any time. Q will be equal to k equilibrium only under equilibrium and then we said we basically showed what is the expression for Q or k.

And we showed that it is nothing, but the summation over all this sorry multiplication over all the terms where the reactants or the products are you take the activity of that particular thing and raise it to the power of their stoichiometric coefficient, but this coefficient will be positive for products and negative for reactants. So, that we say we need what is the stoichiometric coefficient for A; we will say always minus nu A; we will never say that it is a nu A or that way.

So, the or I mean ah; so, the negative sign has to be included and similarly at if it happens at equilibrium; that means, it is a equilibrium constant. And then we talked about the effect of external agents like a effect of temperature as well as pressure. Initially we talked about pressure and then we talked about temperature and that actually explains how if we want to make a change that system will always try to counteract that change which is related to a principle which you studied in high school known as Le Chatelier principle and we explained why the Le Chatelier principle is like that we showed you that how if the pressure wise how the degree of dissociation changes.

We also showed you how if the temperature varies how basically and exothermic or the exo endothermic reactions are control. And so, this is basically the summary of this part which we call as equilibrium. And then we will discuss one application actually two applications of on thermodynamics on or the equilibrium thermodynamics one is the electrochemistry part where we talked about what is the electro motive force of a electrochemical cell and galvanic cell how basically it generics electricity and how we can write the electro motive force and connect it to the standard reaction free energy.

And the second thing we will discuss and that is on surface chemistry part or again it is a equilibrium surface chemistry in the sense that you have a surface and our are an interface between two bulk phases. And how you can actually formulate the thermodynamics of the interface, how we can say that whether the molecules will trend prefer to stay in the bulk phase more or in the interface more. And then we can also classify the molecules based on that particular characteristic. So, these two things we will discuss in the next lecture.

Thank you.