Introduction to Chemical Thermodynamics and Kinetics
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Lecture – 21
Chemical Equilibrium – Part 1

Hello everyone, today we will start our discussion on chemical equilibrium. Now in this lecture will cover, the how, what happens, when several systems reactants and products are in equilibrium and the chemical reaction is happening. What happens to how we can predict the spontaneity or the directionality of the chemical reaction and what happens to the reactant mixtures, like what happens to the concentrations of the reactants and the products when equilibrium is attained.

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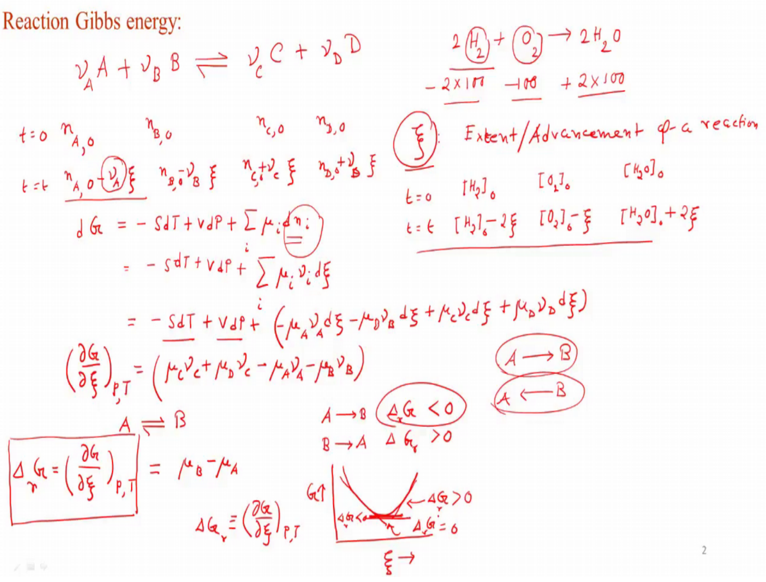

Reaction Gibbs energy:

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$$

$t=0$ $n_{A,0}$ $n_{B,0}$ $n_{C,0}$ $n_{D,0}$

$t=t$ $\underline{n_{A,0} - \nu_A \xi}$ $n_{B,0} - \nu_B \xi$ $n_{C,0} + \nu_C \xi$ $n_{D,0} + \nu_B \xi$

$$dG = -SdT + VdP + \sum_i \mu_i dn_i$$
$$= -SdT + VdP + \sum_i \mu_i \nu_i d\xi$$
$$= -\underline{SdT} + \underline{VdP} + (-\mu_A \nu_A d\xi - \mu_B \nu_B d\xi + \mu_C \nu_C d\xi + \mu_D \nu_D d\xi)$$
$$\left(\frac{\partial G}{\partial \xi}\right)_{P,T} = (\mu_C \nu_C + \mu_D \nu_C - \mu_A \nu_A - \mu_B \nu_B)$$

$2 H_2 + O_2 \rightarrow 2 H_2O$

$-\underline{2 \times 100}$ $\underline{-100}$ $+\underline{2 \times 100}$

ξ: Extent/Advancement of a reaction

$t=0$ $[H_2]_0$ $[O_2]_0$ $[H_2O]_0$

$t=t$ $[H_2]_0 - 2\xi$ $[O_2]_0 - \xi$ $[H_2O]_0 + 2\xi$

$A \longrightarrow B$

$A \longleftarrow B$

$A \rightleftharpoons B$

$$\boxed{\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T}} = \mu_B - \mu_A$$

$A \rightarrow B$ $\Delta_r G < 0$

$B \rightarrow A$ $\Delta G_r > 0$

$$\Delta G_r \equiv \left(\frac{\partial G}{\partial \xi}\right)_{P,T}$$

Now to begin with we will define a quantity advancement, but to understand why we need an advancement let us consider particular situation.

Suppose, we have our reaction which we are writing as a, nu A A, nu A is the stoichiometry of the reaction. Last, nu B of B plus this way and suppose it is in equilibrium with C and D, say nu C of C and nu D of D.

Now you know when we discuss the rate of the reaction or the kinetics of the reaction, will use the similar concept. Now let us take an example for example, say hydrogen and oxygen forms water and you know that the balance equation, will be 2 H 2 plus O 2 is 2 H 2 O. Now suppose I talk about how much reaction has proceeded in say 1 minute and say for example, 100 molecules of oxygen has been consumed in that in the 1 minute duration. And we are saying say how many number of hydrogen will be disappearing in 1 minute that will be 200 times of course.

Now, in order to ask this question how much the reaction has proceeded, if you look from oxygen's perspective it is 100 molecules if you look at hydrogen perspective it is 200 molecules. So, we need to actually quantify the extent of the reaction independent of the constituents like whether it is a hydrogen whether it is oxygen, something like that and also you can you could actually, explain the extent of the reaction based on the products also in 1 minute, we see that again 200 number of molecules are produced.

Now from the reactants perspective if we say then we will see that this number of molecules has been reduced. So, we can actually use a negative sign for that, but from the products perspective it is actually positive because those number of molecules has been generated.

So, you have to in order to maintain a consistency, that how much reaction has preceded 1 has to keep those things in mind, whether it is a reactant or the products and the stoichiometry, but if we want to get rid of all these things.

So, whether it is a reactant or whether it is a product or it is independent of the stoichiometric, we want to find something which will tell the extent of the reaction in 1 minute how much the reaction of has happened that quantity will be independent of whatever we are choosing like whether it is a reactant or whether it is a product, and that quantity we call as the advancement or the extent of the reaction.

So, we call it as a extent, or sometimes advancement of a reaction and we denote it by a symbol, and the symbol is a Greek letter is called xi. So, xi is denoted as the advancement of a chemical reaction, now to give you an example suppose for example, I have some amount of say for 1 minute, I say that the reaction has proceeded by xi amount. So, which means from reactants perspectives, the hydrogen's perspective the number of moles that will be present or not that will be consumed say at time 0, we had nu say a H 2 concentration was something like H 2 0, oxygen concentration was O 2 0 and water concentration was say H 2 O 0.

So, the suffix 0 means actually, the at time 0, now similarly we can ask this question that at time t suppose the reaction has preceded by xi amount, that is the extent of the reaction. So, here the amount of hydrogen after that specified time will be nothing, but H 2 0, and then it will be negative off because I am using negative, because it has consumed negative for 2 times xi, similarly for oxygen it has also been consumed. So, it will be oxygen minus xi.

So, it is the stoichiometry including the xi, whether it is a reactant inconsiderately as a negative sign, and if it is a product it will be either a positive sign and for water we can say that it is H 2 O initial concentration plus 2 xi. So, xi is actually independent of whether it is a reactant of the product the total amount of the reactant of the product which is at time t will be either reduced or increased, but that will be proportional to xi and that proportionality constant will be just as stoichiometry constant including the xi.

Now, then we will have defined a quantity which is very much independent of the reactant of the product and that I basically tells how much the reaction has advanced. So, that showing calls it as an advancement or the extent of the reaction, now what is say that we have in that in that notation that we have we are writing it.

So, suppose the initial amount was n A 0. So, you can write it as n A comma 0, and similarly nu B was n B 0 nu C was n C 0 and nu D was n D 0. And then we can say that how much again how much amount stoichiometric amount has been I mean remained, how much amount is remained at time t. So, this will be nothing, but minus nu A into delta xi.

Suppose, I am calling this as delta xi amount has been reduced, or delta z it is the extent of the reaction in an interval say delta t. So, similarly a from in this perspective it will be n B 0 minus nu B into delta xi, from n C is perspective it will be n C 0 plus nu C into delta xi, and from n D is perspective it will be n D 0 plus mu C nu D into delta xi. So, delta xi is the advancement in delta t time. So, we can ask this question fine, so what is the free energy that is associated or what is the free energy change that is associated with this reaction. So, we know that the amount which we are talking about is nothing, but the Gibbs free energy which we can write it as a delta G. Now we already know that delta G is nothing, but minus SdT plus VdP plus mu i dni up some over the mu i dni.

So, that we can write it mu i dni, so that is a basically the amount instead of delta G you can write it as dG. Now we are asking this question, what is the amount of dni, now if you think from this equation we can easily calculate, what is the amount of dni? So, instead of the delta notation we can we can just use say at time t, we had xi advancement just like we did it for the in the example of water, and then now we can differentiate.

So, this was at time 0, and if you differentiate it you will see that if I differentiate any every quantity, what will be left with is this thing because n A 0 is constant, n v 0 is also constant. Similar for mc 0 and m d 0, so what I will be leaving it a left with for the a reactant a will be minus nu A d xi for dni. So, what will be what we can write it is nothing, but minus SdT plus VdP plus some of our i and we can write it as say, in this case it will be minus mu A d xi, minus mu B into d xi plus mu C. I am just taking the summation into d xi, it will be basically minus nu A sorry, it will be minus nu A or we can write it once again as in terms of mu and i.

Let it is use the same notation some of our i, it is mu i into the stoichiometry, which is nu i including the sign remember and then it will be nothing, but into d xi because I am just taking the derivative. So, what do we notice here, is that at dG, if I take the derivative with respect to say d xi that will be nothing, but the difference between the all the reactants and products such as just expand it and then it will be clear. So, what I am saying here is that it will be minus SdT plus VdP plus, now you expand we have nu A and nu A, but nu A was the minus sign remember.

So, it will be minus nu A d xi minus, will have say nu B nu d d xi plus, will have nu C nu C because nu C had a plus sign into d xi plus will have nu D into n D into d xi. So, if I take this derivative delta G, del G del xi, at constant pressure and temperature then these 2 terms vanish because I am taking constant pressure and temperature.

So, I will be left to it nu C nu C plus nu D nu D minus nu A nu A minus nu B nu B. So, that quantity now let us think for a moment suppose we had a very simple reaction like A is going to B, and this is an equilibrium reaction and. So, what is happening a here in that so in this case, A is the reactant and B is the product.

So, this del G del xi at constant pressure and temperature that will be nothing, but it will be nu B minus nu A you can easily figure that out. So, what I am doing is that, I am taking basically the difference mean that gives free energies and the difference is taken from the reactant gives free energy minus the product gives free energy. So, what I see is that it is difference I can actually call as some difference, in the Gibbs free energy, when the reaction happens.

So, you can call it as a reaction Gibbs free energy and we denote it as delta G and since this delta corresponds to some reaction we put a suffix r here. So, reaction Gibbs free energy is defined as the derivative of the Gibbs free energy with respect to the advancement of the reaction at constant pressure and temperature.

Now, the question is whether, the reaction will be spontaneous in this direction A to B or the reverse direction is spontaneous that we can easily figure out. So, if A to B is spontaneous then this direction is the forward direction, then we will see that the delta G r should be negative, because we know that at constant pressure and temperature the changes in Gibbs free energy if it is negative that gives the direction of spontaneity, and in this case if that is so.

Then the B to C direction or the B to A direction, I should say for that actually the delta G r, if that is say more than 0, it is positive then actually it is not spontaneous, but what happens here is that in we are not talking about 1 particular reaction going in the spontaneous or non-spontaneous reaction. What we are saying is that the overall reaction Gibbs free energy must be negative. Now what it means is that if we want to plot, the say Gibbs free energy versus the extent of the reaction.

So, then we will see some curve like say this and what it means; it means that for the reactant when A is going to product I will have a slope, which is negative. Now this slope is nothing, but what is the slope of this curve if the slope of this curve is del G del xi, at constant pressure temperature which is nothing, but by definition is the reaction Gibbs energy. So, if the reaction Gibbs energy is negative then which means the slope is negative.

So, A to B is actually taking the reaction towards forward direction; however, if the reaction Gibbs free energy slope is positive which is B to A then actually it is actually taking it to the non spontaneous direction. So, what will happen at the both these, so here actually what I am saying, is that del r G sorry, the r the suffix r should be here and del r G, if it is greater than 0 the curve will be like this and del r G, which is less than 0 the curve will be like this. And what is happening here the forward reaction is happening then the reactant, I mean it’s is a gaining in I mean amount more and more B's from.

So, the B is actually given that you to a and then what will happen these 2 Gibbs free energy, as we have seen that they will actually try to minimize the overall Gibbs free energy, which is something like this because we know that the overall Gibbs free energy has to be minimum.

Now delta r G greater than 0, or delta r G greater than less than 0 those are basically 2 sides of the total Gibbs free energy, which is basically downhill slope and one is basically negative slope, one is basically positive slope and then when the equilibrium is attained, we know that the changes in Gibbs free energy must be 0 because you can also see that the slope has been it is a flat, it is a basically parallel to x axis. So, we can say that at that point the delta r G is 0 here. So, at equilibrium when the equilibrium is attained, the Gibbs free energy or the reaction Gibbs free energy change will be 0.

So, what we in a long story short what we have said is that suppose you start with a me not a mixer is suppose we start with A only. So, what will happen initially A will form B, but as soon as the B concentration is increasing, B is also forming A. Now the changes in Gibbs free energy for one case actually, it is decreasing and in one case it is basically increasing sorry, B to A is basically increasing.

So, what will happen is that B to A is also actually a reaction, but when we had the reaction free energy when we discussed the slope of the Gibbs free energy with respect to the advancement of the reaction, then we see that for these two reactions, the slopes are either positive or negative.

And the positive and negative slope means actually intend to push the reaction towards or region, where the delta G, or the reaction which we write as delta r G will be 0 that is the concept of reaction Gibbs free energy and when it is 0 the equilibrium has been attained.

Now, we already discussed that this Gibbs free energy, the reaction Gibbs free energy is the difference between the reactant and the product.

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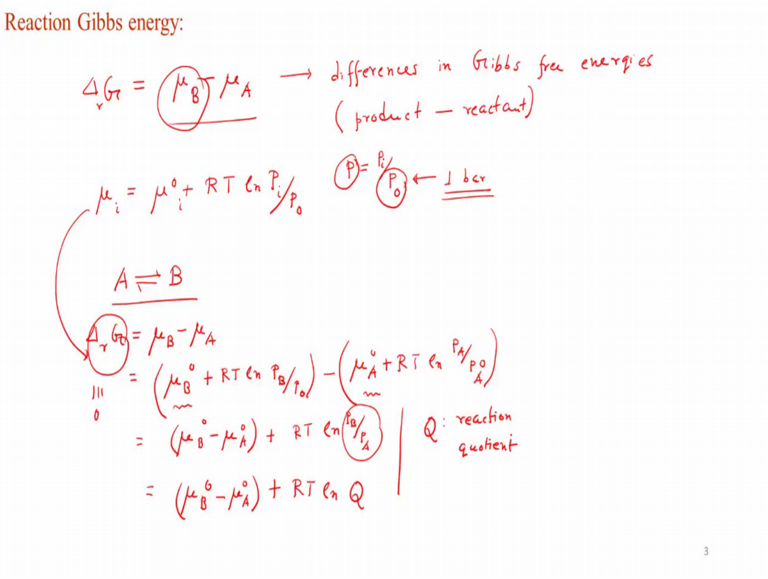

Reaction Gibbs energy:

$\Delta_r G = \mu_B - \mu_A \longrightarrow$ differences in Gibbs free energies (product − reactant)

$\mu_i = \mu_i^0 + RT \ln P_i/P_0$

$P = P_i/P_0 \leftarrow \underline{1 \text{ bar}}$

$\underline{A \rightleftharpoons B}$

$$\begin{aligned} \Delta_r G &= \mu_B - \mu_A \\ &= \left(\mu_B^0 + RT \ln P_B/P_0\right) - \left(\mu_A^0 + RT \ln P_A/P_0\right) \\ &= \left(\mu_B^0 - \mu_A^0\right) + RT \ln \left(P_B/P_A\right) \\ &= \left(\mu_B^0 - \mu_A^0\right) + RT \ln Q \end{aligned}$$

$\Delta_r G \overset{|||}{} 0$

Q: reaction quotient

And we have already argued that this delta r G is nothing, but mu A sorry, mu B minus mu A, which is basically the differences in the Gibbs free energies, differences in Gibbs free energies. So, the difference is taken from product minus reactant it is product minus reactant and if we do it in this way we see that the reaction Gibbs free energy is nothing, but the differences in the chemical potential of the reactant minus product. Now in the general case as we had have seen that these chemical potentials has to be multiplied by the quotients.

So, it is obvious because you have to if you have a different number of moles for B and A, you have to also take that into account. And that is why in the general case we have to also multiply it by the reaction, I mean reaction quotient that will be I mean exploring now, but before that let us.

So, discuss a very general case where we are saying that that any chemical potential say mu of any species, we can write it as mu 0 plus say RT Ln P, and remember that this P is nothing, but P by P 0 now because we have to always say that it is taken with respect to a standard state so, but usually we write it as P. Now for any ith constituent we can write it as something like this, and this P i instead of P i, you can write it as P i by P 0, but if I do not write.

So, it inherently means that we have divided it by P 0 where P 0 is the standard state, which corresponds to 1 bar pressure. Then in many cases actually the standard states used to be like the 1 atmospheric pressure, but we will use the si convention, but we are using 1 bar pressure. Now, let us again take a very general argument like we will see the what happens if I include the nu C nu d all these cases, but for the timing let us say stick to this particular reaction, when the stoichiometry is are also 1 is to 1.

Now for this reaction we already know that the reaction Gibbs free energy change is nothing, but mu B minus mu A, now we can expand it using this equation. So, we can write it as mu B instead of mu B we can write it as mu B 0 plus RT Ln P B. So, let us use the full form PB by PB 0 and similarly, for mu A, we can write it as mu A 0 plus RT Ln we have P A by Pv P A 0. So, we can now take the terms common which is mu B 0 and mu A 0.

So, it will be mu B 0 minus mu A 0, which is the difference of the chemical potentials taken at the standard state plus we have RT Ln, and remember that Ln A minus Ln B is nothing, but Ln A by B and when you do that at the P 0 terms cancel and. So, you will be left with a PL and PB by PA. And when now, equilibrium is attained, so you will have this term is equal to 0 only when equilibrium is added.

Now before that we can actually call these ratios as the reaction quotient, we write it as mu B 0 minus mu A 0 plus RT Ln Q, where Q is known as reaction quotient. So, Q is nothing, but at this moment is the ratio of the pressure of the react products divided by the reactants, but we will see that if I have stoichiometry numbers which are not equal to 1 what will happen we will have we will discuss the more general case now what we found.

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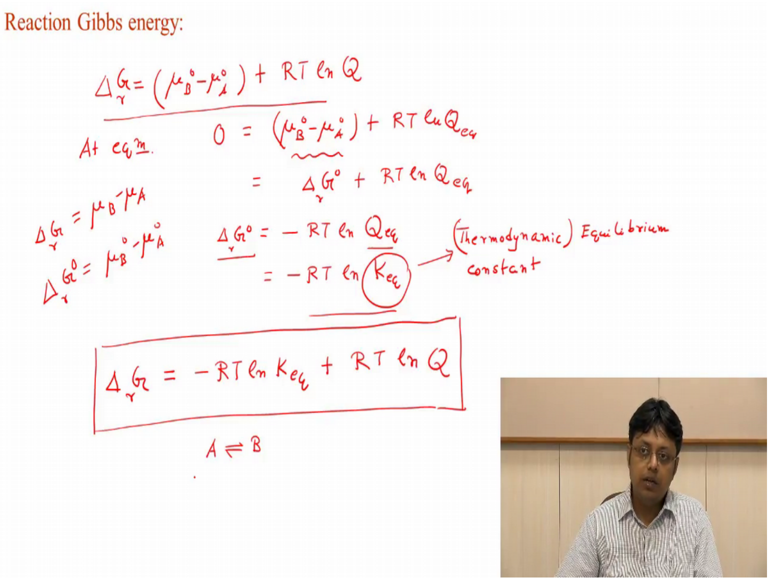

Reaction Gibbs energy:

$$\Delta_r G = (\mu_B^\circ - \mu_A^\circ) + RT\ln Q$$

At eq$\underline{m}$.

$$0 = \underbrace{(\mu_B^\circ - \mu_A^\circ)} + RT\ln Q_{eq}$$

$$= \Delta_r G^\circ + RT\ln Q_{eq}$$

$$\Delta_r G = \mu_B - \mu_A$$

$$\Delta_r G^\circ = \mu_B^\circ - \mu_A^\circ$$

$$\underline{\Delta_r G^\circ} = -RT\ln \underline{Q_{eq}}$$

$$= -RT\ln \boxed{K_{eq}} \rightarrow \text{(Thermodynamic) Equilibrium constant}$$

$$\boxed{\Delta_r G = -RT\ln K_{eq} + RT\ln Q}$$

$$A \rightleftharpoons B$$

So far is the reaction, Gibbs free energy is given by mu B 0 minus mu A 0 plus RT Ln Q. Now at equilibrium we know that the reaction Gibbs free energy must be 0, because the slope of the del G del xi curve was horizontal with respect to the x axis.

So, we will have mu A mu B 0 minus mu A 0, that is RT Ln Q, now look at this equation mu usually the delta rG is nothing, but mu B minus mu A. So, if we have a quantity which is mu B 0 minus mu A 0 we can call it as the standard reaction free energy. So, instead of that we can lets write it as standard reaction free energy plus RT Ln Q. And at equilibrium remember that this Q is now at Q at equilibrium, this is also Q at equilibrium it would not be the same Q as which is the general case.

So, what we found is that delta r G 0 is nothing, but minus RT Ln, the reaction quotient at equilibrium, but instead of writing it as K Q equilibrium we write it as K equilibrium. So, where K is known as the thermodynamic equilibrium constant, we call it as a thermodynamic equilibrium constant because we will see that there are also usually, for when you described say the reaction kinetics and many other things. We actually take the concentrations, but here for a general case this will be not concentration this must be expressed in terms of activities and that will discuss.

So, this is the thermodynamic equilibrium constant which you write as K equilibrium and. So, with what we get is this delta G 0, we can write it as ma minus RT Ln K equilibrium. So, you can now write the original equation as the reaction Gibbs free energy is given by delta G 0, instead of that I am writing as minus RT Ln K equilibrium, plus we have RT Ln Q. So, Q is the reaction quotient when delta G is 0. So, then we will just have K and Q are equal at equilibrium.

So, this is a nice compact way of writing the Gibbs free energy change, for any reaction although we have developed it for a very, very simple reaction, well now see what will happen if we include the stoichiometry numbers, for multiple reaction not only just 1 reactant and 1 product. And then we will see that how we can express the reaction, Gibbs free energy, in terms of the reaction quotients and what will happen what are the conditions that will dictate that the equilibrium has attend.