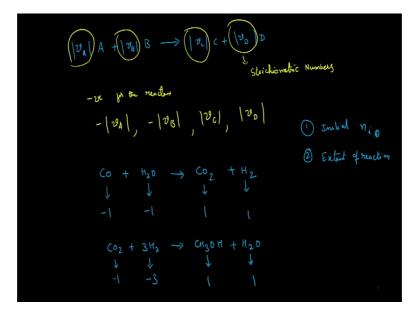
Chemical Engineering Thermodynamics Prof. Sasidhar Gumma Department of Chemical Engineering Indian Institute Technology, Guwahati

Lecture – 39 Chemical Reaction Equilibria

Hello and welcome back. We are talking about Chemical Reaction Equilibria in the last class and we discussed how we handle the enthalpy change due to the chemical reaction, what standard states are and how to calculate enthalpy change for a reaction from heats of formation data. We also mentioned that just like enthalpy change due to reaction other thermodynamic variables such as Gibbs free energy change upon reaction can also be calculated on similar lines. What we will do today is to lay the theoretical background so that we can analyze chemical reaction equilibria through thermodynamics.

Let us start with the quantity called a stoichiometric number. We already talked about it during enthalpy change upon reaction discussion; what it is essentially it is the number of moles of a particular species that are reacting in a balanced reaction or that are produced in a balanced reaction.

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So, for example, if I have something like this nu A time nu A moles of A plus nu B moles of B reacting to give nu C moles of C and nu D moles of D then we call each of these quantities nu A, nu B, nu C and nu D as the stoichiometric numbers right. Notice that we

have used an absolute sign here so that they are always positive in the way a balanced chemical reaction is written, but stoichiometric number actually is negative for the reactants.

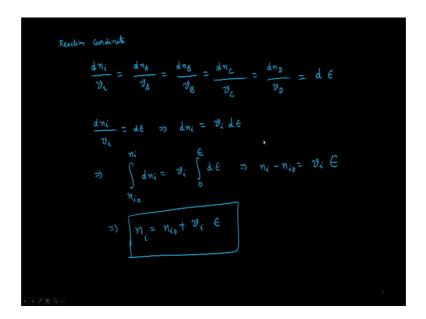
So, in that sense for A the stoichiometric number is actually negative of nu A, for B is negative of the absolute value of B nu B, for C it is positive for D it is positive. So, these are the actual stoichiometric numbers for each of the 4 species that are present in that particular reaction. If I have something like a water gas shift reaction for example, CO plus H 2 O giving CO 2 plus H2, in this particular reaction the stoichiometric number for carbon monoxide is negative one because it is a reactant and the number of moles in this particular reaction for CO are 1, for H 2 O also it is negative 1, for carbon dioxide it is 1 and for hydrogen it is 1. So, all the products get the positive sign, the reactants get the negative sign and then with the appropriate number of moles that are present in this particular reaction.

Similarly, if I have a direct conversion of CO 2 to methanol reaction for direct conversion of CO 2 to methanol for example, CO 2 plus 3 H2 giving CH 3 O H plus H 2 O in this particular reaction the stoichiometric numbers for carbon dioxide is negative 1, for hydrogen is negative 3, for methanol it is 1, for water it is 1 all right. So, this is the quantity we call as stoichiometric number this plays an important role.

Now, in addition to this, notice that the number of moles at any instant in time during a reaction is going to depend on two things; one the initial number of moles let us call that as n i and because it is initial we will call it as n i naught. So, it will depend on initial number of moles for each of the chemical species and also it will depend on the extent of the reaction how far the reaction has proceeded right. The number of moles of A that react will be related to the number of moles of B that will react according to the stoichiometric numbers that would also be related to the number of moles of C and D produced according to these stoichiometric numbers because the reaction has to proceed.

So, in that sense the final composition of a mixture in a chemical reaction is going to depend in addition to initial number of moles it will actually depend only on one other variable and we can call that as the extent of the reaction. In general for good bookkeeping what is done is a new variable is defined that to enable us to do this and we will call this variable as the reaction coordinate.

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And the way we define reaction coordinate is by defining the quantity d ni over nu i right where dni is the change in number of moles nu i is stoichiometric number it is positive for products negative for reactants etcetera. And, this quantity as it turns out is going to be constant irrespective of what species we are considering right; if that species is present in the reaction then this quantity is going to be constant.

So, for example, in the previous case, then the dni by nu i for A will be dn A by nu A, nu A being negative for the reactant dn B by it will also be equal to dn B by nu B again nu B is negative it will also be equal to dn B by nu C because C is a product nu C is positive and dn D by nu D again D nu D is positive right. So, this ratio is constant and we are going to call this ratio as d epsilon and this epsilon is the quantity we are going to identify as reaction coordinate. So, d epsilon is the differential change in the reaction coordinate.

Now, I can actually write the final number of moles in terms of the initial number of moles and the reaction coordinate for each of the species using this expression for example, as it turns out since for any species i dn i by nu i is d epsilon what I can do is integrate this particular expression. If I integrate it from the initial condition of n i naught that is the initial number of moles to the final number of moles let us say is n i dn i is going to be nu i that is a constant integral of 0 to how far the reaction has proceeded.

If the reaction coordinate is epsilon that is when we get in a final number of moles n i let us say then it will be integral from 0 to epsilon d epsilon and if I take this it will be n i minus n i naught is going to be nu i times; nu i times epsilon or n is going to be n i naught plus nu i times epsilon this is n i. So, the final number of moles is going to for each of the species is going to be related to the initial number of moles n i naught and the reaction coordinate epsilon.

So, only thing I need to calculate the final number of moles present during a reaction is simply the reaction coordinate of course, in addition to the initial number of moles we have taken for that particular reaction. So, I do not need to identify the number of moles for each of the species or track them for each of the species along the reaction I just need to track the reaction coordinate and at any instant in time I can readily calculate the number of moles for each of the species and that is again because each of them are related we are the stoichiometric number for that particular reaction.

Now, what this will help us is to calculate the number of moles, but in general in our thermodynamic analysis as you can recall what we are interested most of the times is the mole fraction. And in fact, we can do a little bit of manipulation for this reaction sorry we can do a little bit of manipulation for this particular equation to get the mole fraction also.

 $M = bitch number of nubers = \sum_{i} (n_{i0} + v_{i} \in)$ 6= 6 800 E 29 $n, + v \in$

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Let us say the mole fraction is y i and if n i is the number of moles for each of the species, then the total number of moles will drop the subscript will call n to be the total number of moles and it is simply going to be sum over all n i's. And because n i we call it as n i naught plus nu i times epsilon right this is summation over all the species i present and this will be summation over i for all the species present n i naught plus summation over i for all the species present n i times epsilon.

And because we are summing it over all the species I let us call this quantity as n naught which is the total number of moles at initial condition and notice that the second term is sigma nu i times epsilon we can do a little bit of manipulation to this term sigma nu i times epsilon is going to be epsilon time sigma nu i epsilon is constant irrespective of the species.

So, it can come out of the summation and we have sigma nu i instead of writing sigma nu i each time, we can write it as simply nu; nu being summation over all nu's for each of the species. So, this equation then reduces to n naught plus nu times epsilon this is the total number of moles at any time t and total number of moles at the initial time is n naught.

Now once I have n and I also had n i from the previous expression, then y i is simply going to be n i over n sorry and that would be n i naught plus nu i times epsilon over n naught plus nu times epsilon. So, the numerator is the change for the species i plus the initial number of moles for i and the denominator is the change over all change for the reaction the number of moles overall change in the number of moles for the reaction plus the initial total number of moles n naught. So, that would be essentially y and of course, it makes sense right.

So, if there is a single reaction present then the mole fraction is simply given by this particular expression and we know what each of these terms are right n i naught is the initial number of moles for i, n naught is the initial total number of moles, nu i is the react sorry stoichiometric number for i, nu is the total stoichiometric number which is sigma nu i and epsilon is the reaction coordinate.

So, once I know epsilon I can calculate mole fraction at any point in time during the course of a particular reaction this is for single reaction what we will do is quickly work on one example to illustrate the concept of calculating the mole fraction or the

expressions for mole fraction in terms of the reaction coordinate before we move on to look at how we handle multi reaction scenario all right.

Example Solution 26=13

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So, let us take an example. Let us say I have the same example water gas shift reaction. So, the reaction reads CO plus H20 giving CO 2 plus plus H 2 that is a water gas shift reaction the initial number of moles n i are given here let us write this n i naught for CO for H2O for CO 2 for H 2 and it turns out in this particular reaction there is also an inert nitrogen present. So, we will write the initial number of moles for nitrogen also.

So, the initial number of moles for CO are 4, for water it is 2, for CO 2 it is 2, hydrogen is 1 so some of the products are still present at the initial time and there is an inert present for most of inert present right. These are the initial number of moles for each of the species. Remember all the reaction is occurring only for these 4 species we also need to include the inert because essentially inert will influence the mole fraction. So, we will still write the number of moles for inert as well right.

Now what we want to know is, find expression for y i and because now we have 5 species although only 4 are in the reaction there are a total of 5 species, so we want to find the expression for the mole fraction for all the 5 species in terms of the reaction coordinate epsilon that is what we want to do ok. So, to do that we will use what we just discussed. The first thing we want to find is the total number of moles at the initial

condition n naught which is sigma n i naught and that turns out to be 4 plus 2 plus 2 plus 1 plus 4 at 6 8 9 13 those are the total number of moles at the initial condition.

Now, we also want to find the overall stoichiometric number which is nu which is defined as sigma of nu i right what I will do is just for sake of easiness I am going a write nu i this thing in yellow is something I am writing it is not given in the problem statement I am writing it for our understanding nu i for CO is negative 1; obviously, because it is a reactant, for water it is negative one again because it is a reactant and one mole is going into this balanced reaction shown here.

For CO 2 it is 1, for hydrogen it is 1 and from nitrogen it is an inert it is not participating in the reaction. So, stoichiometric number is going a be 0 for nitrogen. Now with these values of nu i, if I sum sigma nu i what I get is negative 1, negative 1, positive 1, positive 1 and a 0 that would add up to 0.

So, for this particular reaction including the inert present the overall stoichiometric number nu is going to be 0. Now once we have that sorted out its pretty straightforward to write the expressions for y i recall the expression for y i is n i naught plus nu i times epsilon over n naught plus nu times epsilon that is the expression we had earlier. So, we are going to use our expression to write y i for each of the species, for CO it is going to be n i naught CO n i naught for CO is 4 are the stoichiometric number nu i is negative 1 times epsilon so that is 4 minus epsilon over n naught so since we have this what I will do is the denominator is common for each of the species.

So, I am going write n naught plus nu times epsilon is going to be 13 plus 0 times epsilon is 0. So, the denominator is going to be 13 for each of these and it is constant. So, that is going to be the value for n naught plus nu times epsilon now that is for the first species. So, the mole fraction of CO is 4 minus epsilon over 13.

So, if I know epsilon I can calculate the mole fraction for CO. Similarly for water it is going to be n i naught for water is 2 minus nu i for water is minus 1 times epsilon over 13 so it is 2 minus epsilon over 13. Similarly for CO 2 n i naught; n i naught for CO 2 as you can see from the table is 2 nu i for CO 2 is 1 so it is 2 plus 1 times epsilon is 2 plus epsilon over 13.

And finally, for hydrogen y H 2 is going to be initial number of moles for hydrogen which is 1 right plus epsilon nu i again for hydrogen is 1 so it is 1 plus epsilon over sorry 1 plus epsilon over 13. So, these are for the species that are present in the reaction, in fact, we have one more species which is an inert that is nitrogen y for n 2 is going to be n i naught for n 2 which is 4 plus nu i for nitrogen is 0 so 4 plus 0 is 0 over 13 right.

So, these are the number of moles in my particular reaction or sorry these are the mole fractions for each of the species in my particular reaction at any point in time and the only thing that you need to know to calculate them is the reaction coordinate right. In fact, one other thing I usually do when I solve problems such as these is make sure that all the mole fractions add up to unity right make sure that sigma y i is going a be 1. And if you actually go through the math you will see that the numerator the denominator is same the numerators all add up to 13. So, that sigma nu i y i is going to be 1 that is how I cross verify whatever expressions I usually write for these type of problems right.

So, that is how we handle a single reaction scenario for the sake of a practice let us do one more problem right this had a overall stoichiometric number equal to 0 so the denominator does not involve the reaction coordinate, but in certain cases it can let us see an example.

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N2 = Emin = 4+15+1=20 n. + 26 = 20 - E E 33H2= 15-

This time the reaction we are looking at is for formation of ammonia everything in the gaseous phase again half N 2 plus 3 by 2 H 2. So, the moles do not have to be necessarily

integers there can be fractions as well as in this scenario will give me 1 mole of ammonia, this is the reaction I am looking at and as earlier let us write the initial number of moles and nu i. The initial number of moles are given right for N 2, for H 2 and for ammonia. The initial number of moles are 4, 15 and 1 and what we want to find is expression for in expression for y i in terms of the reaction coordinate epsilon.

So, unlike the previous case now there is no inert, but what we want is expression for y i which as we recall is n i naught plus nu i times epsilon over n naught plus nu times epsilon right. So, which means I need to know the reaction sorry the stoichiometric numbers as well. So, as earlier let us write stoichiometric number for nitrogen is negative half it is a reactant, similarly for hydrogen it is negative 3 over 2 and for ammonia it is 1.

Once I have the stoichiometric number, what I can do is go back and calculate the denominator first n naught sigma n i naught it is 4 plus 15 plus 1 which is going to be 20 and similarly nu is going to be sigma of nu i which is negative half negative 3 over 2 plus 1. So, that is negative 2 plus 1 which is negative 1 and because n naught and nu are known now I can write the denominator n naught plus nu times epsilon the denominator is going to be 20 minus 1 times epsilon is epsilon.

So, now in the denominator I have the reaction coordinate term also unlike in the previous case and I have that because the overall stoichiometric number is not 0 in the previous case it was 0. But anyway the denominator now is 20 minus epsilon if I want to write the expressions for the mole fractions y N 2 is going to be n i naught for N 2 which is 4 plus nu i for N 2 which is negative half times epsilon over 20 minus epsilon.

Similarly, for hydrogen it is 15 minus 3 by 2 times epsilon by 20 minus epsilon and for ammonia is 1 this time it is a product so nu i is positive 1 plus epsilon by 20 minus epsilon right. So, those are the expressions for each of the mole fractions and as in the earlier case we can cross check and it turns out that if you add all these mole fractions it will be 1 which it should be right. So, that is how we cross-check what we just derived. So, those are a few examples on how we express the mole fractions in terms of the reaction coordinates when we have a single reaction.

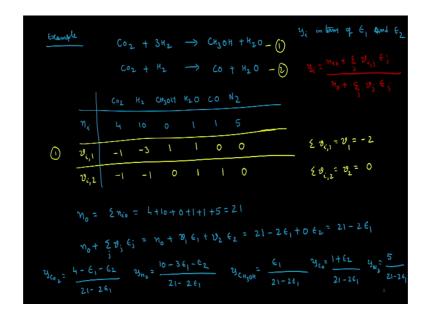
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Now, let us consider the case of a multiple reactions and in case of multiple reactions what we will do is will identify the stoichiometric number as nu i, j. So, this is the stoichiometric number for species I in reaction j. Earlier we only had one reaction, now we have more than one reaction. So, in each of these reactions the stoichiometric number for species i might be different so we will identify as nu i, j and similarly we also have a reaction coordinate this reaction coordinate for each of the reactions might be different.

So, we will denote it by a subscript j. So, epsilon j stands for this reaction coordinate for reaction j right this being the case the species the change in number of moles of species i dn i is simply going to be as it earlier it is going to be n i naught the initial number of moles plus the change due to each of the reactions. So, what I need to do is sum it over all the reactions j nu i, j epsilon j. If there is one reaction then it will be simply nu I times epsilon if there are more than one reactions then we have to taken for changes in each of these so it is going to be nu i, j times epsilon j right.

And to calculate the mole fraction we can derive this expression, but we will just write it down it would be simply ni naught plus sigma over j nu i, j epsilon j over n naught plus sigma over j nu j epsilon j right. And here nu j is again defined as the overall stoichiometric number for reaction j which is summation of nu i, j s for all the species in the reaction j right that is how we define it and this will be the expression for mole fraction of species i when there is more than one reaction occurring right. Again we can demonstrate this calculation using an example.



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So, let us take one quick example. We will consider the case of data conversion of carbon dioxide to methanol CO 2 plus 3 H 2 gives methanol CH 3 O H plus water all of them are in the gaseous phase at high temperature and pressure. And a side reaction occurs as well CO 2 plus H 2 is going to give CO plus H 2 O this is what we call as the reverse water gas shift reaction right both these reactions occur simultaneously. And let us again write what is given ahem CO 2, H 2, CH 3 O H, H 2 O CO and n inert N 2 is also present in the reaction. The initial number of moles for each of these species n i is 4, 10 moles of hydrogen, 0 moles of methanol, 1 mole of water, 1 mole of CO and 5 moles of N 2.

So, this is what is present and what we want to calculate is y i in terms of epsilon 1 and epsilon 2. So, this we are identifying we are identifying this as reaction 1 and this as reaction 2. So, epsilon 1 is for reaction 1, epsilon 2 is the reaction coordinate for reaction 2 and we want to find expressions for y i each of the species i in terms of this epsilon 1 and epsilon 2. Now to be able to do this what we will do is we will write these stoichiometric number for each of the species i in the reaction right.

So, what I will do is nu i in reaction 1 and nu i in reaction 2 right. In reaction 1, we will use the same table in reaction 1 CO 2 it is negative 1, for hydrogen it is negative 3, for methanol it is positive 1, for water it is positive 1 there is no CO, there is no N 2 right

and summation of nu i 1 is what we call as nu 1 the overall reaction coordinate; the overall stoichiometric number for reaction 1 and this turns out to be negative 1 negative 3 is negative 4 plus 2 is negative 2.

Now, for the second reaction CO 2 is again negative 1, hydrogen is also negative 1 there is no methanol in this particular reaction water is again positive 1 CO is positive 1. And, there is no nitrogen and so nu i 2 for summation of nu i 2 is going to be what we call as the overall stoichiometric number for reaction 2 which turns out to be 0 in this case negative 1, negative 1, plus 1, plus 1 is 0.

So, once I identify this, the next thing I want to do is calculate n naught right calculate n naught and from the given information it is sigma of n i naught and from the given information this value is 4 plus 10 plus 0 plus 1 plus 1 plus 5 which turns out to be 14 15 16 and 20 21 right. And the denominator term let us write that expression for y i one more time here y i as we know is n i naught plus sigma over j nu i, j epsilon j for reaction j over n naught plus sigma over j nu j epsilon j that is the expression right.

Now, let us first write the denominator because it is common for each of these species like in the single reaction case let us write that down n naught plus sigma of nu j epsilon j running over all j. So, it will be for both reactions 1 and 2. So, we can ext expand it; it will be nu one epsilon 1 plus nu 2 epsilon 2 and that would be 21 nu 1 is negative 2 times epsilon 1 plus 0 times epsilon 2. So, that is going to be 21 minus 2 epsilon 1 in this particular case, that is going to be the common denominator for each of the species.

Now, I can write the expression for mole fraction y for CO 2 is going to be initial number of moles for CO 2 which is 4 minus nu for CO 2 in the first reaction which is negative 1 times epsilon 1 plus nu times nu for CO 2 in the second reaction which is again negative 1 times epsilon 2 over the denominator which is 21 minus 2 epsilon 1. Similarly for hydrogen it is going to be 10 the initial number of moles minus nu for hydrogen in the first reaction is 3 times epsilon 1 in the second reaction is 1 times or negative 1 times epsilon 2 over the common denominator which is 21 minus 2 epsilon 1.

For methanol it is there is no initial moles for methanol and it is produced only in the first reactions and nu for methanol in that reaction is 1 times epsilon 1 nothing in the second reaction over 21 minus 2 epsilon 1 y for CO is going to be the initial number of moles which is 1 nothing in the first reaction for CO it is nu for CO in the second

reaction is 1 times epsilon 2 over 21 minus 2 epsilon 1. And finally for N 2 the initial number of moles is 5 does not at the stoichiometric number in both the reactions is 0. So, the numerator is going to be simply 5 over the denominator is 21 minus 2 epsilon 1.

So, those are the 5 expressions I am looking at for the mole fractions in terms of epsilon 1 and epsilon 2 and notice that because there are 2 reactions now I need 2 reaction coordinates to calculate each of the mole fractions and again as earlier if you add all these mole fractions the summation should go to 1 and in this case as well it does right.

So, that is how we handle the scenario for a multi reaction equilibria we can express each of the mole fractions in terms of the reaction coordinators of as many reactions as are present. Now once we identified that all I need to define the mole fractions is simply the reaction coordinate for each of the reactions that is occurring the next logical thing to do is analyze the thermodynamic equilibrium when there is a reaction right. We will do that when we come back in the next class.

Thank you.