Introduction to Chemical Thermodynamics and Kinetics

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Lecture – 23
Chemical Equilibrium – Part 3

All right; so, we are now going to discuss the general case for a stochiometrically balanced equation.

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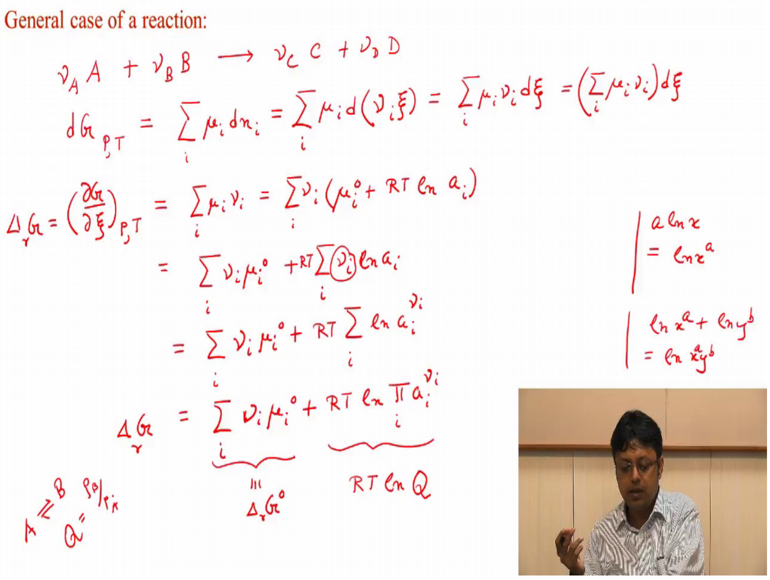

General case of a reaction:

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

$$dG_{P,T} = \sum_i \mu_i dn_i = \sum_i \mu_i d(\nu_i \xi) = \sum_i \mu_i \nu_i d\xi = \left(\sum_i \mu_i \nu_i\right) d\xi$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi}\right)_{P,T} = \sum_i \mu_i \nu_i = \sum_i \nu_i (\mu_i^\circ + RT \ln a_i)$$

$$= \sum_i \nu_i \mu_i^\circ + RT \sum_i \boxed{\nu_i} \ln a_i$$

$$= \sum_i \nu_i \mu_i^\circ + RT \sum_i \ln a_i^{\nu_i}$$

$$\Delta_r G = \underbrace{\sum_i \nu_i \mu_i^\circ}_{\equiv \, \Delta_r G^\circ} + \underbrace{RT \ln \prod_i a_i^{\nu_i}}_{RT \ln Q}$$

$a \ln x$
$= \ln x^a$

$\ln x^a + \ln y^b$
$= \ln x^a y^b$

$A \rightleftharpoons B$ $\quad Q = p_B/p_A$

So, by general case, what do you mean is that if we write the equation as nu A into A plus nu B into B is going to nu C into C plus nu D into D. Now the question is what will be the most general form of the reaction quotient and the equilibrium constant for this reaction. Now as before you can write it as the dg or the change in Gibbs free energy and we are not writing the minus sdt plus vtp term.

So, we are right away writing the constant pressure temperature term and that will be sum over all the constituents i and that will be nothing, but mu i dni something like we started with and dni, we know that it has to be multiplied by the stoichiometric number times, we can just write it introduce another step. So, this is nothing, but nu i and remember when I am writing for A, it will be minus nu A because we have to include the sign because it is being consumed in to xi; xi was the advancement of the reaction. So, we can write it as for a differential amount it will be nothing, but mu i nu I; mu i is a constant into d xi.

So, that we can actually write that this sum; remember d xi does not have any index because it is independent of reactant or the product we can write it as mu i nu i. This sum times d xi. So, we can actually take now the derivative of Gibbs free energy at constant pressure and temperature and we called it as the reaction Gibbs free energy and that will be nothing, but sum over i nu i and we write it as mu i into nu i and we already know that what is mu i mu is nothing, but mu i 0 plus RT ln activity of that spaces.

So, I am writing the nu i term at the beginning and then I am writing it as mu i 0 plus RT ln activity of i. Now, if we write it in this way see the beauty here. So, and now, I am going to expand it just to or before expanding it we can also write it in terms of just the summation notation. So, you see here that I can actually write it in 2 different terms, one is basically some of our all the mu i 0s and the other one is basically sum over the RT is a constant we can actually keep it outside and we will have nu i ln ai.

Now, we already know what is ln ai and ln ai, if I just write the notation let me just write it here. So, what is ln a i nu i ln a is what is say a ln x that we can write it as ln x to the power a that we know. So, that way I can actually use this factor nu i and as an power of the logarithmic term. So, we can write it as nu i nu i 0 or let me just use the next line we can write it as sum over i nu i mu is 0 plus r t and then sum over i ln a i raise to the raise to a nu i and then we are summing up; now, what is the sum up of l n sum up of ln means what is say ln x plus ln y it will be nothing, but ln x y.

So, it is basically taking the logarithm of the product terms. So, that we can write it further and in this case there was already a power here. So, x was raised to say a and y was supposed raised to b. So, it will be something like x raise to a y raise to b something like that. So, we can write it as nu i nu i 0 plus RT and the ln of product of all these terms mu; mu i a i to the power nu i. So, that is our equation and that is basically the reaction Gibbs free energy expressed in terms of the reaction and all these activities of the reactants and the products now this if you. Now, remember that delta G of the reaction was nothing, but the first term will be delta r G 0.

So, that we can always equate and this will be nothing, but RT ln Q. So, you can see what is the expression for Q; Q is not just the for the general equation which we were at for a specific equation which we considered like a; B we wrote it that time Q is partial pressure of B divided by partial pressure of A, but now, we are writing it in the more general sense in the sense that we are writing it as Q is nothing, but sum over or we can just write it in this way here is nothing, but.

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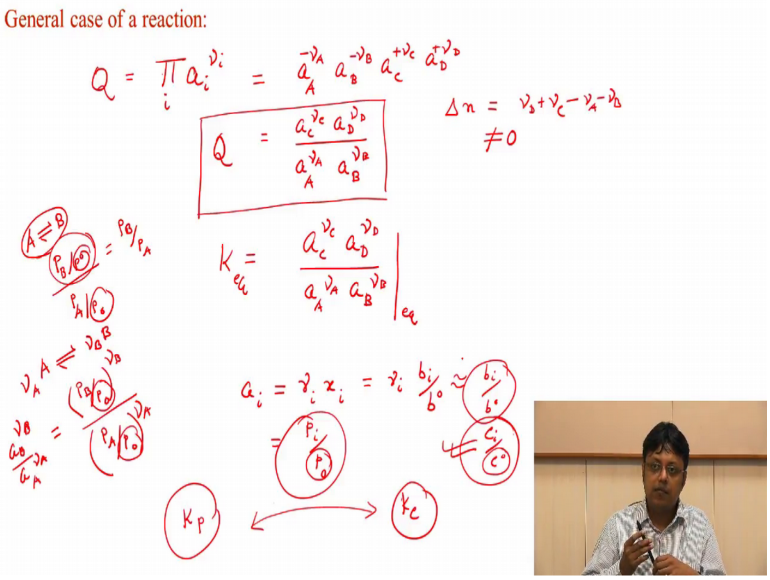

General case of a reaction:

$$Q = \prod_i a_i^{\nu_i} = a_A^{-\nu_A} a_B^{-\nu_B} a_C^{+\nu_C} a_D^{+\nu_D}$$

$$\boxed{Q = \frac{a_C^{\nu_C} a_D^{\nu_D}}{a_A^{\nu_A} a_B^{\nu_B}}}$$

$$\Delta n = \nu_D + \nu_C - \nu_A - \nu_B \neq 0$$

$$K_{eq} = \left.\frac{a_C^{\nu_C} a_D^{\nu_D}}{a_A^{\nu_A} a_B^{\nu_B}}\right|_{eq}$$

$$A \rightleftharpoons B \quad \frac{P_B/P^0}{P_A/P_0} = P_B/P_A$$

$$\nu_A A \rightleftharpoons \nu_B B \quad \frac{a_B^{\nu_B}}{a_A^{\nu_A}} = \frac{(P_B/P_0)^{\nu_B}}{(P_A/P_0)^{\nu_A}}$$

$$a_i = \gamma_i x_i = \gamma_i \frac{b_i}{b^0} \approx \frac{b_i}{b^0} = \frac{P_i}{P_0} \neq \frac{c_i}{c^0}$$

$$K_P \leftrightarrow K_c$$

So, it was RT ln Q. So, it is sum over a i to the power nu i. So, for example, for the reaction which you wrote for that it will be nothing, but first think about the reactants which was nu A. So, we can write it as activity of a raised to nu A, but there was a negative sign remember, then activity of B.

Similarly, this was reactant and similarly activity of c this was product nu c and activity of d that was also product and that is why we have to take the positive sign. So, we can write as nu c activity of t nu D divided by activity of A nu A activity of B nu B. So, this is the reaction quotient. So, we have we see that we have to take the numerator all the activities of the products raised to their concentration and then multiply all for each product divided by the same for the reactants. Now you see a very interesting situation if we can actually write in terms of the activity we can write the partial pressure also, but for this generally equation when you wrote as A to B.

So, we wrote that it is basically the A by P A 0 or P A 0 does not make sense, it is basically divided by P 0 because P 0 is same for everything and divided by PB by P 0 and that P 0 actually got cancelled and that is why wrote has PB by PA. This should be PB by

PA; however, you see that if we want to write it in this way, I will have actually pressure of C divided by or you can actually think about you can just modify this equation little bit let us say that we write this equation as nu A into a is going to nu B into b and this is these stoichiometries are not equal, then I will have a very interesting situation I can write the activity of B divided by activity of A and then it has to be raised to the exponents B and A here.

So, what we can write actually A is PB by P 0, we have to always take the PB divided by P 0 because it is the standard state notation raised to nu P divided by PA by P 0 raise to nu A. So, if the nu A and nu B are not equal, then I cannot cancel the P 0 terms which is here. So, that is the importance of the thermodynamic equilibrium constant it is not just PB by PA or the concentration of B by A in the dilutes case, you have to take the division by the standard set and then you have to take the exponent you have to take the not the exponent you have to take the power. So, these P 0 things do not necessarily cancel all. So, we can say that q is this and then what will be K and already we know that K is nothing, but the equilibrium constant we wrote it as K equilibrium.

So, K will be the same activities, but at equilibrium. So, q is the general activity for any condition and K will be nothing, but the same thing, but at equilibrium at equilibrium. So, that is how we can actually explain K and Q. Now this question is how they write the activities. So, we wrote that we already discussed the activity can be expressed as activity coefficient times the mole fraction, but not for or not always actually, but first a dilute solution you can write it or sometimes you actually write it in terms of molality also where you write it as say it is the more the activity coefficient times the molality which we write as b i divided by the standard state always you have to keep that in mind or instance of pressure we write it as a pressure of the constant i divided by pressure of the standard state which is just one mole per one bar and in the very dilute concentration instead of the molality.

Ah we could also write it. So, we know that for dilute concentration it will be nothing, but b i by b 0 similarly we could also write it as c i by c 0. So, if I express these activity in terms of pressure, then the corresponding equilibrium constant is known as the equilibrium constant with respect to pressure we write it as KP, if we express it with respect to concentration, we write it as K suffix C and of course, there is a relationship between KP and KC you know that that you can actually write it, you do not be actually equal into I mean you can actually write it in terms of something and then you can actually figure it out like; what will be the relation between KP and KC, already you know the relation, I mean how to how to get you have to write the pressure in terms of concentration and then we easily figure out what is the relationship.

However the point here is that there will be some P 0 terms or the C 0 terms that will not cancel out. So, because the addition of all the nu c nu ds and these addition of all the nu A nu ds and when you take the difference between those addition which we sometimes know right it is as delta n which is nothing, but this sum basically nu d plus nu c minus nu A nu B which if it is not equal to 0, then the pressure terms do not cancel out the concentration terms the P 0 terms or the nu 0 c 0 terms, they do not cancel out and you have to keep that in mind. So, we are actually dividing it pressure divided by 1 bar.

So, that we make it as unit less. So, we express the pressure as bar and then divided by one bar means it actually it is just a number and similar thing is for also for the concentration or for the molality you can actually easily convince yourself that it is just a number, but not something that we are we have to think about like we have to it is just you have to treat it just a pure number.

Now another thing which we are going to discuss in the next section is how these equilibrium constant gets affected by change in pressure or change in temperature or what are the con what are the contributions of the external any disturbance in terms of pressure or in terms of temperature. So, that we are going to discuss in the next section.