# Introduction to Chemical Thermodynamics and Kinetics

**Dr. Arijit Kumar De**

**Department of Chemistry**

**Indian Institute of Science and Education Research, Mohali**

## Lecture – 22

## Chemical Equilibrium – Part 2

Before we proceed, what is the expression for the reaction quotient? Let us now discuss little bit about the division from the ideal behavior, for a say mixture. Now we already discussed, the thermodynamics of mixtures where we discussed a Raoul's law as well as henrys law, now remember.

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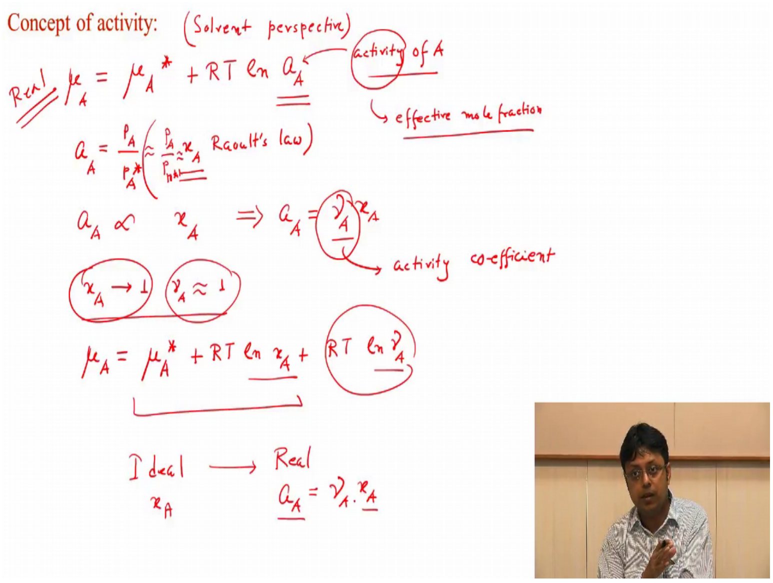

Concept of activity: (Solvent perspective)

Real $\mu_A = \mu_A^* + RT \ln a_A$ ← activity of A ↳ effective mole fraction

$a_A = \frac{p_A}{p_A^*}$ ( $\approx \frac{p_A}{p_A^*} \approx x_A$ Raoult's law)

$a_A \propto x_A \Rightarrow a_A = \gamma_A x_A$ → activity co-efficient

$x_A \to 1$ $\gamma_A \approx 1$

$\mu_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A$

Ideal ⟶ Real

$x_A$ $a_A = \gamma_A \cdot x_A$

In Raoul's law, we wrote to the chemical potential as mu A star were mu A, say chemical potential of any component A and we wrote the start notation to designate, that it is in the pure state. Like it is a pure solvent say for example, say pure water and then of course, there was a deviation for the Raoul's law and we wrote it as RT Ln P A by P 0 that is a correct equation.

But that P a by P 0, we wrote it to be equivalent to the mole fraction which was not correct. Now we are writing it, fine let us just define a quantity, which will explain everything in the limit of dilute solution, in the sense that this quantity a small a will actually describe the behavior over entire range of mole fraction. So, that quantity we call it as a activity.

So, this is activity of one component in this case it is activity of a, now what is what do you mean by activity. So, in Raoul's law, so this was activity we could actually replace activity is nothing, but in this case PA by PA star, which was taken to be the mole fraction of A that was Raoul's law.

So, this activity you can think of as an effective mole fraction, in the sense that it is not exactly the mole fraction, because we saw that if I take it to be xA. Then in some range it follows Raoul's law, but not for all range and you saw that for a fairly dilute concentration, when you talked about dilute solution from the solvents perspective it is, but from the solids perspective it is not.

So, from solvents perspective Raoul's law was, but as we increase the mole fraction of the solute it we saw a huge departure, and that sort was the problem with Raoul's law. And now we are saying that everything can be explained with this quantity, which is known as activity it can be replaced by mole fraction only in the dilute concentration, dilute solution and.

So, this activity can be thought of as an effective mole fraction, and we can always write this activity is suppose somewhat some way actually proportional to the mole fraction. And this proportionality constant, we write it as something like at regulated gamma and we call this gamma as activity coefficient.

So, gamma is known as the activity coefficient and of course, you can see that for a Raoul's law to be valid gamma should be equal to 1. So, what it means is that as the mole fraction of the solvent let us say I am keeping A as a solvent, and I will write B as the solute. So, if the mole fraction is tending to will be 1 the gamma is tending to be 1, so that activity becomes the mole fraction.

So, that is the concept here and, so activity can be I mean anything, but like for example, in a very concentrated solution we are saying that that there of itself it will be proportional to xA, but it wouldn't be equal to xA it will be equal to gamma a into xA, but that gamma A. Now the question is how to calculate the gamma A for the concentrated solution that we are not going to discuss.

We are going to say that this it will be still proportional to mole fraction, but all this departure will be now content within the gamma A, if you can make or if we can come up with a theory, which nicely shows how basically gamma A or the activity coefficient is going from value of 1 to something else. In a very, very non-linear fashion then you can think about that the this, we can actually have a very real situation which can explain everything.

So, gamma is not actually exactly a constant it also depends on the mole fraction, that is very, very important. If I take gamma to be say that, we are saying that gamma tends to 1, when mole fraction is tends to 1. Which means actually I cannot take gamma to be 1, for the entire inch of mole fraction. When the mole fraction of a is actually, I mean decreasing or x A is actually decreasing from 1, or we are going a doing a departure from the pure solvent to the solution thing we are adding more and more salute to it.

Then we see that there is a departure, and the departure we can account for if we can adjust the gamma, which means gamma has to be dependent on x A, or mole fraction it is not exactly a constant. Now we can actually write it you know way like mu A is nothing, but mu A star plus RT Ln x A plus RT Ln gamma A. Now I am just writing it in terms of a, I mean activity and x A into gamma A, and remember that this is what we have discussed.

So, far is with respect to the solvent perspective, so it is basically the concept of activity from solvent perspective, we know that from solids perspective it is very different and what is the difference, so we already know that. Now, for dilute solution which means that we can when x tends to 1, we can write gamma to be tending to 1 or we can actually write it that the gamma is almost equal to 1. So, we can actually ignore this term and then it reduces to Raoul’s law as you can see. So, that is the entire concept, and now the, what happens from the solutes perspective, now from the solutes perspective.

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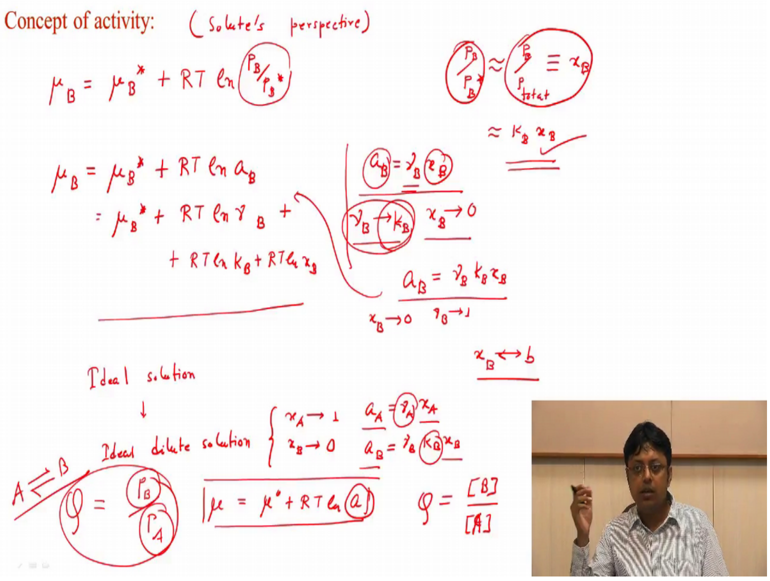

Concept of activity: (Solute's perspective)

$\mu_B = \mu_B^* + RT \ln \left(P_B / P_B^*\right)$

$\frac{P_B}{P_B^*} \approx \frac{P_B}{P_{total}} \equiv x_B$

$\approx K_B x_B$

$\mu_B = \mu_B^* + RT \ln a_B$

$= \mu_B^* + RT \ln \gamma_B + RT \ln K_B + RT \ln x_B$

$a_B = \gamma_B x_B$

$\gamma_B \to K_B \quad x_B \to 0$

$a_B = \gamma_B K_B x_B$

$x_B \to 0 \quad \gamma_B \to 1$

$x_B \leftrightarrow b$

Ideal solution

↓

Ideal dilute solution $\begin{cases} x_A \to 1 & a_A = \gamma_A x_A \\ x_B \to 0 & a_B = \gamma_B K_B x_B \end{cases}$

$A \rightleftharpoons B$

$\varphi = \frac{P_B}{P_A}$

$\mu = \mu^\circ + RT \ln a$

$\varphi = \frac{[B]}{[A]}$

We know that, we have to take henrys law and that was basically for ideal dilute solution, and then what we are writing here is that it is the same way we can just write it as mu B. We were writing A for the solute just like here and we are writing mu B is mu B star plus RT Ln PB by PB star, which is basically the activity now you see here that this equation is not very correct you already know that.

The reason is the pures solute in a solution. So, you can actually a think that whenever it is a dilute solution of course, for a concentrated solution it is very a lot, but even for a dilute solution it the from the solids perspective, we see a huge departure henrys law sorry, Raoul's law is valid from the solvents perspective, the reason being in the solution the you can think that it is almost the similar environment just like in a pure liquid or pure solvent.

But from a solids perspective it is very, very different. So, this is not very correct equation from the solutes perspective, now you know that we can write it as we already discussed about henrys law. And henrys law said that this thing, which is basically PB by PB star, which was approximated to be P by PV P total, and which is of course, equal to the mole fraction, which was Raoul's law, it is not correct if we just take it as PB by PB star. So, that thing is not correct this equating this with this is not very correct for the solutes perspective and.

So, what henry told that it can be instead with the thought of as some kind of proportionality with respect to the mole fraction? So, then we already see that we have to define now the activity how to define the activity of the salute with respect to all these equations. So, we write remember that activity is nothing, but we the way we are writing it is as PB by, and we can write the actual equation in terms of activity, because the way activity is defined is that that equation will explain everything for all range of solute concentration or solvent or the solute concentration.

So, the real equation will be nothing, but mu B is mu B star plus RT Ln activity of B. Now this activity of B again as before, we can write it as activity coefficient plus times the mole fraction, and we can write it as RT Ln xB plus or mole fraction, which is you can write actually a B is gamma B into x P. Now this gamma now this will be slightly different in this case, now remember that this at what condition we can write it in to be equal to x B that is the thing here, now you can write it to be equal to xB you.

In fact, you cannot write it to be equal to xB because already henrys law we know that it cannot be proportional to xB, it is some constant into xB and that constant we have to measure experimentally. Now, what it means is that when I have a very, very dilute solution. So, it is already ideal solution that is why we talked about a departure in Raoul's law by in incorporating a term arbitrarily which is activity, and it is trying to connect this activity with mole fraction which is for the real solution.

So, all this discussion on activity is on making it as a effective mole fraction was to see the real life situation. So, this is a real situation, which is a deviation from ideal behavior and remember this was an approximation in the Raoul's law. Right one more line here that pA by pB was taken to be pA by P total, which is the mole fraction. So, that is basically Raoul's law, here and now we introduce activity that will explain everything for the real solution.

So, from ideal solution we are going to real solution and the way is that from ideal solution if we go to real solution. So, we see that this real solution you have to always write it in terms of activity, ideal solution you could write it as activity sorry and the mole fraction. And the activity is connected to the mole fraction through the activity coefficient, but of course, if these two will be equal for a dilute solution, when actually your mole fraction is almost equal to 1. Now from the solutes perspective we know that even for a dilute solution there is a problem. So, we are saying that for a already we know that in that case we have to use a B into x B.

Now, think about it if I say that gamma B is tending to 1, when 1 x P tends to 0, x B tends to 0 means actually it is now di dilute solution, remember that form a for a dilute solution means it is a mostly solvent and very less amount of solute which means x A tends to 1 and x B tends to 0. So, if we impose that condition now if I also say that gamma B tends to 1, then we have a problem then actually have Raoul's law which is already wrong we know.

So, we can write that gamma B is tends to kB then it is fine then it is again behaving as an ideal dilute solution which is the henrys law. So, we can write instead of activity that it will be nothing, but you can write it as before gamma B plus we can write it as or we could actually define it in a slightly different way. Instead of writing it like this, we can actually use our old convention that I will know actually, I will not use gamma B tends to kB, but rather I will just write it as a B is equal to gamma B into kb into xB.

So, that I can say that when these x P tends to 0, for an ideal dilute solution this gamma B tends to 1 then I have satisfied everything. So, then if I just put the value of activity here, so I will have RT Ln gamma B plus RT Ln k B plus RT Ln x B. So, then we are we have basically satisfied everything and you see that the clear there difference in the day I mean definition that how will you write it. So, you know that there you have it is a little bit confusing that you had two situations.

So, one is actually have only one situation, but you are looking at from two perspectives. So, one is solvent perspective, another is solutes perspective and we already said that when we have ideal solution let me again write it ideal solution means actually. So, which will show some ideal behavior, now this ideal behavior just like in ideal gas, when you see the ideal behavior when the pressure of the gas is too low, which means the density is very low the same thing we are seeing here.

So, density of what is law that is basically the solids density is law, solids mole fraction is law. So, in a limit of dilution any real thing should behave as a ideal system. So, in the limit of if it is a fairly dilute solution or we can write it as a if it is an ideal dilute solution. So, then we can say that x A intends to 1, and x B will tends to 0 because that is the condition for dilute solution in that case we can actually write recover or Raoul's law, by writing x A into gamma A into x A. And then we can write our this other equation, which is the henrys law as activity of B it will be nothing, but gamma B times k B into xB.

So, in either case you can see this activity is actually proportional to mole fraction or it is telling some effective mole fraction, but again keep that in mind that this gamma is not a constant, it is basically it will take it will vary with respect to the concentration. Similarly, here the kB is taking care of everything, we can write it in two different ways either you can include the kB inside gamma and then you can say that there gamma is actually varying with respect to x P, that will also you can think of and now the point here is that we introduced this part in discussing reaction quotient.

In the sense that we need to know right the as you know that what is the reaction quotient it is nothing, but the differences in the pressure and we wrote it as PB by PA, for in reaction which is going like A to B, but will now use general equation and ask this question how the to write this reaction quotient. Now this we got by writing the mu in terms of the pressure like PB by PA, but now we are what are you going to do we will we are just going to write it as in instead of writing it in terms of pressure.

We are going to write it as mu 0 plus RT Ln, activity of the situation by the way when we write it as activity. So, when I use this equation of course, you have to in real life situation you usually connect it to the concentration, because this mole fraction is also connected to the concentration and usually you connect it to molality of the solute and there are equations are we the mole fraction to the molality.

And then you just write the henrys law in terms of just kB in to B something we discussed and then we will replace the activity with concentration, but that strictly is valid only for the dilute solution limit, When the solution also behaves ideally with respect to the solid perspective as well, but we often use it even for any concentrated solution also we will often use this reaction quotient as the ratio between the product versus the reactant, and that is not very correct from the thermodynamic point of view because as we see that the energetics are not very correctly a explained.

So, that is why we wrote these equilibrium constant, when you wrote it we specifically said that it is a thermodynamic equilibrium constant. Whenever you are using the thermodynamic equilibrium constant you have to be very careful, 1 is that you have to divide it by the standard state pressure and. Secondly, you have to for a real system you have to always consider the activity and not the concentration.

So, that way we will I mean we will keep this notation for a future perspective, now in the next section we are going to discuss, how we can actually consider the general case something like we already discussed like, if I you have stoichiometry equation where the stoichiometry is are not necessarily one, and then what will be the general expression of the reaction quotient or the equilibrium constant for this equation that is what we are going to discuss now.