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Lecture-17

Soil Solution-Solid Phase Equilibria and Sorption in Soils (Contd.)

Welcome friends to this second lecture of module 4 and of this NPTEL course of environmental soil chemistry and in this lecture, we will be discussing about the different, you know, how to calculate the different species of ions in the soil, as well as, we will be talking about ionic activities and their implications. And also, we will be talking about the stability diagram. Now in the previous lecture, we are we are talking about the speciation of the soil solution.

And I started on one example if you remember, so let us consider, let us continue that. In that example we, we, we started to calculate the we we were, we are basically calculating the concentration of different calcium species present in the soil solution from a basic soil and we assumed that at a pH of 7.9, when the total calcium concentration was 3.715 multiplied by 10 to the power -3 mole per liter.

So, we assume that the calcium occurs as either free hydrate, you know, as free hydrated calcium 2+ ion, or as complexes with inorganic ligands like carbonates to form calcium carbonate, sulfates to form calcium sulfate, and chloride to form calcium chloride okay. So, I I showed you that.

Then we have presented this, the sum of the free and complexed ion in this form of equations. And then we have calculated we have shown the conditional stability constant or conditional equilibrium constant for each of these complex forms like calcium carbonate, then calcium bicarbonate, then calcium sulfate and calcium chloride okay, we have expressed them in the forms of in the, you know, in terms of conditional stability constant or conditional equilibrium constant.

And then by taking this calcium 2+, as a common factor we have converted this total equation into, in the form of this algebraic equation where we can multiply the conditional, conditional stability constant of each of these, you know, each of these compound with their concentration of that particular ligand. So, for example you can see K1 conditional. That means the conditional stability constant of calcium carbonate, multiplied by the concentration of the ligand or carbonate.

Similarly for bicarbonate and then sulfate and chloride. So, basically we have reshaped that the equation in forms in the form of conditional stability constant. Now, we want to in we want to calculate this total relationship, by inputting the values of this conditional probability constant. Now we have already used several models, there are several computer models, which have this database of this conditional probability constant.

So, I was giving you an example using one particular complex. Let us consider this calcium bicarbonate and in this calcium bicarbonate, we can we can see that calcium plus H+ plus carbonate forms this calcium bicarbonate. So, in this calcium bicarbonate if we know the conditional stability constant that is 9.33 into 10 to the power 10 at 298 Kelvin temperature.

We can express this equation in, you know, like this like, you know, the concentration of calcium bicarbonate is basically 9.33 into 10 to the power 10

and concentration of calcium concentration of H^+ and concentration of carbonate. Now, if we input the concentration of calcium concentration of protons or H^+ and concentration of carbonate, then we can calculate the concentration of that particular compound. So, by that way, this similar way we can calculate the concentration of each and every compound which is present in the soil solution.

So, once the free concentration, so what I mean that once this free concentration of Ca2+ H+ and CO3+ are determined, the concentration of the complex, that is calcium bicarbonate can be calculated. So, the calculated concentration of various metal species. For example, calcium carbonate, calcium sulfate, calcium chloride, calcium phosphate, calcium nitrate, calcium hydroxide.

So, all these can be checked by inserting them into the mass balance equation and determining if the sum of the equal to the known total concentration. So, basically once we calculate, once we calculate the concentration of calcium carbonate, calcium sulfate, calcium chloride, calcium phosphate, calcium nitrate, calcium hydroxide and input those values and then we can see whether the summation of all these is equivalent to the Ca T. Then we can see that yes, this is the correct calculation. So, let us see one example.

So, in this table we can see the concentration of free metals, free ligands, and then total metal complex by each ligand and total concentration of metals and ligands in soil solution. So, in our case we know that our total concentration of metal of calcium is 3.715 multiplied by 10 to the power -3. So, the total metal complexed by each ligand in case of carbonate is this, sulfate, chloride, phosphate, nitrate, hydroxide and free metals is this. So, inputting these values.

If we input these values all these value, we can see we can see basically the calculation is coming around 3.715 10 to the power -3, which is almost equal

to 3.717 10 to the power -3, which is the value of Ca T. So, this is how we calculate the sum of free ions and complex species from the model and then we can see that is the close to the Ca T values. So, again how we start, we start by inputting the conditional probability constant from the models.

And by inputting the conditional probability constant and then we calculate the individual species concentration of the individual species and from there we can see the concentration of the compound and from and inputting the values of the concentration of the compound from the table, we can see if the summation is equal to the total, you know, Ca total, you know, total metal consumption or not. If these are 2 same if these 2 are same then we can see that okay, these are the concentration of individual. We have seen that this is the justified speciation of that particular metal in the soil solution.

So, then let us consider another important thing that is ion activity and activity coefficients. So, the single ion activity coefficients are basically activity coefficients are calculated using the extended Debye-Huckel equation. So, the extended Debye-Huckel equation, we can calculate this activity coefficient where this log of activity coefficient is basically -A Z i square I to the power half + 1 Ba i I to the power half, where A and B are the constant relating these A and B are the constant related to dielectric constant of water.

And generally we take their value as 0.5 and 0.33 at 298 kilo 298 Kelvin. And a i is basically the size of the ion in angstrom, Z i is basically the charge of the valance of the ion in solution. And I stands for the ionic strength. So, so ionic strength basically is a measure of degree of interaction between the ions in the solution. And it is related to total electrolyte concentration.

And is expressed as basically in the form of this summation, where C i basically relates to the concentration of i th species in mole per liter, and Z i is basically charge or valence of the ionic species, where the summation extends

all over the ions in the all the ions in the solution. So, whatever ions are present, we can we can sum them for these for their respective concentration, as well as their charge or valence squared, and then we can get the total ionic strength.

So, if we consider the ionic strength of different, you know, different ions. For example, in case of H +, you know, values of single ion activity coefficients at various inorganics, you know, various ionic strength at 298 Kelvin. So, you can see in case of H + we know, we get their ionic strength, you know, single ionic activity coefficient. Basically the single ion activity coefficient, how their coefficient changes based on the ionic strength okay.

So, at different ionic strength and particular, you know, ionic radii. So, for this lithium, then sodium bicarbonate, then orthophosphate and all these we can get their values of ion active active activity coefficients, from this table. So, and also this is for the inorganic ions of charge of 2 + as you can see, Mg 2+, beryllium, calcium, copper, zincs, then tin and then iron, then nickel, cobalt and so on so forth. And this is inorganic ion of charge 3+ as you can see, L 3+, Fe 3+, then chromium 3+, Selenium 3+ and so on so forth.

So, what is the relationship between the ion activity and activity coefficients? So, when the ionic strength is greater than 0.2 mole per liter the single ion activity coefficients are basically calculated from extended Debye-Huckel equation derived from the actual values which you have seen recently. However, for more concentrated solutions with ionic strength, less than 0.5 mole per liter we generally follow Debye's equation.

And this Debye's equation generally take this form of log of activity coefficient equal to -AZ i squared then I to the power half 1 + I to the power half -0.3 I, I is the ionic strength, whereas A is the, you know, constant and Z i is basically the valence, or the charge okay.

So, let us see some example mathematical solution, some sample problems of calculation of ionic coefficients. So, here the first question says the calculate the ionic, calculate the I for 0.10 mole per liter for potassium nitrate and 0.10 mole per liter K2 SO4 solution. So, I for 0.10 mole per liter potassium nitrate we can use this formula where C i, we already know that the concentration is 0.10 mole per liter.

And in case of potassium, it is +1. And in case of nitrate it is -1, so we get the value of 0.10 mole per liter. And I for basically 0.01 mole per liter K2 SO4, if we can see if you want to. If you want to calculate it for the K2 SO4, obviously, then the, it will be basically 2 into multiply into 0.10 + 1 because it is K2, and then, SO4. We know that SO4 has the valency of - 2, so it will be squared. So, 0.10 + -2 whole square. So, we are getting a value of 0.30 mole per liter. So, this is how we can calculate I from the concentration, from the valency of the cations, as well as the associate anions.

Now another question is calculate the activity coefficient for cadmium 2+ at 298, Kelvin. When the ionic strength is 0.01 mole per liter. And we can extend you can, we can use the extended Debye-Heckle equation, we can input those values, we know that - A, that means it is basically 0.5. We have already seen we can default, we are using the default values of 0.5 for a and for b we are using the 0. you know value of 0.33. These are two constant based on the dielectric constant of solution. And then, cadmium Z i square.

So, from there, we can also, you know, using this formula, we can calculate that 0.17, and then log of value and from there we can get the value of 0.67 okay. Again, we are basically using -A Z i square +1 + B a i you know, and then I to the power half as you can see, we are using 0.01 value of ionic strength here, and this is 0.33 we are using the value of B, constant, which is basically depends on the, the dielectric constant of the solution. So, this is how you solve the ionic coefficients and ionic strength calculations.

So, another thing generally comes to our mind what is the difference between dissolution and solubility processes. Now there is a difference between these two terms. Well, you know, dissolution is basically dissolving of a soil solid into the soil solution, whereas solubility is the process of deposition or precipitation of a substance from the soil solution. So, again dissolving of the soil solid into the soil solution is known as the dissolution.

Whereas solubility is the process of deposition or precipitation of a substance from the soil solution. And in case of dissolution it occurs only when the soil solution is under saturated. However, the solubility occurs when the soil solution is supersaturated. So, basically these are two opposite processes. In case of dissolution soil solution has less solute than in equilibria. However, in case of solubility, soil solution has more solute than in equilibria.

So, as a result of that, due to the supersaturation, there is a precipitation or there is deposition. However, when there is a less strength or, you know, less solute than in equilibria obviously, there will be further dissolution to maintain the equilibrium. Now, dissolution and solubility basically determine the fate of inorganic mineral components of the soil and dissolution-precipitation, equilibria affects the weathering as you know, soil formation and the contaminant mobility, obviously, this dissolution and precipitation highly, you know, control the concentration of differing, you know, concentration of different solid phases in different stages of the weathering.

Whether they will further weather away or not based on these dissolution and solubility process, obviously, due to the solution due to the solubility of different minerals, the weathering basically goes on. And when there is a, when there is no further solubility of the mineral obviously the weathering process stop there okay and also soil formation basically depends on this dissolution and solubility. And precipitation also and contaminant mobility is also depend on this dissolution and solubility process.

Now in case of calcareous soil like gypsum dissolve relatively rapidly and congruently. Now congruent mean after dissolution, the stoichiometry properties in the solution is same as those in the dissolving mineral. So, basically when calcium and sulfate combines together to form the calcium sulfate, or gypsum. It is at stoichiometry, you know, the stoichiometry proportion remains same. So, this is how this reaction is known as the congruent reaction.

However, many soil weathering reactants are reactions are incongruent also, and this is due to the precipitation of a new solid phase, because when there is a, you know reaction, and formation of a new solid phase when that solids, you know, for example, when there is a constant, when there is a reaction between two species and the new species which is being formed is getting precipitated of a as a new solid phase.

Then either separately or on the surface of the original mineral undergoing dissolution, then it is obviously changing the stoichiometric proportion. And as a result, this is called incongruent process. Now, silicate minerals, in case of silicate minerals, they dissolve to form various secondary minerals. For example, as you can see in this slide obviously anorthite, which is an important silicate mineral or, you know, this is an important feldspar also.

Calcium feldspar when they are reacting with the carbon dioxide or water. In other words, the carbonic acid when they are reacting with the carbonic acid, they are forming the kaolinite. So, this is basically dissolving the primary minerals to form a secondary minerals, as, you know, the secondary minerals are formed from the primary minerals. Here you can see that anorthite which is a calcium feldspar is getting dissolved in the presence of carbonic acid to form the kaolinite and also they are producing the calcium ion as well as the bicarbonate ions. Also you can see here albite.

Also when they are combining with the carbonic acid, they are forming the smectite and also they are forming the sodium ions, bicarbonate ions, and silicic acid and also biotite when they are, you know, reacting with oxygen and carbonic acid they are forming gibbsite, goethite, potassium ions, magnesium ions, bicarbonate ions and silicic acid. So, you can see that how the dissolution of different primary minerals basically, you know, helps in development of different secondary minerals into the soil.

And that is why this dissolution and solubility process are very important for the formation of the soil as well as for the weathering process. Now, in case of silicate minerals, water and carbonic acid, are the major reactants as we have already seen and calcium, magnesium, potassium, sodium and bicarbonate are released into the salt solution, which you have just seen and the extent to which these reactions occur depends on the soil forming factors, obviously, due to the presence of, due to the presence of different climatic condition, whether there is a warm and humid climate.

Whether there is a presence of acids, mild acids, which are exuding from the plants or whether there is a presence of, you know, presence of other factors, basically also topography basically also depends, you know, also determines the dissolution solubility process.

Now, what is the thermodynamic dissolution constant? Now considering the following dissolution reaction in gibbsite. So, this is a gibbsite when it is reacting with the proton in acidic environment, they are basically forming the aluminium as well as water. So, the thermodynamic dissolution constant which is K0 dis from this reaction is basically can be expressed in terms of this okay. So, this is called the thermodynamic dissolution constant.

Now, thermodynamic dissolution, the activity of any solid phase is defined as 1 in its pure form when there is no structural imperfections. So, consider that the activity of any particular solid phase is defined as 1 when, you know, when it is pure form when there is a no structural imperfections, at standard temperature at 298 Kelvin and pressure of 0.101 mega Pascal and the activity of water is also considered 1 since soil solution are indefinitely dilute compared to the concentration of water molecules.

So, assuming the activity for aluminum hydroxide in water as 1, this, you know, thermodynamic dissolution constant becomes this, you know, can be simplified to this. Also, this ratio is known as the thermodynamic solubility product constant. So, this is also known as the thermodynamic solubility product constant.

Now, the thermodynamic solubility product constant is numerically equal to the thermodynamic dissolution constant when the solid phase is pure and aqueous solution phase is infinitely dilute. Obviously these are 2 conditions because in this both the cases the activity will be 1. So the ratio of Al 3+ + H3 + is often referred to the activity product or ion activity product okay, we are basically seeing the ionic activity.

So, when this active when the ratio of this ionic activity product by this, you know, this K0 SO, that is equal to 1, then the solid solution is in equilibrium with the given solid phase, when this ratio becomes greater than 1, then the solution is, then supersaturated with respect to the solid phase, and when these, so, you know, this ratio is less than 1 the solution is under saturated with respect to the solid phase.

So, again if we go back and see, this is the thermodynamic dissolution constant and thermodynamic dissolution constant can be represented in this simplified form in the form of a solubility product constant when the activity of the solid phase is 1, and the activity of the solution phase is 1 because it is dilute and then we can see that in this condition, these 2 values these 2 constants are the same.

That is thermodynamic dissolution constant the thermodynamic, you know, or the, the solubility product constant is same. So, this ratio of the activity of Al 3 + and H+ is often referred to as the ion activity product and this ion activity product by this constant when it is equal to 1, then the soil solution is in equilibrium with the given solid phase when it is greater than 1, then it is super saturated obviously it is the respect to the soil solution phase. When it is super saturated, obviously, there will be precipitation. And when there is less than 1 the solution is unsaturated and then further dissolution will go on for maintaining the equilibrium.

Now for seeing this whole process, we generally use that stability diagram. So, stability diagram are used to determine, or to basically to get stability diagrams gives us 2 basically answers. One is does a solid phase control the concentration of an element in the soil solution. And if it does, what the solid is. So, they are constructed by converting previously solubility relationship into logarithmic terms. And rearrange rearranging the terms to form a straight line relationship.

So, as you can see, the log K0 dis that is thermodynamic dissolution constant can be calculated from the standard free energy accompanying the reaction which is denoted by this. So, if it is the standard free energy of formation is basically this, you know, the can be, can be calculated by these equation okay. Now, this is basically the standard summation of the standard free energy of all the products. And minus the summation of standard free energy of all the reactants. So, considering the, incase of gibbsite, we can see that when the gibbsite is reacting with the protons, it is producing Al 3+ + 3H 2 O, we already have seen this.

So, using the published values, we can calculate the value of this particular delta G 0, which is - 45.92 kilojoule per mole. So, as this delta G 0 is related to the thermodynamic dissolution constant, you know, this delta G 0 can be related to the thermodynamic equilibrium constant with this formula where, you know, this R is basically universal gas constant and T is the absolute temperature.

So, this is the relationship between this thermodynamic equilibrium constant and these this delta G 0. And again, for your, for your recap this delta G 0 is basically the, this delta G 0 is nothing but the standard fee energy of the formation and we calculate this delta G 0 by summing up the delta G 0 of all the products and delta G 0 of all the reactions the reactants. The standard free energy. Remember, this is the standard free energy of formation. So, this is the. So, this is how we can relate the standard free energy of reaction to the, to the thermodynamic dissolution constant.

Now this thermodynamic dissolution constant used by inputting all the values of these, that means RT ln K K0 dis. So, basically when you input, all these values, we will get this value of minus, we get basically we will get this reaction, we will get this equation. So, for the pre calculated value of delta G 0 r, we know that the value will be 8.04. So, the corresponding solubility line is determined by plotted as, so we can see that once we calculate this log value of K0, we can calculate this and from there we can express this straight line equation.

Again, let me go back and this, you know, describe it again. We know that thermodynamic equilibrium constant can be, or thermodynamic dissolution constant is basically the K0 dis dis and the log of K0 dis values can be calculated from the standard free energy accompanying the reaction and the standard free energy accompanying the reaction can be calculated by the standard free energy of the products minus standard free energy of the reactants.

So, considering if we consider particular these this case of dissolution of gibbsite to form the aluminium as well as water. We can use the published values of these free energy of formation and the free energy of formation we can see it is - 45.92 of, you know, we can use this formula of free energy of the products and free energy of the reactants we can calculate these value of the free energy of the thermodynamic free energy of the reaction.

And we know the relationship between the thermodynamic dissolution constant. And this thermodynamic free energy of reaction, you know, can be related using this formula where this R is the universal gas, gas constant and T is the, you know, absolute temperature in Kelvin. So by inputting all these values we can get this relationship and the from the pre calculated values of delta G 0 for gibbsite. We can input these values and we can get this log of this thermodynamic dissolution constant of 8.04. From there we can calculate this linear equation.

So stability diagram basically here the linear equation. If this log of Al 3+ is our, we can we can use this as y axis, this is the intercept, and obviously -3 is the slope. So, we can see that log Al 3 is plotted on the y axis, pH is plotted in the x axis and -3 and 8.04 are the slope and the, you know, y intercept respectively. And from there we can see the solubility. This is called the solubility diagram of various aluminium oxides and hydroxides.

And we can see the solubility of different elements like conundrum, amorphous, Al OH 3, bayerite, gibbsite, norstrandite and then boehmite and

diaspore and all this okay. So, this is called a stability diagram. Now the advantage of a stability diagram is that, you know, the solubility of several different solid phases can be compared at one time and the position of the different lines correspond to the solubility of each solid and the line nearest to the axis is the most insoluble or most stable. So, the lines which are nearest to these both axis are basically the most stable or most insoluble.

So, the anhydrous aluminum oxides, you know, as you can see here the anhydrous aluminum oxides, like gamma alumina and alpha alumina as you can see from here, the gamma alumina and alpha alumina are not usually formed in soils because, as they are high temperature minerals, and the, the order of decreasing the solubility among the remaining mineral is bayerite. So, here you can see the bayerite and decreasing the solubility means the less soluble, followed by boehmite.

And then norstrandite and then gibbsite and then diaspore. So, obviously the activity of Al 3+ is dependent on the pH, and it decreases, you know, 1000 fold for every unit increase in pH as you can see at every unit increase in pH, the activity of Al 3+ decrease, you know, 1000 folds. So, using this stability diagram, we can see which mineral form is stable at which condition and we can we can we can basically see the, the composites or we can we can basically identify the dissolution of solubility of that particular element at that particular pH condition.

So, for phyllosilicates the stability diagram is plotted instead of log, you know, silicic acid at x axis and log aluminium + 3 pH as the y axis. So, you can see this is the kaolinite when it is reacting with the acidic environment with the protons, it is producing aluminium. It is producing the Al 3+ and silicic acid and H 2 O and associated K dis is basically 5.45.

From the rearranging the terms and assuming and activity of 1 for water and kaolinite basically yields this value of 10 to the power 5.45 and taking log on both the sides solves and basically yields this reaction log Al 3+ plus 3 pH equal to 2.73 - log H 4 SiO 4. So, basically we pot plot H 4 SiO 4 or a log of this silicic acid in the x axis and log Al 3+ plus 3 pH in the y axis.

And this is how the stability diagram of different minerals can be found, you know, various primary and secondary minerals in the soil. So, the way the vertical lines as you can see silica, amorphous, chloro, you know, semi amorphous silica, silica quartz the vertical lines are quartz and other sources of silica straight lines. This is because there is no aluminium in the crystalline structure, hence the dissolution reaction is essentially independent of the pH because it is not dependent on aluminium.

So, stability diagram are very useful in predicting the presence of stable solid phases in different soil solid system and the proportion and the portion of the straight line relationship close to x and y axis represent the most stable mineral phase or the most insoluble mineral. 2 is to 1 type of clay mineral like montmorillonite is stable only when the concentration of silicic acid solution in solution is controlled by the solid phase and most more soluble than quartz.

So, this is basically the stability diagram and how we calculate the stability diagram and how we interpret the stability diagram. Let us wrap up our lecture here and in the next lecture, we will be talking about the surface complexes and different types of adsorption isotherms. Thank you very much.