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Environmental Soil Chemistry
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Lecture #28
Kinetics of Soil Chemical Processes (Contd.,)

Welcome friends to this lecture of week 6. This is the third lecture of week 6 and we will be talking about the kinetics of soil chemical process. So in the previous two lectures, we have talked about different transport process as well as we have discussed about the first order reaction and in this lecture we will be talking about the half life, how to calculate the half life and then how to calculate what is the second order reaction, what is the zero order reaction and what are different types of kinetic model into the soil chemical process.

So let us start with the half life of first order reaction. So you can see the half life, which is basically denoted by t half.

As you can see in this slide, the half life is denoted by the t half, is basically timescale on which the initial population is decreased by half of its original value represented by the following equation. So basically at any point of time, the concentration of a particular reactant is basically half of its initial concentration. So after a period of one half life, that is t = t half and we can write basically A = A0 e to the power -kt.

So it is another representation of the first order reaction. We have already discussed it. So from there we can see A half by A concentration = 1/2 = e to the power -kt half. So we can represent this equation shortly in terms of half = e to the power -kt half. So this is how this half life period for a first order reaction can be expressed.

So if you take a logarithm on both sides of this equation, we will get, we have to remember that logarithm of ex = x. So basically, if you take logarithm of both sides, so if you are taking logarithm here and taking logarithm and basically logarithm 0.5 = -kt. So solving for the half life, we will get a value of the half life = 0.693 by k. So we obtain this simple reaction, that is t half = 0.693 by k. So from there, we can calculate from this relationship. We can calculate half life of any first order reaction.

So also this indicates that the half life of a first order reaction is basically constant. So we have seen that the half life does not depend on the concentration of the reactant. It is basically constant. So if you see, it is the time and the concentration of the A. We know we can get an exponential decay. So this is the first order reaction and you can see that the t half is basically constant. So half life is basically independent of initial concentration, however this is not in the case of the other reaction orders.

For example, this is second order, it depends on something others. So in case of first order reaction, the t half or the half life is independent.

Now half life of the first order reaction, we know for the first order reaction, the half life is independent of the initial concentration just we have seen, which is an unique aspect of first order reactions. So only in the first order reaction, we will see the half life is independent of initial concentration. The practical implication of this is it takes as much of time of any reactant concentration to decrease from 1 molar to 0.5 molar as it takes from 0.1 molar to 0.05 molar.

So basically to become half of its initial concentration, it takes uniform time. In addition, the rate constant and the half life of the first order processes are inversely related. As you can see in this graph, it is quite clear, if you plot this time t and this basically this is concentration of the reactant, where the intercept is initial concentration. You can see in both these conditions, we are getting this first order reaction curve.

Here, you can see it is the smaller k, as you know and it is the large K value. So the rate constant is quite high in case of this. So we are getting a steep decay; however in case of this, this is a small case, so it shows the slower decay. Now as we can see the rate constant with the half life of the first order process are inversely related. So in this condition, if you see the half life will be somewhat here. So here it becomes 0, so the half life should be somewhere here.

So the timeframe for this half life is quite low as compared to the timeframe of this half life here. So here the half life is basically this duration. So obviously this duration is quite high. So obviously for smaller k, the half life is more than that of larger K. In case of large K, the half life is less. In case of small k, the half life is more. So that is why the rate constant and the half life of a first order processes are basically inversely related.

So if we go ahead and see, some numerical examples of half life calculation, here for example the half life of first order reaction was found to be 10 minute as a certain temperature and what is the rate constant? So we know that the equation is basically k = 0.693 by t half. So here we are seeing, it is basically 10 minute or 600 seconds. So in terms of second we can get the rate constant here. So this is the rate constant.

Now another question is if 3 gram of substance A decomposes for 36 minutes, the mass of the unreacted A remaining is found to be 0.375 gram. So what is the half life of this reaction, if it follows a first order kinetics. Now we can solve this using two approaches. So the first approach is known as the simple inspection approach and the second approach is known as the brute force approach. So we will see the brute force approach in the next slide.

However, in this slide, we will see the simple inspection approach. So this approach is used when one can recognize that the final concentration of A is basically one-eighth of the initial concentration. So you can see the initial concentration, it is basically 3 grams and the final concentration is 0.375 gram. So basically, whatever have been decayed is basically the final concentration here it is 0.375 is basically one-eighth of the initial concentration.

So 3 times the half life have been implemented here. So you can see here, there are 3 half life one half multiplied by one half multiplied by one half have elapsed during this reaction. So initially if you are getting some value of a reactant concentration and now you are getting one-eighth of this concentration, that means it went through 3 cycles of half life. So basically, if we consider this equation, we know this equation, it is equation of half life for the first order reaction.

If you simplify this, 36 minutes it took for undergoing 3 cycles of half life, so basically if we divide it by 3, we will get 12 minutes. So this approach only works when the final concentration is one half to the power n. Remember here, this is the only condition has to be followed for calculating using the simple inspection approach. This has to be followed. For example, the final concentration is one half to the power n that of the initial concentration.

Then n is the number of half lives that have elapsed. So here we can see it has elapsed 3 cycles of half life. So basically we are dividing it and ultimately we are getting the half life. Otherwise, if it is not the case, where the final concentration is not 1 by 2 to the power n of that the initial concentration, then we have to go for the brute force approach.

What is the brute force approach, let us see. So if 3 gram of a substance A decomposes for 36 minutes, the mass of unreacted A remaining is found to be 0.375 gram, so it is basically the same problem. So here you can see this approach involves solving for k first from the integral rate law equation. We know that A by A0 = half in this case. So from there, we can relate this k into the t half via this equation, we know that here.

So this is basically from the integral equation, if you simplify this integral equation, this is the actual form of this equation. So basically from this equation, we can calculate. If you take the logarithm of both the sides and simplify, we can rearrange it as k = logarithmic of At by concentration of A0 by t. Now we know that at a particular time, the concentration is 0.375 gram and the initial concentration was 3 gram, time elapsed 36 minutes.

So from simplifying, we will get 0.0578 minute inverse. So we know k value from here. Now if you put this k value into the main equation or main relationship of the half life, which is t half = logarithm of 2 by k, that is 0.693 and then we can get 0.0578. So we got the value of k here, so ultimately it will give you 12 minutes. So from here also we can calculate the half life; however, remember this thing you can calculate only when the concentration at a particular time is not basically following half of the n-th order of this condition.

Basically in the first simple inspection approach, we have seen that 3 half order cycles have gone. However, in this case, if that does not follow this simple rule of 1 by 2 to the power n, then we will go for this brute force approach.

So I have some homework for you guys. Home work 1 is basically you have to calculate the half life of the reaction below. There are 3 reactions, I have given here. If 4 gram of A are allowed to decompose for 40 minutes, then the mass of A remaining undecomposed is found to be 0.80 grams. So this is the first. If 8 grams of A are allowed to decompose for 34 minutes, the mass of A remaining undecomposed is found to be 0.70 gram and if 9 gram of A are allowed to decompose for 24 minutes, the mass of A remaining undecomposed is found to be 0.50 grams. So you have to calculate the half life for all the reactions.

Now another homework for you guys is determine the percent H2O2 that decompose in the time using this rate constant and the first condition is the time for the concentration to decompose is 600 seconds after the reactions begins and in the second problem, the time for the concentration to decompose is 450 seconds after the reaction begins. So here you can see, I have given you the rate constant, I have given you the time, you have to basically calculate what is the percentage of H2O2 that decompose in that time. I hope that you can do these 2 homework and I will be sending you the solutions after this week.

So now we have completed the first order reaction and calculation of half life, now let us talk about the second order reaction. Now in the case of second order reaction, integration of the second order rate basically follows as I have told you that second order rate basically follows the square of the concentration of any particular reactant or multiplication or product of the concentration of the 2 reactants.

So here you can see it is basically the square of the concentration of a particular reactant. So the rate is basically following the square of the concentration of particular reactant. So if we simplify it, we will get this form. How we will get this form, I will show you. So basically, this straight line form, we will again get for second order reaction, just like for first order reaction, which is easily rearranged to form equation of the straight line, which you can know that and yields a plot similar to the one shown below.

So here you can see there is a positive slope. In case of second order reaction and we are putting the time and 1 by concentration of A reactant will get a positive slope of A multiplied by k and here the intercept is 1 by A0, where A0 is basically the concentration at time 0. So this is the characteristics of the second order reaction.

Now in case of second order reaction, the half life is given by this formula, where t half = 1 by k into concentration of A0. So basically, it depends on the initial concentration, so in contrast to the first order reaction. So in case of first order reaction, the half life, it was independent of the initial concentration; however in case of second order reaction, the half life is dependent on the initial concentration A0. So that is why, the concept of the half life for a second order reaction is far less useful as compared to the first order reaction.

Now let us consider the second order reaction for a case 1, where the reactants are identical. Now if we consider the two of the same reactant, both of them are A, basically combined in a single elementary step. So you can see here A when you combine with another A will ultimately give the P. So the reaction rate for this step, so basically 2A = P. So basically the reaction rate for this step can be written by –half dA by dt = + dP by dt.

And then the rate of loss of reactant A basically, from this we can calculate dA by dt = -k into concentration of, it is basically product of concentration of A and concentration A, so basically –k into concentration of A square. So from here, this k is basically, we know that it is a second order rate constant with units of molar per minute or molar per second. So therefore, doubling the concentration of reactant A will quadruple the rate of the reaction.

In this particular case, another reactant that is B could be present with A, which we will see in the next slide. However, its concentration does not affect the rate of the reaction that is the reaction order with respect to B is basically 0 and we can express the rate law as this V = k multiplied by A, so basically we can express this rate law V = k into A square into B0, where the partial order for kA equal to here 2 and partial order for B = 0 here.

So this is basically the representation of the second order reaction. So this is the case 1, where identical reactants are there.

In case of another, where there different reactants are present. So if you see the different reactants, then two of the same reactants A and B combine to single elementary step. You can see A + B = P. So the reaction rate for this step can be written as rate that is –dA by dt = -dB by dt = dP by dt. So in other way, we can represent the rate of loss of reactant A is equal to –k multiplied by product of concentration of these 2 reactant concentration.

So where the reactant in order to respect in each reactant, reaction ordered with respect to each reactant is 1 here. This means that when the concentration of the reactant A is doubled, then the rate of the reaction will double and quadrupling the concentration of the reactant in a separate experiment will quadruple the rate. So if you double the concentration of A and quadruple the concentration of B at the same time, then the reaction rate is increased by a factor of 8.

This relationship holds true for any varying concentration of A and B. So this is how we can calculate different rate constant for second order reaction. Remember one thing, in case of first order reaction, the rate of decay of the reactant or the rate was basically dependent on the concentration of one of the reactant; however in case of second order reaction, it depends on either square of the concentration of the reactant or the product of the concentration of 2 different reactant.

So to describe how the rate of a second order reaction changes with concentration of reactants or products, the differential or derivative rate equation is used as well as the integrated rate equation. So the differential rate law basically shows us how the rate of reaction changes in time, while the integrated rate equation shows how the concentration of species changes over time. Now the latter form that means the integrated form when graphed yield a linear function.

We will see that and is therefore more convenient to look at. Now plotting these equation can also help us to determine whether or not a certain reaction is basically second order.

So if you consider case 1 where A + A = P, so here basically 2 reactants are basically identical. So second order reaction with a single reactant basically, so we can see what is their integral formulas. So the rate at which A decrease can be expressed using the differential rate equation we know that we have previously seen that, that is dA by dt – dA by dt is basically k into concentration of A square. Now this equation can be further rearranged by dA by d square = -kdt.

Now since we are interested in the change of a concentration of A over a period of time, then we integrate between t0 and t, that is the time of interest. So if you take integration in both the sides and for t0 to t and from A0 to At, to solve this, we have to take the help of this relationship. We know that integration of dx by x square = - 1 by x + constant, we know that. Now by using this formula, this integrate rate equation will basically come at 1 by At – 1 by A0 = kt.

Now upon rearrangement of this integrated equation, you obtain the equation of this line, that is 1 by At = kt + 1 by A0. This is the one, which we have seen earlier while showing the plot of the second order reaction. So now you know how we got this equation or the straight line equation from the second order reaction.

So basically, the crucial part, basically when we plot this t and then 1 by At, we will get a straight line with a slope of k and an intercept of 1 by A0. So basically the crucial part of this process is not understanding precisely how to derive the integrated rate of law equation, rather it is important to understand how the equation is related to the graph, which provides a linear relationship. So that is important.

How to graph this, because graph can give you, from any empirical relationship on any empirical chemical reaction, if you plot the data that will give you the understanding of whether it follows a first order reaction or zeroth order reaction or a second order reaction. So basically it is very important to see, to understand how the equation is directly related to this linear relationship. So in this case and for all second order reaction, the linear plot of 1 by A versus time will always give this straight line with a positive slope and slope value of k.

So this graph is basically useful in variety of ways. So if we know the concentration of a specific time for a reaction, we then can attempt to create a graph similar to this one. So if the graph is straight line, then the reaction in question must be a second order. So basically if we plot time versus 1 by concentration of a reactant and then we will get a positive straight line, then obviously we will be sure that there is a second order reaction.

In addition with the graph, we can find the slope of the line and this slope is basically k and which is basically the reaction constant for the second order reaction and the slope can be found by finding the rise and then dividing it by the run of the line. So this is how we can calculate this, we can basically plot this second order reaction.

Now the plot of this At versus time would result in a straight line, if the reactions were zeroth order. So if we plot At versus t, then we will get a straight line for a zero order. It does however, yield less information. You can see here, there are 2 graphs, one is for the second order reaction another is for the first order reaction. In case of second order reaction, it also follows the exponential decay in first order reaction, which is also following the first order reaction.

So here we are getting these 2 plot by plotting concentration versus time. So for zeroth order reaction, we will get a straight line; however A2 will give less information for a second order graph. So this is because both the graphs in the first or second order reaction would look like an exponential decay. We can see here it is an exponential decay. It is only another exponential decay. The only obvious difference as seen in the graph below is that the concentration of the reactant approach is 0, more slowly for a second order.

As you can see this, the slope is quite low as compared to the slope of this first order reaction. So it approaches 0 concentration very slowly as compared to the first order reaction and in case of first order reaction, the reactant reaches 0 very fast than that of the second order reaction. So this is the difference between these 2 types of exponential decay function.

Another case, case 2 where second order reaction with multiple reactants. So let us see what is the formula of this? As before, we can see the rate at which A decrease can be expressed using the differential rate equation. So differential rate equation, we are seeing here. It is basically product of the reactants. So 2 situations can be identified. Situation 2A where these A0 is not equal to B0, that means initial concentration of A0 is not equal to initial concentration of B0.

So in this situation, the initial concentration of 2 reactants are not equal, let x be the concentration of e species reacted at time t. So let us assume that x is concentration of e species, which is reacted at time t, so obviously let A0 will be A and B0 will be B, then A at a particular time will be A – x, so it is initial concentration minus x, which is already reacted and for concentration of B at a particular time will be B – x where B is the initial concentration and x is the amount reacted.

So this expression of rate law becomes, this will be simplified to this. This can be represented by this, where concentration of A is basically A0 – x and B0 – x basically represents concentration of B at that particular time, which can be rearranged by this form. Now we integrate in both the sides of this equation. If you take an integration from t0 to t and from 0 to x, so basically we will get the following.

So from solving this previous equation, where we are integrating from 0 to x and integrating from 0 to t, we have to take the help of this partial fraction integration rule. So if you see this partial fraction integration rule, from this partial fraction integration rule, we can express our equation in this form, which is integration from 0 to x dx by initial concentration minus reacted concentration into initial concentration of B minus reacted concentration equal to 1 by B – A, that is B0 – A0 and then taking this logarithmic form.

Now applying the form of the natural logarithm, this equation can be simplified to this equation. So in this left hand side, this will remain as such; however in the right hand side this logarithmic form will be simplified to this. Now if we obtain the integrated rate equation, under the condition that A and B are not equal. So basically, we will get 1 by B0 – A0, then logarithmic of B – A0 and A by B0 = kt. So upon rearrangement, we will get this formula. That is logarithmic of B into A0 by A into B0 equal to k multiplied by this.

So if we get this, from this equation, a linear plot we can get. If you plot time versus this logarithmic of this form. Ultimately, if we go back, it will be clear. So here this is basically constant and so basically when we are plotting time versus logarithmic of this expression, then we will get a slope and this slope will be basically k multiplied by this. So this is a constant, this is a slope and this is where we are getting a straight line for a second order reaction.

So this graph can be used in the same manner as the graph previously, which we have shown and written in the same way. So basically we can further simplify this as logarithmic of AB equal to k multiplied by A0 – B0 into t + logarithmic of A0 by B0. So again you can see here, it is a straight line. In this straight line, y = ax + b, where this is k into B0 – A0 and intercept is this term. So if we simplify this, we can further express in terms of A + Bx.

So this is one solution and we have seen how this can be represented in a straight line. Another solution is situation 2A, where initial A0 = initial B0. So basically, what we are seeing A + B = P. Since A and B react with 1:1 stoichiometry, because they are same. So A = concentration A0 – x and B concentration = B0 – x at any time t, A = B and the rate law will be basically rate = k into A into B, we know that.

Now we can basically replace this B = concentration of A, because both of them are same. So we are getting k = A square, which is basically the first case which we have already discussed. So this is how we can get the second order reaction with single reactant or multiple reactant and this is how we can express their rates and also we can plot them in the form of a straight line. Remember in case of first order reaction, this also gives you the straight line, if you plot basically the logarithmic of concentration of a reactant versus t.

You will get a straight line also, and which will give the negative slope; however in case of second order reaction, it will give you the positive slope when you plot the 1 by logarithmic of a concentration of a reactant and the time. So this is how you can differentiate between first order reaction and second order reaction. Hope you have understood whatever, we have covered so far. If you have any questions, feel free to email me and I will be more than happy to answer these questions.

In the next class, we will be talking about more details about the zeroth order reaction and then how we can apply different types of kinetic models for different soil reaction for explaining different soil reaction. Thank you very much.