Transcriber's Name: DoneDoc10 Environmental Soil Chemistry Prof. Somsubhra Chakraborty Department of Agricultural and Food Engineering Indian Institute of Technology - Kharagpur Module # 06 Lecture # 29 Kinetics of Soil Processes (Contd.,)

Welcome friends to this fourth lecture of week 6 of this online certification course of environmental soil chemistry and in the previous three lectures we have talked about the different types of chemical kinetics and different order reactions. We have talked about some of the rate limiting transport processes and also we have defined what is the first order reaction, what is the second order reaction.

And how first order reaction can be plotted, how second order reaction can be plotted, what is the difference between first order reaction as well as second order reaction and how to calculate the half life of first order reaction, what is the formula of half life for the second order reaction and today we are going to talk about zero order reaction and how we can actually apply these different order reaction to define different soil chemical processes and how to identify those.

So if we start today it is with a definition of the zero order reaction in some reaction the rate is apparently independent of the reactant concentration and the rates of these zero order reactions do not vary with increasing nor decreasing reactant concentration. So basically this is constant. So, in order words the rate of this reaction is equal to the rate constant k of the reaction.

And this property basically you can see that this property differs from both first order reaction and second order reaction where the rate constant is dependent on the reactant concentration. So again in the zero order reaction the rate is independent of the reactant concentration it is constant and so it does not depend on the decreasing reactant concentration or increasing reactant concentration. So there are certain properties, there are certain conditions to fulfill zero order reaction we are going to talk about that.

Now there are two general conditions that give rise to zero order rates. First of all only a small fraction of the reactant molecules are in location or state in which they are able to react. So very small fraction of the reactant molecules are generally go through these zero order reaction. So they are able to react and this fraction is continually replenished from the larger pool.

So only very fraction of the reactant molecules are in location of state in which they are able to react and this fraction is always continuously replenish from the larger pools. Second condition is when two or more reactants are involved the concentration of some are much greater than those of others. So, if we consider there are two reactants one is reactant A and reactant B if we consider the concentration of reactant B is much greater than that of concentration of reactant A. Then that could serve as a condition or prerequisite for zero order reaction. Now this situation you can commonly occur you can see it is commonly occurs when a reaction is catalyzed by attachment to a solid surface in case of heterogeneous catalysis or to an enzyme. So this type of reaction you can see in the catalysis as well as in case of enzyme this type of zero order reaction mainly predominate.

So let us see what is the differential form of zero order rate law? Now you know from our previous lecture that for each rate each order reaction be it a first order reaction or second order reaction each of them can be defined in terms of differential rate as well as integral form. So, similarly zero order reaction also can be expressed in terms of differential form as well as integrated form.

Let us first discuss its differential form. So when the differential form of zeroth order of law basically say as indicated by its definition the rate of reaction which is denote by - dA / dt = k and concentration of A to the power 0 which is basically k. So which is a constant so here rate is equal to constant so this is the differential form of zeroth order reaction where rate is the reaction rate and k is the reaction rate coefficient.

Now in this example the unit of k is M by s that means it is basically concentration versus a concentration per time unit of time. So it is a molar per second it could be mole per second. So the unit can vary with other type of reaction. As you already know in case of first order reaction it is different, in case of second order reaction it is different. In case of first order reactions the rate constant is basically time inverse whereas in case of second order reaction the rate constant has a unit of concentration inverse into time inverse.

So, basically I can see that the unit of the rate constant vary from zero order reaction to first order reaction to second order reaction. So in case of this zero order reaction the unit is concentration per unit time. So the unit for the rate constant is always will be this concentration per unit time and in higher order reaction obviously k will have different units which I have just told.

So if we go ahead and see; the integral form of zeroth order rate law. So, how to derive the integral form of zeroth order rate law? So integration of the differential rate so, we know that this is the general rate law equation. So if we go for the integration of the different rate laws it is a concentration as a function of time you know. So we used to start with the general rate law equation.

So first we write the differential form of the rate law when n = 0 which we just saw in our last slide that is rate = k or dA 0 / dt = k. Now, if we rearrange these things we will get dA = - kdt. So this is the differential form. Now if we integrate both side of the equation from A0 to A and from 0 t0 to t so basically in both sides we are taking the integration and if we solve it ultimately we will get these linear equation form. So basically a straight line where basically concentration of A equal to concentration of A 0 time - kt. So basically the integrated form of rate law allow us to find the population of reactant at any time after the start of the reaction. So, if we see the graphical representation of both the differential form as well as the integral form of zeroth order of rate law we will see this.

So in case of zeroth order of rate law if we see the differential the graphical representation of the differential law we will see that the rate is basically constant so if we plot the rate versus time we will see a slope of 0 we are seeing a constant k. However, in case of zero order integral law if we plot the concentration of A versus time we will see a straight line which is having a negative slope.

As you can see here it is having this k is having a negative slope. The slope is - a k. So this is the graphical representation of the zeroth order of rate law. Now you have seen each of this zeroth order reaction as well as the first order reaction and second order reaction can be expressed in terms of graph and these graph when you plot them they will identity whether this is zero order reaction or first order reaction or second order reaction.

Now you may be confuse that in case of first order reaction also you have seen that there is a straight line with a negative slope so how you can differentiate the graph of a first order reaction to a graph of a zeroth order reaction we will discuss that in details in coming slides.

Now graphing a zero order reaction we have already seen that the zero order reaction integral form can be expressed in terms of this equation where we can express this in terms of y = mx + b that is this formula for straight line where m = -k which is the slope which is the negative slope and y intercept b = A0 that is concentration of a reactant at time 0. Now zero order reaction are only applicable.

You can see this is an integral representation, integral graphical representation of zero order rate law now one thing is clear that zero order reactions are only applicable for a very narrow region of time. Now the linear graph is only realistic over a limited time range. So here you can see the time is basically the x axis. So this straight line will be valid only for a limited time range.

So, if we were to extrapolate of this line of this graph downward to represent all values of a time for a given reaction it would tell us that as the time progress the concentration of our reactant became negative. So if we increase the time and if we see the concentration of a particular reactant you will see that negative concentration sometime we achieve negative concentration which is not possible because concentration cannot be negative.

So that is why zero order reaction kinetic is applicable for describing a reaction for only brief window because if we increase the window of time then the concentration might rate negative which is not possible. So the zero order reaction kinetic is applicable for describing a reaction rate

for only a brief window of time and must eventually transition into kinetic of a different order.

So you will see that eventually as time progress this zero order reaction which is basically very transient one will be converted to other order reaction like first order reaction or second order reactions.

So to understand where the above you know these graph is basically comes from let us consider a catalyzed reaction. So, at the beginning of the reaction and for small value of time the rate of reaction is constant. We know that from these differential representation the rate of reaction is constant in case of zero order reaction and this is indicated by blue line of the figure.

So basically the integral one shows that it is a constant as we increase the concentration will go down and if we plot the rate versus time it will be constant line so this blue line basically indicates that. Now this situation typically happens this situation basically happens when a catalyst is saturated with the reactants. So when the catalyst active sides are already saturated with the reactants then this kind of situation may arise.

Now with respect to Michaelis Menton kinetics you have already know what is Michaelis Menton kinetics. Now this point of catalysis or catalyst saturation is basically related to the maximum velocity that is V max. Now as a reaction progress through time however it is possible that less and less substrate will bound to the catalyst. So initially the catalyst side is saturated with the reactants however as the time progress the catalyst the side is less and less saturated or less and less occupied by the substrate.

Now as these occur the reaction slows and we see a tailing of the graph. Now you can see as the time progress there is a tailing of the graph and is denoted by this dotted line and this portion of the reaction is basically represented by this dotted black line now looking at this particular reaction we can see that the reaction is not the zero order under all condition they are only zero order for limited amount of time.

So that basically says that these reaction is following the zero order law for a brief period of time up to this and after this it is following some other order of reaction. So here you can see the tailing of the graph has been started. So that is why the zero order reaction is very transient one it is actually applicable for very short window of time.

So if we plot the rate as a function of a time we obtain the graph we know that it is basically straight line again the only describes the narrow region of time obviously the time will be very narrow region and the graph is equal to k which is the constant rate constant. Therefore, the k is constant with time. In addition, we can see that the reaction rate is completely independent of how much reactant you put in.

So it does not matter whether you put much amount of different reactants you know the rate constant the rate will be very much constant and so

this is the zero order reaction. Now you can see the differences between zero order reaction, first order reaction and second order reaction.

So how to determine in case of soil now how to determine the reaction order and rate constant as far as the soil chemical processes are concerned. Now there are 3 basic ways to determine the rate laws and rate constant according to the scientist. First of all using the initial rates secondly directly using the integrated equation and graphing the data and third is using nonlinear least square analysis.

Now the second point using the integrated equation in graphing the data we have already discussed for zero order, first order and second order let us discuss what is the use of initial rate and how to use nonlinear least square analysis. So before that let us assume an elementary reaction where there are 2 species of reactants species A and species B. So there are 2 reactants reactant A and reactant B which are basically reacting to form the product Y.

Now here one thing you see that there is a forward reaction as well as there is a backward reaction so it is basically reversible reaction so these in equilibrium. Now you can see here the k1 here basically forward rate constant whereas for the reverse reaction this k - 1 is the rate constant of the reverse reaction. So this is basically equation 4. So let us see what is the implication of this for devising different types of order of reactions.

So if first order reaction rate law can be written from this previous equation we can see dA / dt = -k1 into concentration of A product with concentration of B where k1 is basically the forward rate constant and alpha and beta here are assumed to be 1. Now you know alpha and beta are basically partial order of A and B. Now the reverse reaction which we are talking about is basically dA / dt.

So here you can see it is positive because it is in the reverse reaction basically there is a generation of the reactant. So here you can see this is basically positive here it is the reverse rate constant and this is the concentration of Y which is actually the product in the forward rate reaction and in the reverse rate reaction or reverse reaction this Y become the main reactant.

So here equation 5 and 6 are only applicable far from equilibrium where back or reverse reactions are insignificant. So basically this equation 5 and 6 can be only applicable when these reverse reactions are insignificant where there is a perfect equilibrium the reverse rate is equal to the forward rate. However, when there is not equilibrium then we are assuming that forward rate constant or forward reaction is more predominant.

So if both these reactions are occurring then equation 5 and 6 must be combined so to get the net reaction rate which is basically denoted by dA and dt it is basically summation of the forward reaction rate plus the backward reaction rate or reverse reaction rate. So, you can see the net reaction rate is the difference between the sum of all reverse reaction rate we know that and the sum of the all forward reaction rate. So basically if we arrange this it will be just like dA dt K - 1 Y - K A product B. So this basically satisfied so this is the net reaction rate and this net reaction is difference between the sum of all reverse reaction rate and sum of all forward reaction rates. So this is how we can calculate the net reaction rate for any particular reaction where there is both forward reaction as well as backward reactions.

Now what is the initial rate how we can use the initial rate? One way to ensure that back reactions are not important is to measure the initial rates. So, if we just nullify the back or reverse reaction and we are only focused on the forward reaction then we have to measure the initial rates. The initial rate is the limit of the reaction rate as time reaches the zero. So obviously at time reaches zero there are initial point there is a higher concentration of the reactants.

So there is low concentration of the product so obviously there will be less reverse reaction. So with an initial rate method one plot the concentration of a reactant or product over a short reaction period during which the concentration of the reactant changes so little that the instantaneous rate is hardly affected. So if we just concentrate on the instantaneous rate in the initial rate method then it is so little that the rate is hardly affected.

So thus by measuring the initial rate one could assume only the forward reaction rate so basically while you are talking about the initial rate we are basically nullifying the reverse reaction rate and we are only focusing on the forward reaction rate in the equation 4. So in the equation 4 we have seen there are two equations, one is forward reaction and another is backward reaction or reverse reaction. However, in case of measuring the initial rate we are nullifying the reverse reaction.

Now this would simplify the rate law they are given in equation 5. We have seen in the equation 5 that dA / dt = -K1 into multiplication of concentration of A reactant and concentration of B reactant which is basically showing a second order reaction. Now we know in case of second order reaction the rate is basically proportional to the product of both the reactant concentration.

So this is how we can see it is basically a second order reaction it is following a second order reaction. So, forward rate constant is following a second order reaction in case of two different reactants. Now equation 4 under this condition would represent basically a second order elementary reaction. Now to measure the initial rates one must have available technique that can measure rapid reaction such as relaxation method and accurate analytic system method.

So we will talk about the relaxation method in our coming slides. So these methods are very useful for measuring the concentration changes with very short amount of short period of time. So these methods are required for measuring this initial rate.

So just one example of how we can use the initial rate. So, if a reaction is a first order as you can see in this plot so a plot of logarithm of At

and versus t. So, if we plot the time in the x axis and logarithm of concentration at particular time in y axis then it will result in a straight line we know that it is a negative slope. It is a slope k1 / 2.303. Now why this 2.303 basically come.

So if we convert to natural logarithm to logarithm then we will get this value of 2.303 so basically we are basically that into consideration. Now this example of this first order plot for manganese sorption on this manganese oxide are two initial manganese concentration at one is at 25 micro molar and another is 40 micro molar we are seeing here.

So basically we are seeing the sorption how this manganese concentration changes as time progress on to the manganese dioxide then we get these two types of plots which basically showing the first order sorption process or first order reaction.

Now the Mn2 0 values or the initial Mn values obtain from the intercept of this figure basically are 24 and 41 micrometer which is in very good agreement with the two Mn2 0 value which we have assumed that is one is 25 another is 40 so basically these reaction satisfy our condition. Now the rate constant, constant are 3.73 into 10 to the power - 3 and 3.75 10 to the power - 3 per second at Mn0 of 25 and 40 micromolar concentration.

So, you can see this is the first order reaction so obviously the unit will be per second. Now the rate constant are not significantly change with concentration. You can see here the rate constant are not significantly change with concentration. So this is how we can apply the initial rate to calculate to basically see which order of reaction is basically following for a particular chemical process.

Now integrated equation now integrated equation we have discussed in detail for the first order reaction what should be the initial integrated equation for the second order reaction for the zeroth order reaction. What should be the integrated equation we have discussed and also we have discussed the half life we have calculated the half life for this. So this is also very self explanatory how we can use this integrated equation basically to plot them.

And see how we can use by plotting this integrated equation we can see the straight line for both first order reaction and second order reaction as well as a for a transient time for a zeroth order reaction. So by seeing the shape of this curve we can identify which type of reaction order it is basically following.

The third one is the least square analysis now the least square analysis can also be used to determine the rate constant. Now you know that with this method once we hit the best straight line to a set of points linearly related as y = mx + b. So basically if we just plot two sets of data. For example, let us plot x and y so if you plot two sets of data for different values of x and y and then draw a straight line.

This straight line will be represented by a formula equal to y = mx + b. Now here the slope is m whereas this b is basically the intercept okay. Now how to calculate these lines is basically a least square method. So the least square method says that we will draw this line so that the residual or the summation of the residual or error terms will be least for this line as compared to any other line.

So, although we can draw several lines to connect this point the most optimum line will be drawn by the least square estimate. So, that is why any linear regression will be simple linear regression or multiple linear regression, is known as the least square regression ordinary least square regression. Now one thing is clear that this least square estimate this using this formula you can calculate the slope as well as the intercept b can be calculated using the least square analysis.

For example, in case of m you can calculate by using this formula in case of b you can use this formula to calculate the intercept. So this is basically the calculation based on the least square analysis where n is the number of data points and the summation are all data point in the data set. So basically it is basically drawing a straight line from a sample or a set of points where you have both x and y. You have predicted as well as you have the target variable. So basically it is calculating the slope based on the data as well as calculating the intercept and then drawing the line. So this is how we use the least square estimate.

Now curvature implication: Now curvature implication now this curve which you have seen in case of first order reaction, zero order reaction, second order reaction. You will see sometimes there are some curvatures or abrasions. So this curvature may result when the kinetic data plotted. So this abrasions or curvature maybe due to incorrect assumption of reaction order.

For example, in case of first order kinetics the reaction if we assume the first order kinetic and the reaction is really a second order then you will see a downward curvature. Now secondly if the second order kinetics is assumed, but the reaction is really first order then you will see upward curvature. Now curvature can also be due to the fractional third or higher mixed reaction order and non-attainment of equilibrium often results in downward curvature.

And also remember the temperature changes during the study can also cause curvature. So guys you have understand what is in this lecture you have understand what is zero order reaction, how you can plot the differential form of zero order reaction, what are the condition of zero order reaction and what is the integral form of zero order reaction, how you can plot the zero order reaction and what are the methods.

Three methods initial rate integrated form as well as least square method for identifying the order of the reaction in the soil we have discussed. So in the last lecture, we will be discussing about several important soil chemical processes in which the chemical kinetics are very important.

So, let us meet in the next lecture in the last lecture of week 6 to discuss the practical implication of these order reaction in defining different soil chemical processes. Thank you very much.