Environmental Quality Monitoring Analysis
Physical and Chemical properties of interest
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Lecture - 8
Partition Constants

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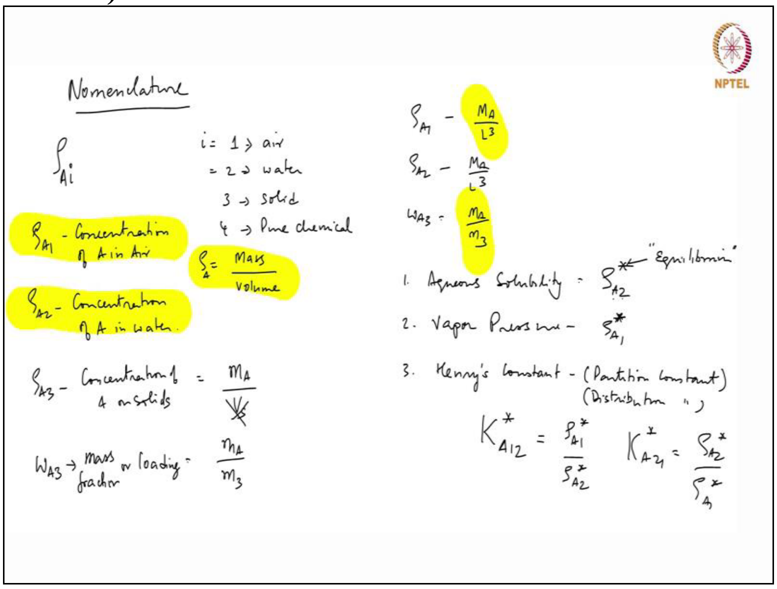

So, we will start today's class with the nomenclature that we are going to follow for this course should have done it in the last class, skipped out. Ah, our main quantity of interest is concentration. And we are looking at mass concentration. So the mass concentration symbol is Rho, so Rho of A and in some medium. So, it is concentration of A in water, air or some such medium. So here, I have indices for I have to put some number here to indicate whether something here to indicate it with air or water.

So, I will, so will have "i" here, "i" equals 1 is 'air', "i" equals 2 is 'water' the symbol 3 corresponds to 'solid', 4 corresponds to 'pure chemical'. This is a general nomenclature. So if I write Rho A1 it is so Rho is itself, Rho is Rho of A is mass by volume, it's a density unit. Mass concentration or density. Rho is the symbol for density whatever in chemical engineering terminologies we use C. C is concentration in terms of moles per metre cube. That's the convention.

When you write Rho it is of mass so, all our calculation will be in terms of mass. Rho is not convenient because our mass per unit whenever we go to the analysis section they are all mass per volume. So no moles per volume, we are not working that range, ok, so this is ah, when we say concentration, it is by default in this class is mass concentration. In air when we say Rho A2, this is concentration of A in water.

So, what about soil? So in soil, you can also write Rho A3, just concentration of A on solid. But the problem is some of these this means we are looking at M of A divided by volume of solid. Lot of times volume of solid is not very easy to obtain. So if we take soil for instance, and it's porous media, it's heterogeneous, different sizes. For me to get actual volume is very painful. Ah, because of the properties of soil also and it's laborious to do it.

So, instead we don't do this, we do a M A over M3. It is the mass of the solid itself, so it is the mass fraction, mass fraction symbol is 'w' or 'Omega' or 'w' whatever you can call it. This is this is Mass fraction, we also call it as 'L oading', 'WA3'. So I also like to use dimensions instead of using units and all that. So will will call in terms of dimensions Rho A1 is MA by L cubed. This L is 1, volume of air. Rho A2 is MA by L cubed again, WA3 is MA by M3, ok.

So in this context, when we will when we use when we apply this nomenclature to whatever we did in the last class we we are to three physical properties. The first one is aqueous solubility.
We call it as Rho A2 but we indicate that it as an equilibrium property by putting a star there, ok. So, whenever this star appears anywhere it is something to do, something in equilibrium with something. It relates to equilibrium; some mention of equilibrium is there.

So, it is equilibrium of A with water, pure A with water. This is equilibrium concentration of A in water. Similarly, Vapour pressure is Rho A1 Star. Equilibrium of A, it's equilibrium concentration of A in air. So, yeah, then we also looked at Henry's constant, so Henry's constant is a ratio, ok. It's a ratio and we usually have this, this partition constant kind of Concept, so this is a partition constant or a distribution constant.

Student: sir, what is the difference between Rho A1 and Rho A2?
Professor: it is this one Rho A1 is concentration of a chemical in air and that concentration of chemical in water 2 is water. So if you look at this. See, you look at this this, Rho A1 is concentration of A in air and Rho A2 concentration of A in water that's that's all. So, when you are representing the concentration of A in air, we write it as Rho A1?
Student: sir, the mathematical formula is same that we are writing sir

Professor: no, Rho A1 is I don't know it's a mathematical formula it's it's just a representation.
Student: sir that you have written in the right side, top of the right side.
Professor: Yeah, right, no that's a dimension. That's that's a unit. See definition of that is mass by volume.

So I am writing this mass by volume as MA by L cube. Volume is L cubed, dimension is L cubed. MA is mass of A and M3 is mass of the solid. It is mass of A over mass of solid. So this is definition and dimension of the atoms that we are using so that's all. There is no other. So this is distribution constant also. So we will give generic term K capital K. There is lot of confusion small K capital Ks you please be careful. So normally when you are writing a problem we you have to define whatever whatever is that you are defining in words so that there is no confusion.

So this is only for convenience there are other symbols people other textbooks use and all that. So this is I have found this to be the most because there is a large number of interfacial things this is the most unambiguous representation but there there are some text books which have evolved some other notation. So they will use that so I am not contesting all that. There is no right or wrong way to do this, this is a matter of convenience and sometimes matter of convention. So I would recommend suggest that you don't get stuck with those definitions or those abbreviations, ok. So here we are representing the equilibrium of A between two phases which means both the phases have to come in this definition here. So we are now talking about Henry's constant we are we are talking about the partitioning of A between 1 and 2. One is air and two is water. If you write it like this and we put a star here, it means that it is in equilibrium quantity.It is the ratio of Rho A1 to that of Rho A2 so both of these are in equilibrium with each other. That's already mentioned here. If you want, you can put a star sign here and a star sign here, both of them are in equilibrium with each other. Whenever you put a star it essentially denotes this is in equilibrium with something. So that's the that's the easy notation for you to remember so that later on when we write look at transport this becomes easier for us to represent. So this is the Partition constant, so I can write different partition constant. This is one this is for air and water this is we are air here and this is water.

So this defined as the ratio I put A A1and 2 which means 1 goes to numerator 2 goes to denominator. If I write this as KA 21 star, I will write it as Rho 1 star, that's all. So this makes it unambiguous, whatever the partition constant however you define it this is this is the way it is, right. Any doubts in this, any questions?

So, sometimes you have this four, pure chemical whenever it comes we will discuss that sometimes it is there. We will look at it. In fact, aqueous solubility is like a partition constant between pure substance and water, a pure substance its pure substance and vapour. So you can write, but ratio of the we can't write in terms of ratio of concentration, concentration doesn't have any meaning there. So it's pure phase but sometimes we write in terms of activity people write that, people write activity in terms of 1 and all that. So we won't get there. So we will stay clear of that.

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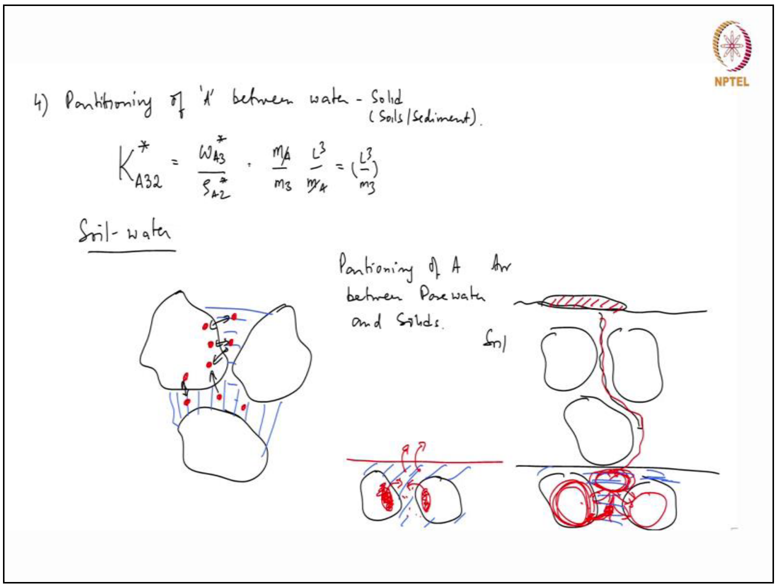

So, we have now had properties of aqueous solubility, Vapour pressure and Henry's concept. The fourth property that we are interested in is the partitioning of a chemical A between water and solid. By solids we mean we mean soils or sediment or any such thing, yeah. So, we can write this in terms of we write we write it as KA. I can write it as 32, arbitrary like I can write it as 32. General convention is people write this KA number as a ratio of things. So, here we are writing as KA32, this will be W A 3 over Rho A2. Because we are writing this in the equilibrium of a chemical between water and solid. So, it's the solid concentration, so don't worry about this star here. I am just putting it now here to indicate that is equilibrium you don't have to put it all the time just have to remember it and if it makes it convenient put it otherwise you know what it is don't need to, ok. So, here look at it the units here are again 'mA' by 'm3' and this is 'mA' by 'L cube'. So the dimension of this is 'L cube' by 'm3'.

Unlike the Henry's constant this not Henry’s constant both the units will cancel so it will be some number, it’s a ratio of concentrations, mass concentration. Here it’s not so ‘L3’ by ‘m3’ so it has units of metre cube per kilogram or some such thing, ok. So now, this is a general definition, this is partitioning of chemical between water and the solids so this is relevant. So when we are looking at soil-water systems, for example you have groundwater and you have you have water here.

I think let me let’s erase the that thing. So I have water in the middle of the solids, yeah. Suppose there is a chemical here. So we have a chemical here we will call it we will say some Chemical A, this will partition to the solid between the solid and this thing there is a ratio in which it will exist between this and the water, pore water. So this is the partitioning of A and the solids. So the system is static or moving slowly are whatever it is. You don’t worry about it right now. It is in equilibrium with it, so it is equilibrating between this point. So there is another there are other solids sitting here on the surface somewhere and the, there is exchange between the pore water, chemical in the pore water and this, why is this relevant? Relevant because if you take the case of, if you take a scenario of say somebody there is say there is soil, air somebody dumps a large quantity of chemical on the soil, ok. So we will put it as this.

Somebody dumps a large quantity of chemical in the soil and the so the chemical tries to go down it goes down, it travels down by percolation, going in and it goes all the way say to the groundwater, ok. The groundwater you have again, this is groundwater, so this chemical is travelling, so this chemical is travelling all the way to the groundwater and depending on its property it will sit there, right. It is sitting here in the ground water, what will happen, immediately this is pure phase chemical sitting on ground water, while it is sitting there you just focus on this first, don’t worry about this part. We will come to that later. What will happen to this? What will happen to the chemical that is sitting in at that first sees the pore water? As soon as it comes in contact with pore water what will start happening to it to the chemical? It will?
Student: dilute
Professor: It will dissolve it will dissolve into the water, when it dissolves into the water it will also comes in contact with the solid.

So when it dissolves into the water, it can also come in contact with solid from the water, it can enter the get accumulated on the solid. And it keeps happening as there there is pure chemical being supplied from wherever from the source and it keeps accumulating on the solid till a point just like solubility, at some point it cannot accumulate anymore, it reaches equilibrium between the concentration that is there in the pore water and the solids, ok. And then at some points that will stop.

This is how contamination of solids occurs over a period of time. And then the reverse can happen. So when there is a lot of there is chemical that is sitting here, and this chemical there is some chemical here, and if this chemical leaves this place, there is a non-equilibrium that is setup and chemical from solids will now get into pore water and then move, move away. So this is a reverse of this thing, ok. All this takes a long time we will come to all that later.

It takes several decades sometimes to happen for this to happen because processes are very slow. For for this reason, the presence the the partitioning of chemical between solid and water pore water become very important, very critical in terms of what happens in terms of fate and transport of the chemical in the system, ok.

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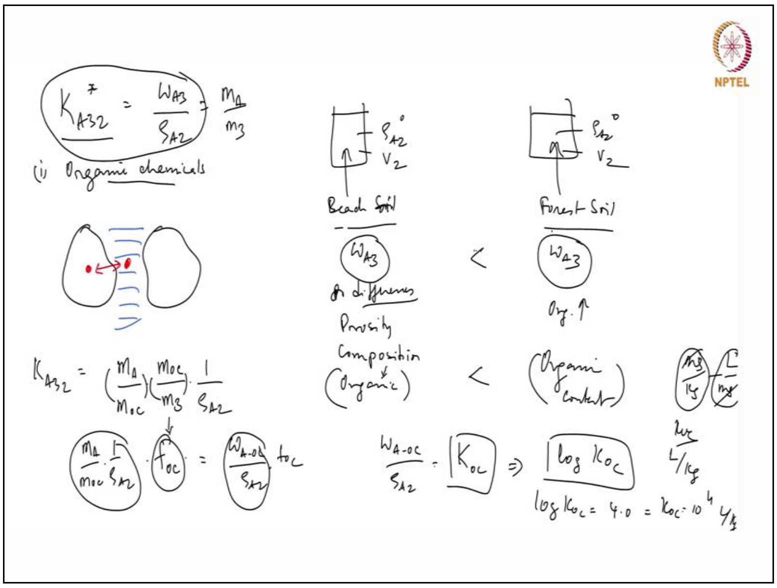

So, if you looking at the KA 32 this is ‘wA3’ by ‘Rho A2’ now, you have 2 conditions, 2 possibilities here one is for Organic Chemicals. This is true for organic or inorganic chemicals. Either of this can partition. Inorganic and organic both can partition for a large amount of our discussion we have organic chemicals so will start with that first. So, organic chemicals, ok. So, organic chemical is there in water and it it it is in contact with the solid, ok, this partitioning of organic chemical between this thing and solid.

So we will now have to invoke what is this solid material, so the one one of the this things is here, if I want to measure, if I want to get the partition constant of any chemical here, suppose say I look at partition constant of a chemical in IIT, versus the partition constant of chemical in say Bangalore or Hyderabad or Delhi? What do you think that number will be? Will the number be different, same? I am talking about partition constant.

Henry's constant is it the same or different in different places. Henry's constant is is it different in Chennai and Delhi and Hyderabad? Our aqueous solubility is
Student: same sir
Professor: is the same. What about KA 32 star? Same, how do you know? On what basis do you say that? This ratio of KA32 star 'wA3 by Rho A2' the ratio, the equilibrium ratio. KA 32 on what basis are you saying that? If this is true, what else has to be true?

Let us say that I take a soil sample from Marina beach, the beach, the beach and one soil sample from inside the campus here and I put it I make a solution of chemical A, ok. And I take one same solution so I'll start with Rho A20 and start with Rho A20 in this case I add beach soil and this case I add a forest soil same concentration, same volume, ok.

When I put the I put a 1 gram of beach soil and one gram of beach forest soil, in both cases and I shake it, at the end of some period of time say 2 days or 3 days, how much of the chemical would you think will be on the soil in the case of the beach and the soil in case of the forest? Which one would be higher? So if I if I want to estimate WA3 here and WA3 here, which one do you think will be greater? Will they be the same?

Do you understand the problem what I have posed? I have added the same amount of chemical in the water aqueous phase in the initial here and I've added the same amount of solid in both cases, but I have added different solids: one is from the beach, one is from the forest soil. You think it will be same or different? Why, why will it be different?
Student: Properties of
Professor: ah?
Student; the properties of
Professor: properties of the soil are different. What properties of soil are different, likely to be different?
Students: porosity

Professor: Porosity, ok, anything else?

Student: composition

Professor: what composition? So what is specifically in composition? What do you think will? So if if A is organic chemical, what do you think will, will be the factor, determining factor? Which one will be higher? This or this? From your general observation of beach soil what is the difference between beach soil and the forest soil? Ah?

Student: water content

Professor: No, no, soil. I'll check I will go to the beach and take soil and go out check. Water content may or may not be different. Is there anything else, any other major compositional difference? Hmm?

Student: Pores.

Professor: pores. Somebody said something, I couldn't hear, any other difference, big difference?

Student: Loose soil

Professor: ah?

Student: beach soil will be loose

Professor: loose, ok. Now I can make this also loose, I can make this also loose like a property this thing. Ah?

Student: in forest there will be organic content.

Professor: there will be organic, more organic content. So if you have organic content, that's a composition one of the main this thing is organic content for Organic chemicals.

You have to recall some discussion that we had earlier about organic matter. Now, which one of this will be greater? So, the organic content of forest soil is higher, so the organic content of beach is less than organic content of the forest soil. 'wA3', what do you think how do you think it will behave?

Student: It will be more in beach soil.

Professor: It will be more in the?

Students: beach

Professor: It will be more in beach, why? If organic content is less why will it be more in the beach? So, if organic content is high what does it imply?

Organic content is part of the soil of the solid phase, what does it imply? If organic content is high what can it do? Where else do you use organic solids? Any application that you are aware of?

Student: Agriculture

Professor: in the?

Professor: Agriculture, something more, more common more. What do you use in Agriculture for?

Student: manure

Professor: That's a different application. With reference to water, do we use organic solids for anything? May be in water treatment, ah

Student: activated carbon

Professor: activated carbon, what do you use it for?

Student: treatment of water

Professor: treatment of, water, what? treatment means what exactly?

Students: adsorption

Professor: Adsorption means what is the more general description of adsorption? If I don't know the word adsorption, how can I describe it? What is adsorption? Removal of yeah, removal of, no no activated carbon is used there for specific reason. Why do have carbon? So if we look at the organic property or organic carbon, large background, backbone of carbon so it likes carbon.

So if organic carbon content is high, organic carbon likes other organic chemicals. This is, this is true. More or less if you have a large organic content it is likely to attract organic compounds, ok. So you are likely to find that the if the organic content is high here, you are also going to find this in the same direction. Large amount of organic Chemicals are also likely to go to the forest soil than this. So, this is, this leads to more accumulation this has then we have a problem.

If you want to describe KA32 for a particular chemical I have to then go and get the organic content of all the this things and I have to refer to I have to do an experiment to actually get what is the, so I can't have a uniform property, I cannot say KA32 of a chemical between two particular soil KA32 of a chemical itself I can't classify because I need to know about the organic carbon content and I need that also information I need.