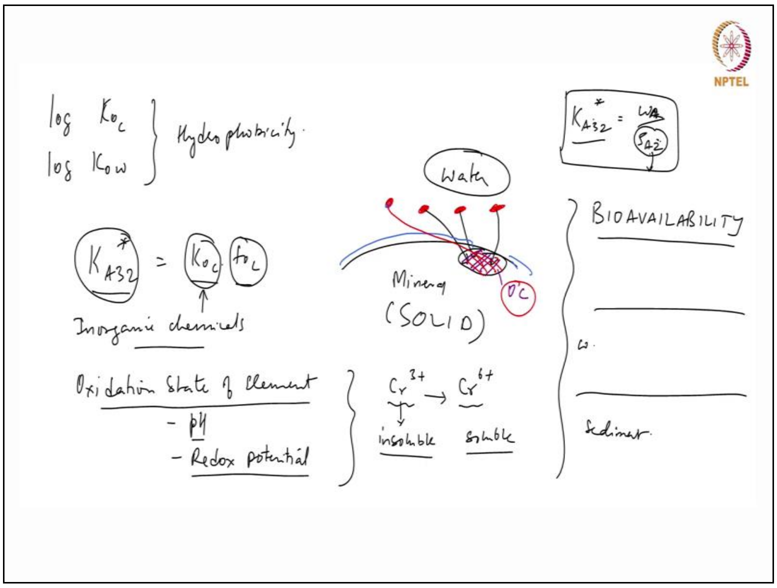
Environmental Quality: Monitoring and Analysis
Prof. Ravi Krishna
Department of Chemical Engineering
Indian Institute of Technology Madras

Lecture - 9
Soil-Air partition constants

(Refer Slide Time: 00:32)



Issue of log K oc we determine that log K oc and log K ow these are two properties of a chemical which characterise the fibre hydrophobicity? So, in the context of environmental feet and transport these numbers are important from in soil and sediments and we will do the example, immediately following days. The assumption is like this so if you are writing K A32 star, we write K A32 star as K oc times F oc rather than writing it simply like this. So what we are doing is this is a property of chemical itself and this F oc is what we represent site wherever you are taking it from.

It is very large organic carbon that taking care of this business the overall partisan constant depends on both the organic carbon content and the nature of chemical. So, this is number which you actually used in transport scenario but this is the property of the chemical is easy for us to quickly get an assessment when you will look at the number itself, you know that this is likely to be in this phase or in this phase judgements based on that.

So for the case of inorganic so we said for inorganic chemicals this does not apply because when we say for Organic Chemicals the assumption is that all organic compounds will only adhere and here only bind to organic matter present in these things. So, the mineral component in the soil or sediments does not attract. It is not does not attract has lesser affinity for organic compounds especially when you have water in the system.

So when there is water, water prefers absorb, the surface prefers water than inorganic compound. You have a mineral surface and of this is the one component of organic compounds this is organic carbon and rest of it all mineral. So, if there are organic compound here in the water, this is water this will only bind; this can only bind to here the reason is does not want to bind on this mineral surface. It cannot bind because this is already occupied by water.

The water forms thin-layer or just continue there is fully saturated already there lot of water is there. So, there is no there is no opportunity or location site on which the mineral can accommodate and organic molecule so does not allow any water. So the only place the minerals are the organic carbon can go through is the organic carbon. This organic compound phase that is why this equation become important that assumes that there is no absorptions there is no binding on the minerals for the organic compound in the presence of water in the system.

For inorganic chemical this does not apply, the organic chemical nature of binding is very different and it is more to do with the surface charge that is present in the in the system and also its oxidation state of surface charge depends on oxidation state and in what the valence is. So, the property that oxidation state of the inorganic element some ways determines where and what form it is, whether it is bind; how much it binds to the solid phase are does not bind to the solid surface.

And there are no general rules like K oc and F oc kind of system. The rules are based on oxygen; what determines oxygen state of element several things once ph1 dissolved oxygen content of this what is called as a redox potential. So, depending on the amount of; depending on whether the ah ah amount of oxygen is present in systems is oxidation state changes, the redox potential changes. So, redox potential for different elements valence states are different and then and it is a function of whatever is there in the system however it is in the system.

So, for soil it is different from soils, sediments because oxygen content is very different and pH is also different. And it is also a function of any biogeochemical activity that is going on in system so it is little more complicated but one example that is very prominent in the case of this why it is important? The oxidation state and therefore the partitioning and depending on that the partitioning will change if any of these conditions change.

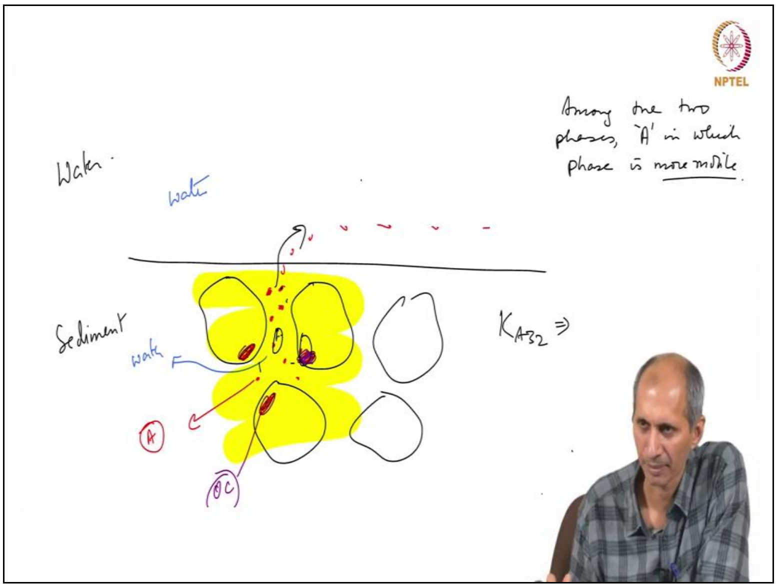
So one examples is for actually one of the permanent example give is Cr 3+ and Cr 6+ so Cr 3+ is chromium valency of 3+ valency of 6+ this is usually present in an insoluble form and this is present in a soluble form is means in the water in presence of water Cr 6+ is likely to be more in the water than CR 3+. Cr 3 + it is there it will be either in insoluble form this not absorption. This is the way it is, so Cr 3+ becomes precipitate Cr 3+ precipitate it is forms of precipitate either as chromium trioxide or it forms oxide or another combination is something else that is present in the soil and sediments.

It is present in soluble form. And when there is a conversion due to some activity where is conversion from Cr 3+ or Cr 6+ comes into soluble form. Even in the case of organic compounds when we look at the K A32, when we look at KA 32 star the implication of KA 32 star is that it determines how much of chemical is present in the in the water? Why is that important? Why are you very worried about being present in the water?

It is the property, like solubility, if the solubility it is very high is very high in the case of water it takes solubility is high or the KA 32 is some value it implies that there is a value, there is a concentration that exist in water. Why it is important? Why do we need to know how much this is the value of this is determined by how much, is this value? Why is this important? This is what is C; let us look at 2 of this numbers.

So I think we will get back to this few minutes I think I will make it more context that thing. Along with this concept of hydrophobicity the significance of numbers KA 32 is in another term that we commonly used in again in Pharmacology and Toxicology and in Environmental Sciences is called bioavailability. Bioavailability means it is it can be seen in different contexts from contexts of human health and patent transport exposure what it means that, say there is a sediment and water and top of it.

(Refer Slide Time: 09:18)


Among the two phases, 'A' in which phase is more mobile.

And we have draw it like this so there is sediments and there is water on top of it and there is lot of solids among the solids you have some organic phase you also lot of the; what is the implication of this diagram. I have drawn this, this is chemical A, and this is the organic carbon and these are all water. What is the implication of this from exposure point of view? Value of KA 32 the value of K 32 how does it influence this ,what is happening in the system? If there is when we say KA 32 in the system, what does this determine, say if you are taking this particular system. If I take this system, what is the value of KA 32 determine in the system.

KA 32 is the equilibrium of a between the solid and the water so it means it will determine, what is the distribution of the chemical between these two phases. So, we can find out what is the concentration of A in the pool water, So how does that matter, why is it important? It is important point of view that which of these phases is more likely to move from one place to another place? Which is more mobile?

We asked this question is more mobile among the 2 phases solid phase A that is sitting on the solid phase or phase A is sitting here which is more mobile in the water for that reason this can move much more easily from one phase from one place to another place because there is a continuum here. There is water here and there is water here it can move out this chemical can go out and travel somewhere else and reach a receptor.

There is the possibility of reaching receptor much more. So, that is the reason the bioavailability can be interpreted in this form in which it is now accessible to some receptor some fish some animals or more human beings downstream somewhere away from the system.

We can move from here to there and therefore it becomes mobile that is bioavailability available biological activity. On the other hand we also use the term bioavailability in the context of treatment.

When we do water treatment solid treatment we are looking at bioavailability is looking specifically at the amount of chemical that is available for microbes to degrade. Degradation of microbial degradation occurs mainly in the aqueous phase in the presence of water they will perform very well for dry conditions and all that. So, the transfer of chemicals from solid phase to microbes occurs through water. The water is the medium by which that occurs therefore that is also a contact in which we can look at bioavailability.

So, the term bioavailability is important showing in the case of chromium, things like chromium it becomes more bioavailable if it is in the soluble form than it is insoluble form. So any condition that will convert Cr 3+ to Cr 6+ will make it more mobile, which is the reason Cr 6+ is considered to be more toxic Cr is Cr because Cr 6+ more mobile. This what you are you will measure away from your particular side for measuring chromium in water it usually it is Cr 6+.

If you have solid phase you measure Cr 6+ and 6+ because there is 6 and 3, 6 will be here and 3 will be here. If I take entire thing and measure you will get total chromium it will be in combination of 6 and 3 I only do it here. If it is pure aqueous phase is only this Cr 6+. So, this becomes an important constituent in terms of partition. Partitioning constant is important from view of bioavailability and then for inorganic compound is bioavailability is influenced by other factors such as pH and oxidation reduction potential and its oxidation State all like that any other conditions that will influence it.

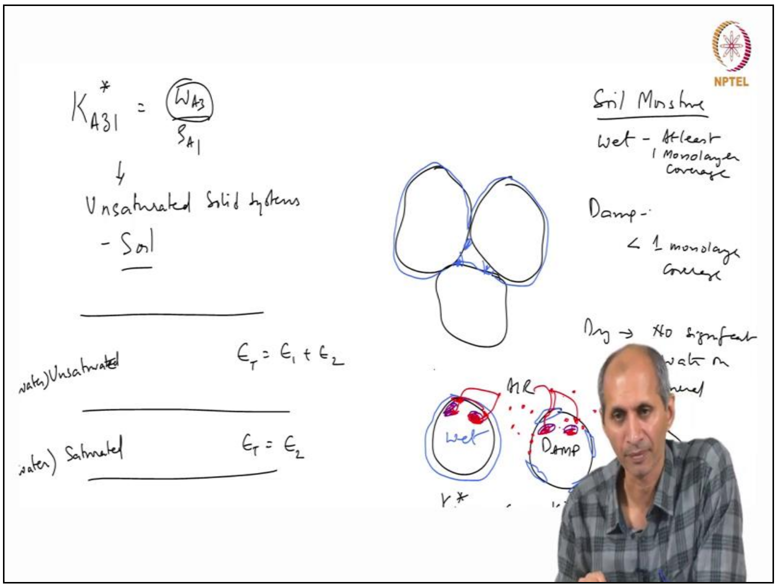
So lot of time for happened is there is say chromium is sitting as an insoluble form in sediment it is deep under the water. You go and dig it up and you turn it and stir it up. You are introducing oxygen in the system and there will be transformation of all the things which are in a lower oxidation State now get to higher oxidation state and they can become more mobile generally. So, this is generally this is; so for inorganic elements you have to measure the partition constant separately each one if you are going to look at;

It is more complicated it is not as straight forward as K oc and F oc. It is possible to get a relationship between partitions concept verses other factors but people usually do not do that they will go to each site and measure the hard way. There is no unifying single normalising parameter for the case of inorganic elements but there are also lot of inorganic elements of interest. We are looking at few heavy metals Chromium, arsenic, Mercury and few of them they are not the whole lot.

So, that see practical aspect is there and there is a very wast subject in aquatic chemistry, biogeochemistry aquatic systems where people look at all is thinking different systems in lake systems, in river systems in groundwater, and in sediments and in oceans so all of this elements that are present in each one of the systems have a different biogeochemistry because there is a different set of biological presence there.

And their all participating in it, so very complex system and so we will look at one chemistry, we look at mercury we will look at mercury in a particular system and then studying everything related to that the inorganic chemistry of mercury in that system.

(Refer Slide Time: 16:56)



$K^*_{A31} = \frac{\boxed{W_{A3}}}{\rho_{A1}}$

↓ Unsaturated Solid Systems - Soil

water) Unsaturated $\epsilon_T = \epsilon_1 + \epsilon_2$

water) Saturated $\epsilon_T = \epsilon_2$

Soil Moisture

Wet - Atleast 1 Monolayer Coverage

Damp - < 1 monolayer Coverage

Dry → No significant water on mineral

So, now we look at the another number which we call as KA 31 star so from the definition of what we are talking about. This is WA31 divided by rho A1. So, what is this correspond to so this is the solid we are talking about solid and air which system does this corresponds to? Which environmental system thus this corresponds to KA 32 corresponds to groundwater saturated groundwater and settlement systems where everything is water you are interested in water.

K 31 which system environmental system is it the soil, unsaturated surface, so soil is mainly relates to what we can broadly classified as unsaturated solid systems, which is things like soil, soil what is biggest example in this? So we mention when will discuss the properties of soil itself where soil when it is groundwater is saturated with water the post phase saturated water. Above that in the unsaturated zone, what we mean by saturated we are saying it is water saturated?

That is what means and we are saying it is water unsaturated it means if I take to porosity of unsaturated soil porosity of saturated = porosity of water the water filled porosity is the same as a total porosity and all the pores are filled with water that what it means. But here it is not true here we can have in the unsaturated zone where there is some air that is present in the pores phase base in addition to water. So, you can have visibly you can look at this sink you can have water and we discuss this water in the gaps like this or it can be a film that is sitting on the surface.

For example if you rain yesterday today evening for example if you go and look at the soil just dig up some soil you would not see any water sitting there water but soil is wet, where is the water? It will be there something like it be like this, either the water will be like this or in place, it will be hang around here because of some surface tension or something or maybe sticking to surface of the thin film. So, these are in which soil the soil in terms of moisture content the soil can be classified as wet, damp and dry.

When you say wet which is not saturated this is still unsaturated. Saturated means everything is full of water but when you say wet here it has full; at least one monolayer coverage which means that the entire surface is covered with water the mineral surface. Damp I mean, let me write it down here again. When you say damp it is less than 1 monolayer coverage when we say dry no water no significant water on mineral surface.

So, the damp is anywhere between these two less than one monolayer and more than damp. When it is wet when we talking about wet, we are talking about complete, when we are talking about full monolayer coverage which means water is there at least one film thin film completely covering this is wet. When you say damp you are saying that there are packets of water some regions where is water. And when you say dry there is no water there is no water at all.

So, what is the implication in case of partioning? When you are exposed to a chemical that is in air so there is air here, there is air in contact with the solid particle and there is a chemical that is sitting here. In the case of in the case of wet where can this chemical go and bind to; when the soil is wet it will bind only to organic compound because there is no water. The water will not allow it to go to; it will go to water, you are right. It will go to water and from the water it can only go through the organic carbon.

It cannot access the mineral sites again it is again the same thing It will access to water and then from water it will go to the; this thing. In the case of damp it can access the organic carbon and the water, It can access the organic carbon directly because organic carbon maybe real no water covering it or it can also access the available minerals surface. There are some mineral surface that is open now it does not have water on it, not competing with water.

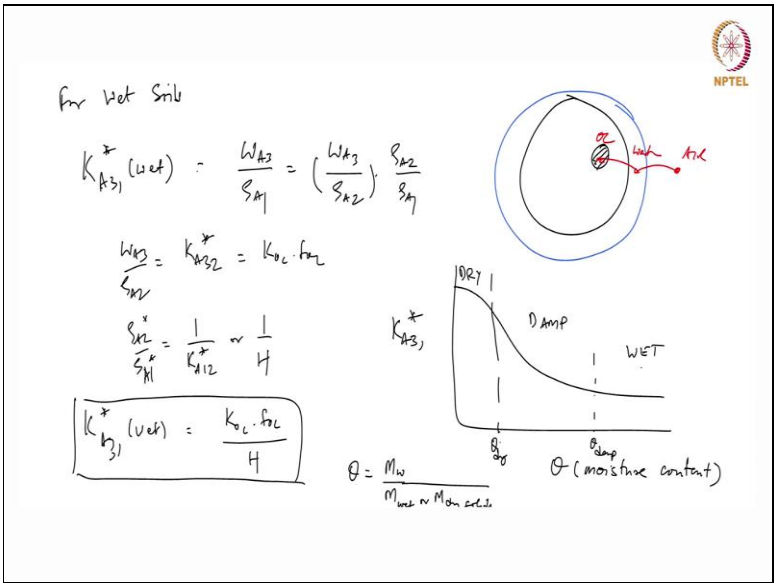
The absorption maybe very small mineral does not like organic body but it will still accepted because no competition they just take it. In the case of dry it has all this it is it can accumulate all organics plus a lot of the surface mineral that is available. As a result of which KA 31 star of this one and the KA 31 star this and the KA 31 star this one which one what is the order of magnitude. See if you remember that this is the definition of KA 31 in which case what is the order in which will go.

KA 31 + 1 for the dry will be greater than for the damp should be greater than wet. There is a complication in terms of soil because soil moisture content varies. It varies diagonally or it varies seasonally all these things happen it varies with depth. The very close to the water table soil maybe very wet because it has water vapour is there it absorb on the surface and also very close to the surface sometimes even if air is humid it will also be higher.

In the middle it can be lower water content depending on the temperature gradient in the system or whatever is humidity so in the very dry places you can see a very simple linear relationship. Very close to surface is very dry as you go to a water table in becomes moisture but in Chennai very humid outside so surface maybe still moist, but it deeper maybe slightly lower. So, any case you have to know the moisture content in order to predict what is going to be KA 31+ but even if it is unsaturated if it is wet?

It is enough, if it is wet then it will behave the partitioning is similar to that of what we look that in the;

(Refer Slide Time: 25:44)



For Wet Soils

$$K^*_{A31}(\text{wet}) = \frac{\rho_{A3}}{\rho_{A1}} = \left(\frac{\rho_{A3}}{\rho_{A2}}\right) \cdot \frac{\rho_{A2}}{\rho_{A1}}$$

$$\frac{\rho_{A3}}{\rho_{A2}} = K^*_{A32} = K_{oc} \cdot f_{oc}$$

$$\frac{\rho^*_{A2}}{\rho^*_{A1}} = \frac{1}{K^*_{A12}} \sim \frac{1}{H}$$

$$\boxed{K^*_{A31}(\text{wet}) = \frac{K_{oc} \cdot f_{oc}}{H}}$$

$$\theta = \frac{M_w}{M_{\text{wet}} \sim M_{\text{dry solids}}}$$

But if it is air to how do we write this for wet systems wet soils. Of course we are writing this S WA3 divided by Rho A1 now, but the contact to the; there is no absorption on the minerals is only on the organic carbon but it has to go through water again as mentioned. So, I can write it WA3 divided by Rho A2 and then I can Rho A2 by Rho A1 what we are saying this is going organic carbon is here and where is a layer of water here and there is air here.

This chemical sitting in the air enter water and from here it goes to organic carbon through this thing. There are two there are two kinds of partitioning will happen when we talk about equilibrium the air and water and water and organic carbon. So this number this W A3 by Rho A2 is the KA 32 you already seen that in the previous cases same as KA 32+ and this is given by K oc and F oc.

What is Rho A2 by Rho A1 it is the equilibrium Rho A2 star by Rho A1 star what is this? This water partition constant reverse inverse of the KA12 star this is nomenclature using kA 12 star when I discuss this in Henry's constant we have looked at it this way. Monolayer constant so this number KA 31 star for wet and can be written as K oc and Foc divided by H. This is a easier for us to estimate if you know that the soil is wet. Now the wet area is the very relative term the wetness of soil in our terms when we say that it is one full monolayer.

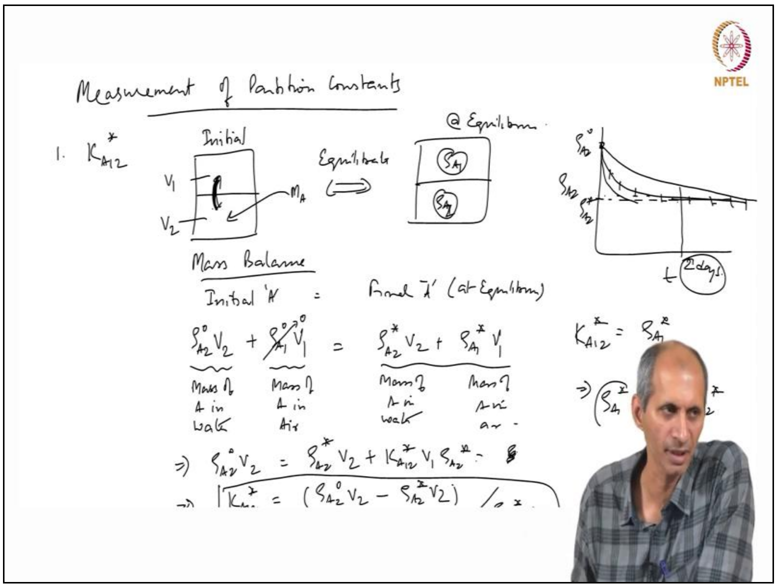
There is no open mineral surface at all, so we are looking at the moisture content that is theta versus KA 31 star when the moisture is very low we are looking at some kind of behaviour like this. So this we are calling as wet this will call this damp. This we will call as dry this theta dry theta damp this numbers will vary depending on the type of solids and all that how much. This is usually measured is usually measured in terms of mass ratio this common nomenclature is the mass of water divided by the mass of wet or dry solids.

Two ways of doing depending on what is convenient at that point in time, typically we will look at wet, mass of wet solids, so, the amount of moisture that is there need not be as long as you know, it can measure that the; this can be calculated from the surface area and all that there are ways to do that. We would not do it here, lot of people just measured it they will measure. Some point that the amount of solid that is moisture that is available goes beyond certain point.

So one way of way of measuring this in the field is to see that if you if you want a complete monolayer, which means that water is completely their present in the system. If you bring it in contact with humid air saturated humid layer there would not be any further accumulation of water will not be any drying the water there would not be mass transfer, we will come that later, only we have to find out saturated if something is saturated already in equilibrium nothing will go there is no change in concentration.

So that is one way of finding out what is the amount of moisture content that is corresponding to wet. So, this is there are ways to do it will come to when we look at measurements, when we come to talk about measurement of partition also; when we look at monitoring analysis method for this when we look at that. Any questions in this any issue here. So for damp and wet there is no; one has to measure it uses of to measure and I will discuss the way in which we measure it. May be I will discuss it now, easier to do it now straight away.

(Refer Slide Time: 31:50)



Measurement of Partition Constants

1. K^*_{A12}

Mass Balance

Initial 'A' = Final 'A' (at Equilibrium)

$$\underbrace{\rho^0_{A2}V_2}_{\text{Mass of A in water}} + \underbrace{\cancel{\rho^0_{A1}}V_1}_{\text{Mass of A in Air}} = \underbrace{\rho^*_{A2}V_2}_{\text{Mass of A in water}} + \underbrace{\rho^*_{A1}V_1}_{\text{Mass of A in air}}$$

$K^*_{A12} = \rho^*_{A1}$

$\Rightarrow \rho^*_{A1}$

$$\Rightarrow \rho^0_{A2}V_2 = \rho^*_{A2}V_2 + K^*_{A12}V_1\rho^*_{A2}$$

$$\Rightarrow K^*_{A12} = (\rho^0_{A2}V_2 - \rho^*_{A2}V_2) / \rho^*$$

It is easier to discuss it now, measurement of partition constants. So,, let us say; let us start with the first one just KA 12 stars is Henry's constant. The definition of equilibrium is the following it is say r if I take a container I have some volume of V1 some volume of V2, V1 is volume of air volume of water. If I if I had a certain amount of mass of A into one of the phases and allowed to equilibrate there will be a concentration of A in n1 and concentration A in n2 at equilibrium.

Theoretically this is the concept of measuring partitioning equilibrium. So, I take two phases I take air and water some volume and externally dump introduce the chemical in one of the phases this chemical then equilibrate what we mean by equilibration? It go from transfer from one place to other phase until it reaches equilibrium at this point. There will be a concentration present here and here.

So I can write in order to express this, what I can write its mass balance equation which will be initial K final A this is a conservation but initially distribution as follows. So, suppose I introduce the way practically this this things are done is I cannot add A into one of the phase, I usually increase A in one of the phase I cannot add it separately. I can add it separately in some cases that we will discuss.

Let us say that that in this case I am introducing a concentration of A in the water phase in air but in the experiment I am introducing all of it in n water so this is 0, after equilibrium it is distributing and can I expect that one of the concentrations will be decrease in the concentration the water will be the increase in the concentration in air phase. And how do I know that this is in equilibrium.

The only way I can find out is that concentration will not change equilibrium. So, if you are doing if you are introducing the chemical in the water phase, we will see that as function as a function of time, this is Rho into 0, it will decrease and it will come to some value not change. Ok so this is Rho A2 star at equilibrium. The only way for us find out when this happens is by measuring the concentration of the of the liquid phase every time I measure here then measure here, I measure here.

And at some point is no change 2 or 3 successive this thing by experience you will know when you are do not change and we will talk about it only talk about the quality control of these things. There is a will be sure, for sometimes you are very close equilibrium assume that in equilibrium all the things error exist so you are absolutely sure that this is equilibrium is reached and nothing is changing.

It does not matter, you can keep it like this for 10 more days may be say that let us say the equilibrium achieved in 2 days. Even if I leave for 10 day nothing will happen it should stay at equilibrium unless somebody comes and the system. In the mass balance what we are assuming is that nothing else is happening to the mass. The only thing that is happening is here is it is transferring from one phase to phase. We are not assuming reaction we are not assuming any other laws are there is no leak nothing.

Ok if there is already add that into the mass balance equation so when we do the experiment to be very careful and nothing else is happening. You have to design the experiment nothing else is happening. Even it happens it should be so small that you are main measurement is valid still valid. Again here this is mass of A in water at equilibrium and mass of A in air. Now we invoke this thing KA 12 star equals Rho A1 star by Rho A2 star it means now I am measuring water concentration and I am not measuring air concentration.

If I am doing that then I will express air in terms of water, so I will write Rho A1 star equals KA 12 star into Rho A2 star therefore I am putting back in to the mass balance equation it becomes Rho A 2 star V2 =Rho A2 2 star V2 + KA 12 star V 1 Rho A2 star and based on the this I can write, I can estimate KA 2 star = Rho A20 V2 – Rho A2 star V2 divided by Rho A2 star V1 this is the equation by which; so here in this equation I am measuring the partition constant by measuring;

I know the initial concentration of water and the final concentration of water and I know volumes of air and water are giving this is not changing I can calculate this is easily. This is usually the way we do any partition constant take two phases, you know, everything else you write the mass balance equation and then you can calculate we can measure what is the; so when you are doing experiment, you need to be careful that when I see that I am measuring when I measure measuring Rho A2 star at some time.

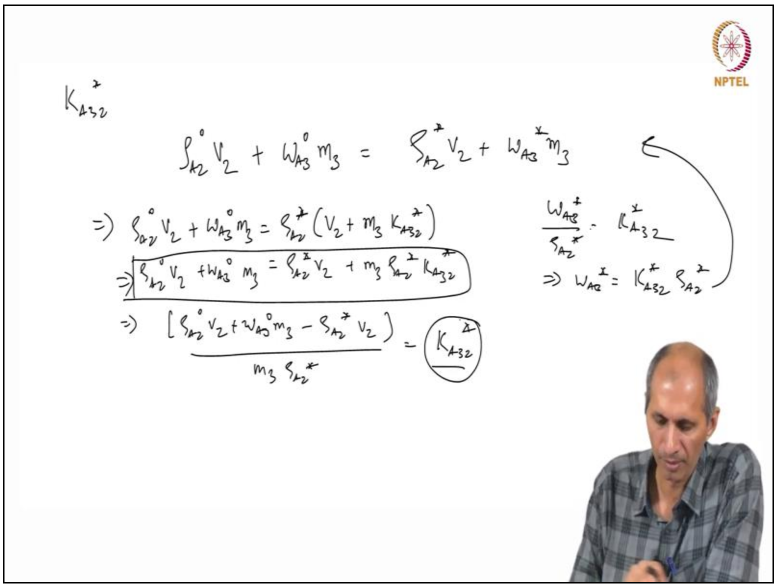
After the first few trial and error experiments whenever you do that, you know that it takes two days, before today is not can happen you do not need 4 or 5 days. So, you will keep the experiment for 3 days and then go and measure 3 days straight forward complete. So when you are developing a method for measurement of partition constant you have to follow that particular system people do this trail and error measurement for that other people were following them do not have to do multiple measurement to see the equilibrium achived.

You say equilibrium will be achieved in 3 days. They will say 3 days is the maximum time it will take for equilibrium. So, keep the system equilibrating for 3 days and then there is a standard method for that. One thing you are learn in terms of mass transfer list is the rate at which equilibrium is achieved will depends on; this is taking long and taking very short and this depends on the way in which equilibration is done.

System has to be mixed this is way to mass transfer we will discuss later. Intuitively you take salt and put into water and if you do not stir it the rate at which will dissolve will be will change and so that is a part of the standard method. When you go and read a method they will say take this much of solid and this much of water in the concentration in the chemical in the water mix it and then stir it or do something agitate it at 100 RPM or 50 RPM one such because that equilibration time.

If you check it 50 RPM for 3 days which means they have done the experiment 3 days the equilibrium is reached under any condition. So, the rate of mass transfer is fast enough so that it is completely cover all cases. So, when you make a standard method people make people study all this and then these parameters become very important. If you have the tools to do with the best ways to measure concentration at different times, you ensure that equilibrium has reached that give you partition constant measurement at that point.

(Refer Slide Time: 41:10)



K_{A32}^{*}

$$\rho_{A2}^{0} V_2 + W_{A3}^{0} m_3 = \rho_{A2}^{*} V_2 + W_{A3}^{*} m_3$$

$$\Rightarrow \rho_{A2}^{0} V_2 + W_{A3}^{0} m_3 = \rho_{A2}^{*} (V_2 + m_3 K_{A32}^{*})$$

$$\Rightarrow \boxed{\rho_{A2}^{0} V_2 + W_{A3}^{0} m_3 = \rho_{A2}^{*} V_2 + m_3 \rho_{A2}^{*} K_{A32}^{*}}$$

$$\Rightarrow \frac{[\rho_{A2}^{0} V_2 + W_{A3}^{0} m_3 - \rho_{A2}^{*} V_2)}{m_3 \rho_{A2}^{*}} = \boxed{K_{A32}^{*}}$$

$$\frac{W_{A3}^{*}}{\rho_{A2}^{*}} = K_{A32}^{*}$$

$$\Rightarrow W_{A3}^{*} = K_{A32}^{*} \rho_{A2}^{*}$$

So you can if you want to same way you can do KA 32 star as well. So here the mass balance will change likely where we are now saying Rho A20 V2 plus instead of Rho A1 we are using WA 30 M3 = Rho A2 star V2 + WA 3 star M3 now you know the WA 3 star by Rho A2 star = KA 32 therefore WA 3 star = KA A2 star into Rho A2 star substitute this back into this equation we get, now we need this is expanded back.

So in most cases if it is a solid is not one this is solid is not contain any thing. So, you can cancel or you can leave both term and leaves terms as it is it becomes the Rho A20 V2 + WA 30 M3- Rho A2 star V2 divided by M3 = Rho A2 star KA 32 star. So, this much balance equation is key from here. You can calculate several things. In this case if I know the partition constant I can use mass balance equation to calculate what will be the equilibrium concentration of A in the water if I start with a particular value of WA 30 this is also important.

Whichever way you want to do it, you can the mass balance. Equation for the equilibrium is tricky thing so you can rearrange equation to get whichever quantities of interest you. When you are doing the calculation measurement of KA 32 in this way, but once you know KA 32 it is used as a property use KA 32 in the estimation of concentration of water. What will happen if this much of contamination is there in the water or this much of contamination there in the sediment, how much will be the concentration in the water so on? So the mass balance is key we able to write mass balance for different kinds of systems.