K 31 which system environmental system is it, it is the soil, unsaturated surfaces, so we have soil, this mainly relates to what we can broadly classified as unsaturated solid systems, which is things like soil, soil is biggest example in this. So we mentioned when we discussed the properties of soil itself that soil when it is groundwater is saturated with water the pore space is saturated water. Above that in the unsaturated zone, what we mean by saturated we are we are we are saying it is water saturated. That's what it means.

And we are saying it is water unsaturated, which means that if I take the porosity of the unsaturated soil, this porosity of saturated equals porosity of of the water, the water filled porosity is the same as a total porosity so then all the pores are filled with water that's what it means. But here it's not true here you can have, in the unsaturated zone there is also some air that is present in the pores space in addition to water, yeah. So, you can have visibly you can look at this thing you can have you can have water and we discuss this long way, you can have water in the gaps like this or it can be a film that is sitting on the surface.

For example, if you go it rained yesterday, so, 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, but soil is wet, where is the water? It will be there something like this, the water either be like this either be if if it is in place, it will be hanging around here because of some surface tension or something or it will be sticking to surface as a thin film, ok. So, these are in which the soil the soil in terms of moisture content the soil can be classified as wet, damp and dry.

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

So, the 'damp' is anywhere between these two, less than one monolayer and more than damp, ok. So which means that in 'wet', when we are 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' we are saying that there are pockets of water some regions there is water. And when you say ‘dry’ there is no water, there is no water at all, ok.

So, what is the implication in this in terms of partitioning? When partitioning when you expose this to a chemical that is in air so this is air here, there is air in combi 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 can only bind to the organic carbon again 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 through water and from the water it can only go through the organic carbon.

It cannot access the mineral sites again, ok, this is again the same thing. So, it will it will access to the 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 in a region where there is no water covering it, yeah, or it can also access the available minerals surface. There is some mineral surface that is open now which does not have water on it, so this not competing with water.

Its absorption maybe very small because it does n’ mineral surface still does not like organic body but it will still accept it because there is no competition let’s take it. In the case of ‘dry’ it has all this it has it can it can accumulate on the organics plus a lot of the surface mineral that is available. As a result of which, the KA the KA31 star of this one and the KA 31 star in 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 this will go.

KA 31 plus for the for the ‘dry’ will be greater than the damp it should be greater than the wet. There is a complication in terms of soil because soil moisture content varies. It varies diurnally or sometimes it varies seasonally all these things happen it varies with depth. Because very close to the water table soil maybe very wet because it is water vapour is there and it can adsorb on the surface and also very close to the surface sometimes ‘cause the if the 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 towards the water table it becomes moist but in places like Chennai it's very humid outside so surface maybe still moist, but deep inside it may be slightly lower. So, in any case you have to know the moisture content in order to predict what is going to be the KA 3 plus but the point here is 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 looked at in the;

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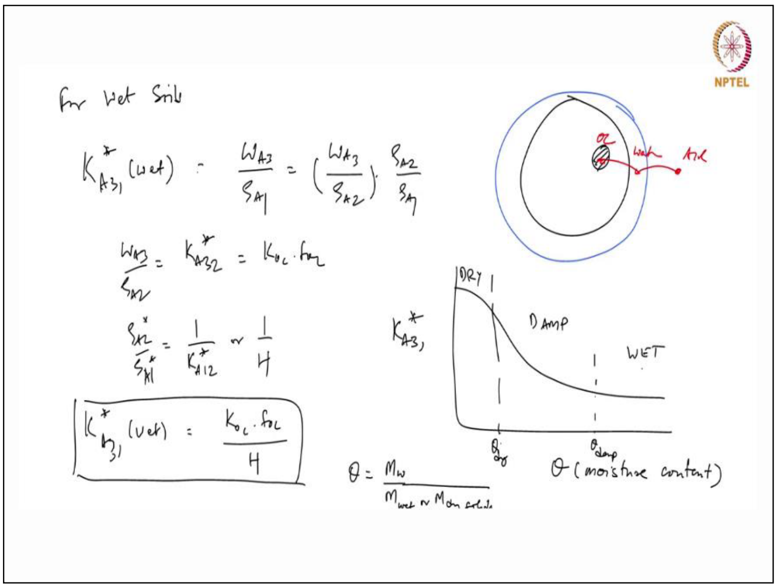

For Wet Soils

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

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

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

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

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

but it is air, so how do we write this for for wet systems for wet soils equals we are writing this as wA3 divided by Rho A1, yeah, now, but the contact to the; here there is no adsorption on the minerals it's only on the organic carbon but it has to go through water again as you mentioned. So, I can write it as this is wA3, so wA3 divided by Rho A2 and then I can Rho A2 to Rho A1, so what we are saying is, it is going, organic carbon is here and there is a layer of water here and there is air here, yeah. So this chemical this chemical that is sitting in the air has to enter water and then from here it goes to organic carbon through this thing. So there are two there are two kinds of partitioning that happens equilibrium when we are talking about equilibrium, the air and water, and water and organic carbon. So this number, so this W A3 by Rho A2 is the KA 32, we have already seen that in the previous cases this is same as KA 32 plus and this is given by K oc and f oc, yeah.

What is Rho A2 by Rho A1, which is at equilibrium Rho A2 star by Rho A1 star, what is this? This is air-water partition constant, it's the reverse, inverse of the this is KA12 star. You just mind the nomenclature we have been using kA 12 star when I discuss this in Henry's constant, this is the Henry's constant, we have looked at it this way. One over Henry's constant so this number KA 31 star for wet can be written as K oc and foc divided by H. This is easier for us to estimate if you know that the soil is is wet. Now the wet is a very relative term the wetness of soil in our terms when we say wet it is one full monolayer. So there is no open mineral surface at all, so we are looking at the the moisture content which is ‘theta’ versus KA 31 star, we expect that when the moisture is very low we we we are looking at some kind of behaviour like this. So, this we are calling as ‘wet’ I will call this as ‘damp’. This we’ll call it as dry this this the theta-dry, theta-damp this numbers will vary depending on the type of solids and all that how much. So this is usually measured, so ‘theta’ 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.

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

See this also one way of way of measuring this in the field is to is to see that if you if you want a complete monolayer, which means that there is water is completely there present in the system. If you bring it in contact with humid air saturated humid air there won’t be any further accumulation of water there will not be any drying the water cont the the there won’t be mass transfer, we will come to that later, that’s the only way to find out if this is saturated if something is saturated it’s already in equilibrium nothing will go there is no 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, ok. So, this is there are ways to do it, will come to when we look at measurements, I will come to, will talk about measurements of partition constant also; when we look at monitoring analysis methods for this, when we look at that. Any questions in this? this issue here? So for damp and wet there is no; one has to measure, you just have to measure and I will discuss the way in which we measure it. May be I will just discuss it now it is easier to do it now, straight away.

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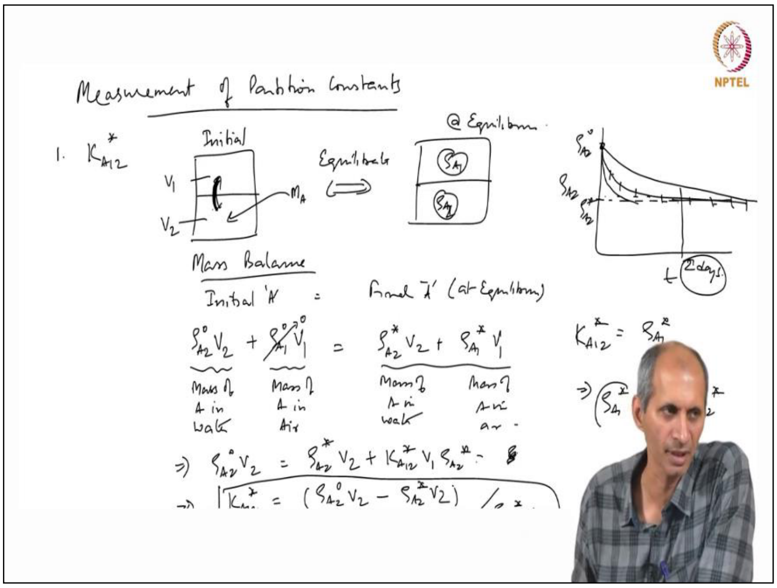
Measurement of Partition Constants

1. K^*_{A12}

Mass Balance

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

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

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

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

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

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

It is easier to discuss now, measurement of partition constants. So, let’s say; let’s start with the first one, this is the KA 12 12 star this is the ‘Henry's constant’. The definition of equilibrium is the following it is, say 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 add a certain amount of mass of A into one of the phases and allow it to equilibrate, there will be a concentration of A in in 1 and concentration of A in 2 at equilibrium.

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

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

So let us say that that in this case, I am introducing a concentration of A in the water phase here in air but in this experiment I am introducing all of it in in water so this is 0. After equilibrium, this is at equilibrium, V1, it’s distributing and I expect that one of the concentrations there will be a decrease in the concentration in the water, there will be an increase in the concentration in air phase. And how do I know that this is at equilibrium.

The only way I can find out is that concentration will not change at equilibrium. So, if if we 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 A2 zero, it will decrease and it will come to some value and it will not change, ok. So this is Rho A2 star at equilibrium, yeah. The only way for us to find out when this happens is by measuring the concentration of the of the liquid phase at every time I measure here then measure here then I measure here and at some point there is no change in 2 or 3 successive this things. With experience you will know when you are don't don't change and we will talk about it when we talk about the quality control of these things. So there there is a we have to be sure, so sometimes you are very close to equilibrium and you may that assume that it is in equilibrium all those things errors exist, so you are absolutely sure that this is equilibrium has reached and nothing is changing.

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

If there is all that you have to add that into the mass balance equation so when we do the experiment you have to be very careful that nothing else is happening. You have to design the experiment such a way that nothing else is happening or even it happens it should be so small that your main measurement is is is valid still valid. So here again here this is mass of A in water at equilibrium and mass of A in air, yeah. Now, we invoke the this thing, we say KA 12 star equals Rho A1 star by Rho A2 star which means now I am measuring water concentrationI am not measuring air concentration.

So if I am doing that, then I will express the air in terms of water, so I will write Rho A1 star equals KA 12 star into Rho A2 star therefore I put it back into the mass balance equation it becomes Rho A 2 star V2 equals Rho A2 Rho A zero V2equals Rho A2 star V2 plus KA 12 star

V 1 Rho A2 star, ok, and based on the this I can write, I can estimate KA 2 star equals Rho A20 V2 minus Rho A2 star V2 divided by Rho A2 star V1,

$$\boldsymbol{\rho^0_{A2}V_2 + \cancel{\rho^0_{A1}V_1} = \rho^*_{A2}V_2 + \rho^*_{A1}V_1}$$

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

$$\boldsymbol{K^*_{A12} = \frac{\rho^0_{A2}V_2 - \rho^*_{A2}V_2}{\rho^*_{A2}V_1}}$$

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 assuming this is not changing I can calculate this is easily. This is usually the way you do any partition constant you take two phases, you know everything else, you write the mass balance equation and then you can calculate you can measure what is the; so when you are doing an experiment, you need to be careful that when I is it that I am measuring when I measure if I am measuring Rho A2 star at some time.

After a first few trial and error experiments whenever you do that, you know that it takes two days, before two days it’s not going to happen and don’t need 4 or 5 days. So, you will keep the experiment for 3 days and then go and measure 3 days, straight forward, simply. So when you are developing a method for measurement of partition constant you have to follow that particular system people do this trial and error measurement so that other people who are following them don’t have to do multiple measurement to see if equilibrium has achieved.

So you say that 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, so there is a standard method for that. One thing you have to learn in terms of mass transfer is which is the rate at which equilibrium is achieved depends on the; this is taking long or taking very short and this depends on the way in which equilibration is done.

It means system has to be mixed this is relates to mass transfer which we’ll discuss later. But intuitively if you take salt and put into water and if you don’t stir it and you put salt and stir it the rate at which will dissolve will will will change and so that is the part of the standard method. When you go and read a method they will say take this much of solid A and this much of water put 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 or some such because that equilibration time. If you say shake it at 50 RPM for 3 days which means they have done the experiment they say that at 3 days the equilibrium is reached under any condition. So, the rate of mass transfer is fast enough so that it is completely covers 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 it the best way is to measure concentration at different times and you ensure that equilibrium has reached and then that gives you the partition constant measurement at that point.

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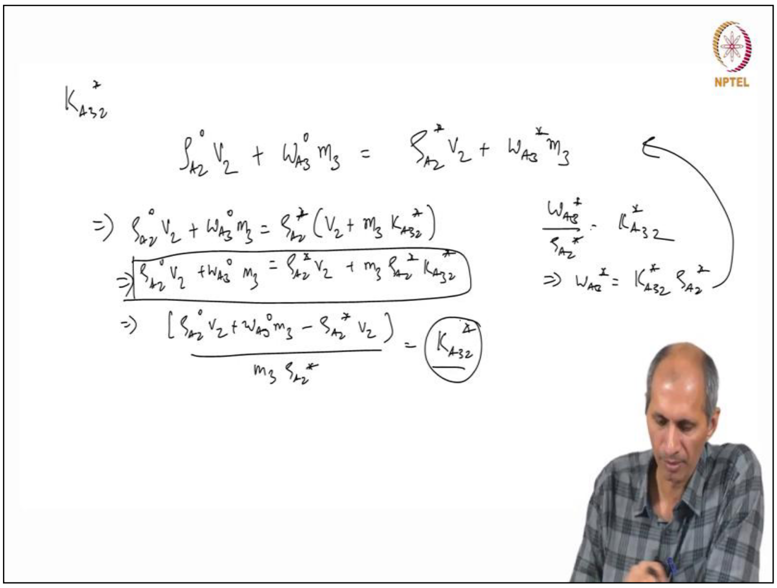

K^*_{A32}

$$\rho^0_{A2} V_2 + w^0_{A3} m_3 = \rho^*_{A2} V_2 + w^*_{A3} m_3$$

$$\Rightarrow \rho^0_{A2} V_2 + w^0_{A3} m_3 = \rho^*_{A2} (V_2 + m_3 K^*_{A32})$$

$$\Rightarrow \boxed{\rho^0_{A2} V_2 + w^0_{A3} m_3 = \rho^*_{A2} V_2 + m_3 \rho^*_{A2} K^*_{A32}}$$

$$\Rightarrow \frac{[\rho^0_{A2} V_2 + w^0_{A3} m_3 - \rho^*_{A2} V_2]}{m_3 \rho^*_{A2}} = K^*_{A32}$$

$$\frac{w^*_{A3}}{\rho^*_{A2}} = K^*_{A32}$$

$$\Rightarrow w^*_{A3} = K^*_{A32} \rho^*_{A2}$$

So you can if you want to same way you can do KA 32 star as well. So we are here the mass balance will change slightly where we are now saying Rho A20 V2 plus instead of Rho A1 we are now doing WA 30 m3 equals Rho A2 star V2 plus WA 3 star M3, now you know the WA 3 star by Rho A2 star equals KA 32. Therefore, WA 3 star equals KA 32 star into Rho A2 star,

$$\rho^0_{A2} V_2 + w^0_{A3} m_3 = \rho^*_{A2} V_2 + w^*_{A3} m_3$$

$$K^*_{A32} = \frac{w^*_{A3}}{\rho^*_{A2}}$$

$$w^*_{A3} = K^*_{A32} \rho^*_{A2}$$

when we substitute this back into this equation we get, now we don’t need this, we will expand it expanded back again.

$$\rho^0_{A2} V_2 + w^0_{A3} m_3 = \rho^*_{A2} (V_2 + m_3 K^*_{A32})$$

$$\boxed{\rho^0_{A2} V_2 + w^0_{A3} m_3 = \rho^*_{A2} V_2 + \rho^*_{A2} m_3 K^*_{A32}}$$

$$\frac{\rho_{A2}^{0} V_2 + w_{A3}^{0} m_3 - \rho_{A2}^{*} V_2}{\rho_{A2}^{*} m_3} = K_{A32}^{*}$$

So in most cases if if if a solid is not one this phases will not contain any thing. So, you can cancel or you know both both of them contain something you can leave this terms as it is, so, it becomes Rho A20 V2 plus WA 30 M3 minus Rho A2 star V2 divided by M3 Rho A2 star equals KA 32 star. So, this this mass balance equation is key, from here, you can calculate several things. So, in this case, I can also if I know the partition constant I can use this 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 to you. When we are doing the calculation measurement of KA 32 you do it this way, but once you know KA 32 it is used as a property, when you 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 you have to be able to write mass balances for different kinds of systems, ok.