Course on Analytical Chemistry
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Module No 03
Lecture 11: Chemical Equilibria

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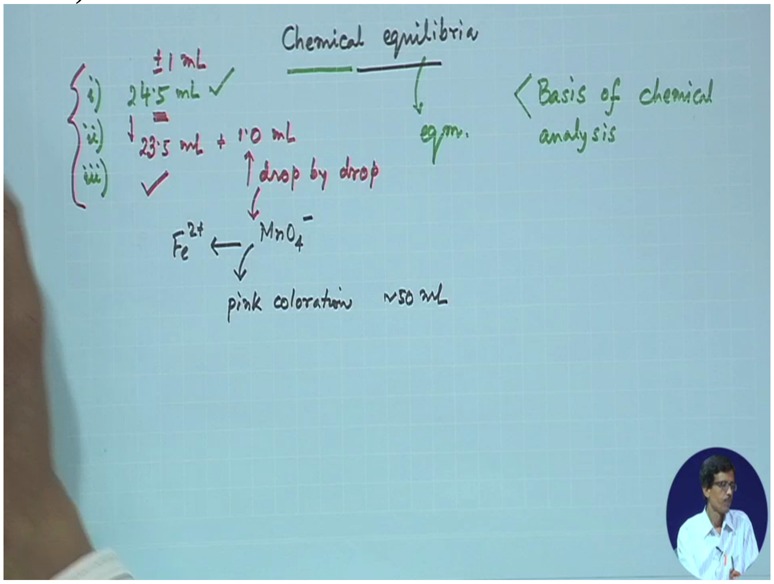


Chemical equilibria

↓ eqm.

< Basis of chemical analysis

±1 mL

i) 24.5 mL ✓

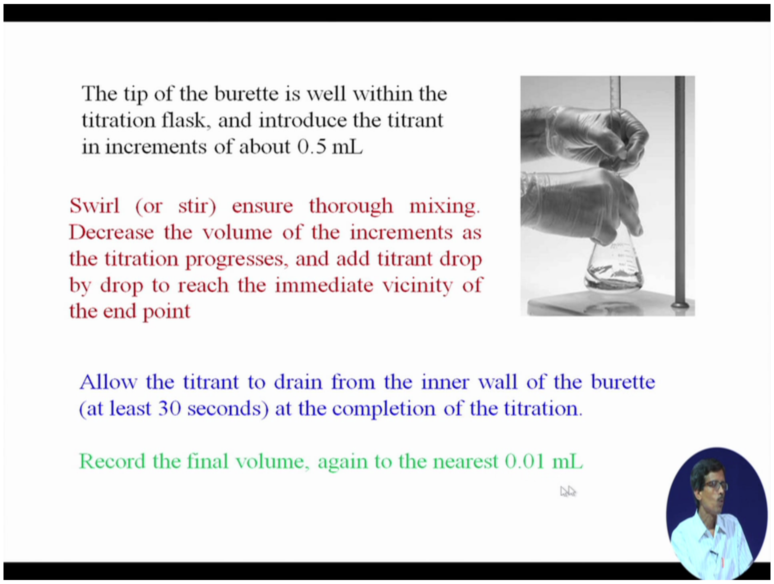
ii) ↓ 23.5 mL + 1.0 mL

↑ drop by drop

iii) ✓

$Fe^{2+} \leftarrow MnO_4^-$

↓ pink coloration ~50 mL



The tip of the burette is well within the titration flask, and introduce the titrant in increments of about 0.5 mL

Swirl (or stir) ensure thorough mixing. Decrease the volume of the increments as the titration progresses, and add titrant drop by drop to reach the immediate vicinity of the end point

Allow the titrant to drain from the inner wall of the burette (at least 30 seconds) at the completion of the titration.

Record the final volume, again to the nearest 0.01 mL

Hello, good evening everybody. So today we will start a any part of this particular course where we will be talking about chemical equilibria equilibria which has something related to that of our particular equilibrium process and this basically or fundamentally connected to the chemical analysis. So basis of chemical analysis, how it can be related to that of a simple chemical equilibrium.

So before going to that, what we can finish today, the last part what we are talking in our previous class is the titrametric analysis where we are doing, so we have the typical holding of this particular burette and in the conical flask, what was there, atypical reagent. So the reagent of the analyte is there and we are adding reagent from the burette. So we introduce that particular thing what is actually reacting with that of our analyte.

So if our analyte has FE2 + ion as I told you earlier and the titrant can be any oxidising agent when we are talking about the corresponding reduction oxidation or oxidation reduction reaction what we see or sometimes in abbreviated form, we say it as the redox titrations. So this particular reagent will be the corresponding oxidising agent such as potassium permanganate and potassium dichromate that we know.

So this is the typical process how we hold with the gloves hand, how we hold the burette and how we hold the corresponding conical flask for a particular titration and in an increment of 0.5, we drop by drop we add the titration because we will be reaching somewhere where the thing what we will be discussing today is the equilibrium process. That means A is reacting with B producing C + D. And when the complete reaction of A + B is taking place, C is here, say Bis over here.

So C and D will be forming there within this particular flask but we have to detect this value because all the titrametric processes, the titrations we can visually understand or we can visually detect the endpoint where the entire A has been consumed by the B. So at an incremental level of 0.5 ml we should introduce that volume from the burette which is graduated volumetric thing. From drop by drop addition of those volume, we basically add those titrant to the conical flask.

So after the addition, what we do? We basically go for the stirring for the thorough mixing where the decrease of volume of the increment as the titration progresses. So we start at the very beginning we have enough volume, say this has been taken as almost 25 millilitres and we are adding another 25 millilitres of the solution from the burette such that if they both have a comparable concentration range, then only we expect that after the addition of the teeth right of same volume what is there in the analyte, we get the endpoint.

So initially we add basically the 1st addition of those titrants but slowly we should as we proceed towards the end, that means after to addition of 20 ML or 21 ML of that particular reagent or the titrant which we are writing in this fashion, the as the titration progresses, the titrant we should add drop by drop in the immediate vicinity of the endpoint. Suppose your endpoint is coming at say 24.5 ML, so this is the 1st titration what we do.

Then we have the second titration and then we have the 3rd titration. So once we get the 1st titration value, so the volume for the 1st titration what we can expect at the 2nd titration when we do because we have to take the average of all these 3 having some concordant values. So in the 2nd case also, we straightaway add say 23.5 ML. So you require still 1 ML of this volume. And this we should add drop by drop.

So that is written in the language in the PowerPoint slide basically. So drop by drop endpoint addition of this particular extra 1 ML volume after the addition of 23.5 millilitre of volume, what does it mean? This basically we should be very much careful whether this 24.5 millilitre of the 1st volume is accurate one. If it is not, the 2nd endpoint might come at 24.4 or 24.6.

So this we should be precisely knowing that whether the value is exactly 24.5 or it is + - 1 ML. So within this + - 1 ML if we add drop by drop, during th 3rd titration we should be able to detect the exact value what is required because we know now because from your experience, from the 1st titration, the 2nd titration and 3rd titration, we should be precisely pick up the actual addition of this, that means the last drop when we go for the drop by drop addition, the last drop of the titrant whether we are adding say MNO4 - in a solution of FE2 +.

So you require the last drop. So that last drop of addition of this potassium permanganate to FE2 + solution is basically not consumed wholly say half of this, it can be consumed by FE2 + and the remaining half of this is giving a pink colouration the whole solution because the potassium permanganate solution as we know is a self indicating solution. So when when we have extra 1 or 2 drop of the solution say in a volume of 50 millilitre, we can detect nicely by our naked eyes, the endpoint for this particular titration.

So that is why we are saying this that the drop by drop addition as you reach the endpoint for this particular titration. Then allow to drain from the inner wall of the burette at least 30 seconds at the completion of the titration. How you detect that particular completion of the titration or the complete formation of this particular C + D? We just allow 30 seconds for this colour to remain because you can have something some other reagent present which might consume your extra potassium permanganate solution which is giving you the colour.

So if the colour is persistent for 30 seconds, we will consider this as your and the point. So the record of the final volume against the nearest 0.01 ML is not 0.01 ML, so is 0.01 ML. This 005 is basically the volume size for a particular type of drop if your burette is a good one. So within this particular value, only 2 drops of that will you gain.

So we are looking for a endpoint with one drop of addition, is not that 4 or 5 drops you are adding and you get the endpoint. So is basically a mustering of this particular technique through your experience you will be able to detect that that one drop of your solution giving a permanent colouration of this thing whatever is the colour it can be from the potassium permanganate or it can be from any other indicator present in the solution, in case of acid-base titration, in case of this particular redox titration or in some other complexometric titration.

That individually we will consider one after another when we go into the respective chapters for the detailed discussion. Okay, so what we can see now? that how we can go back and for a particular type of chemical equilibrium and the nature us giving us so many results.

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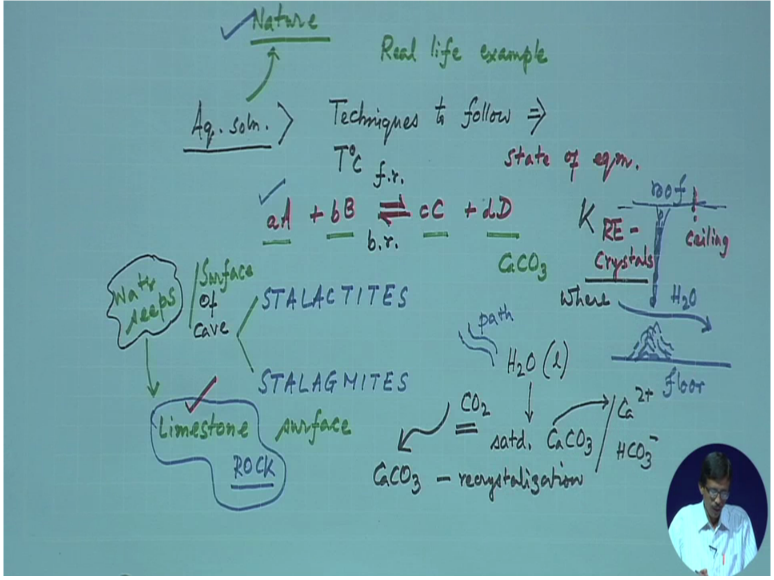

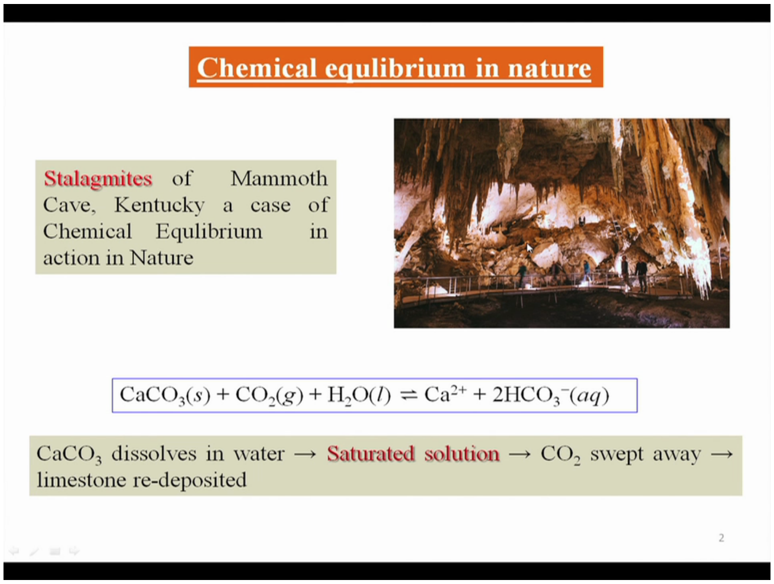

Chemical equlibrium in nature

Stalagmites of Mammoth Cave, Kentucky a case of Chemical Equlibrium in action in Nature

$$CaCO_3(s) + CO_2(g) + H_2O(l) \rightleftharpoons Ca^{2+} + 2HCO_3^-(aq)$$

$CaCO_3$ dissolves in water → **Saturated solution** → CO_2 swept away → limestone re-deposited

So basic idea of this particular course is that how we can understand or how we can follow the natural process what is happening over there. So we will take 1 or 2 such examples such that thing will be very much useful to understand the chemical equilibria in terms of the real-life examples. So our basic idea is for a particular type of example what we are facing, what we are seeing, the nature is doing for us and we are handling everywhere that we know that the corresponding chemical equilibrium in aqueous solution.

So if we talk about the water pollution, if we talk about acid rain, if we talk about the corresponding marble formation or the deposition of any other material, everything we are getting from aqueous solution. So something what we can have should be soluble in this particular aqueous solution. So this particular thing that means we will have or we will follow several techniques, so what are those techniques basically?

So basically, initially, we will be looking for those manual techniques, that means your burette and pipette, what we are talking about that the burette and pipette you can take. So these techniques will be utilised to follow that particular state of equilibrium where just now we were talking about A + B giving rise to C + D. Okay? So a moles of A and b moles of B, c moles of C and d moles of D is reacting.

And this particular symbol is telling us that a particular reaction is going to some point and then all these 4 species are present together within the solution. So after that, after some time, equilibrium has reached and we can have all the solutions but initially what you see, if the equilibrium is such that the reaction is is going towards completion, that means 90 percent of A is converted to C or B is converted to D.

So what we can see that the only 10 percent, so the equilibrium is giving rise to the concentrations of all these of different ratios. So for this chemical equilibrium to follow, why we are understanding this chemical or why we are studying this particular type of chemical reaction is that that most of these techniques basically is dependent on the corresponding equilibrium process. We chemical reaction between A and B, if they are present with the formation of C and D, so equilibrium is there.

And this particular equilibrium process, we basically able to detect. So if we think what nature is doing for us, we will take a very simple example what is given in your book, the scoogs book also, the chemical equilibrium what is present in nature. So this is something within a cave, something is forming from the roof and something is getting deposited from the bottom. So basically geologists say that these are the formation of the the stalactites and stalagmites.

So stalactites and stalagmites. So this you also probably would have studied from your school days is this basically name of some chemical compound when they are forming in a particular way. So what are these? These are nothing but the deposition of limestone what we know which is calcium carbonate. So there are huge amount of calcium carbonate is getting deposited within this particular cave.

So this is beautifully formed, so they are basically crystallised form. So how these are forming? So this is a real-life example of your chemical equilibrium what nature is controlling. So stalagmites of Mammoth Caves. So this is a typical photograph of that Mammoth Cave which is there in Kentucky in USA. So this is a real example of a case of chemical equilibrium in action in nature.

So how a chemical equilibrium is possible for the formation of this particular process? So as I told you that this A and B is there, forming C and D. So you can have more than one equilibrium prognosis also there but initially, the most simplest example of the most simplest form of this equilibrium is that A is reacting with B forming C and D. So what is forming for this particular stalagmites formation is that your calcium carbonate is there which is reacting with CO2 in presence of water.

So that means, you can have a corresponding saturated solution of these. So if they are reacting in a typical fashion, we are getting basically calcium 2 + and the bicarbonate anion. So instead of talking in terms of the corresponding M + B, we have A + B and water is there in the medium because we are talking everything in aqueous medium. So we should not consider this, the corresponding concentration of water present in this particular solution.

But what is happening over there as the corresponding leaching out of the calcium ion, so we all know that the limestone is calcium carbonate which is very solid one. So the dissolution of this particular calcium carbonate can take place in presence of this extra carbon dioxide which is present in the environment. So the carbon dioxide present in the air in presence of that water which is there also in the solution, so there is definitely a flowing water and water can also have some dissolved carbon dioxide.

So dissolved carbon dioxide in this particular water can go for the dissolution of this particular Ca2 + and bicarbonate ion. So if you have a limestone surface, so limestone surface is there and on that limestone surface, the water is water seeps on it, because this water is coming from the surface of the cave, so it is coming from the surface. So is a typical natural process. So surface of cave it is coming.

So if water is sweeping inside, so it is reacting with this and forming bicarbonate ion. So this water what we are writing in this equation, so this H12, the liquid one which is basically this water which is coming over there, and this water when it is flowing through that limestone surface, it is flowing through this particular limestone surface. So it gives us a saturated solution of calcium carbonate. So when this saturated solution of calcium carbonate, that means it is, we are saying that it gives in presence of CO2, it gives Ca2 + and HCO3 -.

Basically some amount of this calcium as calcium 2 +. That means some amount of calcium is leaching out from the limestone and we are getting this particular thing. So if we have the equilibrium, that means this is there, that means one head of this arrow, so this is the forward reaction and this is the backward reaction. So depending upon the magnitude of this equilibrium constant, the corresponding chemical equilibrium and we can have some idea that how much of C and how much of D is there.

That means how much of this HCO3 - and how much of bicarbonate is there because one of the component of that particular reaction is the gaseous carbon dioxide which is present in the environment or which is present in the dissolved form in the liquid water. So if this is not available, if it is going away, that means if CO2 is going away, what is happening them that if CO2, this is your CO2. So B is CO2 if you consider that calcium carbonate + CO2 giving rise to Ca2 + and HCO3 -.

So this CO2 is going away. So if somewhere if the water not having the enough CO2 for the dissolution, what will happen? The saturated solution of this calcium all mixture of all these, basically will try to deposit a fresh amount of calcium carbonate. So this is basically the corresponding formation or the recrystallised form of the limestone. So this recrystallisation can take place that recrystallisation of that limestone is taking place.

So we can have a huge rock sample. So what we are talking about, the usual rock sample we can have. Not sample is nothing but your limestone and on it, water is flowing which is saturated with CO2. So some amount of Ca2 + is leaching. When CO2 is not there, what is happening?

The reverse collection or the reverse process is favoured and the reverse process what is being favoured is that what I wrote in the reaction that the reverse reaction is taking place, that means more and more calcium carbonate will be deposited over there.

So just position now take place depending on the drops, how these drops are forming from the roof of the cave or how they are getting deposited from the floor. So these are the 2 things. That is why we have two different names. One is which is coming out from the roof and one is getting deposited on the floor. So this nice ice like , this small road like as if they are basically the crystals of ice, but is not, is the Crystals of calcium carbonate.

So basically they are getting, so is a beautiful structure what we get in this particular inside of this cave is basically due to this particular equilibrium. And how this water because you have this water and water path is defined. So on the path of this water where the flowing water is taking place, so there the ground deposition, so water is flowing. So you have this water is flowing. So on the top so depending upon this, so on the flow water because this is a continuous process, this is a natural process, so flowing water is there.

And from that flowing water, what we are getting? We are getting a process where the crystals of these things because the deposition is taking place is now from a saturated solution of calcium carbonate, so saturated solution of calcium carbonate what we are getting is basically crystals of those calcium carbonate. So these crystals of those calcium carbonate originally we have this limestone rock we are dissolving. So it is a typical dissolution process.

So how the road is getting going for the dissolution process and when the CO2 is being removed, is basically going for re, we are writing capital RE. So is the recrystallisation process. So recrystallised form and recrystals are there. So recrystallised are different shapes and different sizes and different structures that we are getting for one type is stalactites and one type is the stalagmites. So basically when this is basically from the roof, water droplets are dripping, so they are basically dripping from the ceiling.

So ceiling is there, so these water droplets are coming from the ceiling and we have the floor also. So the formation of these, so where these are forming? So if we ask a very simple question that where because we will be discussing again in details at some point of time that how and where this recrystallisation can take place. If we use or test-tube, if we use our beaker, so the beaker surface, the inside surface of the beaker or the inside surface of the test-tube is the place where the crystals are getting deposited.

Similarly, there are certain positions where you know that we are not talking in terms of something else where this temperature is, so temperature in Kelvin or temperature in degrees centigrade which can also follow this particular value of K, the K is the corresponding equilibrium constant for this particular process has a particular value for a particular temperature. So if some point of (())(23:54) we get that that than the low-temperature zone auto temperature within the cave because cave is definitely not getting sunlight, is some cold regions are there.

So there will be faster recrystallisation processes also can take place over there. So this we have seen that way that CACO3 what is being dissolved in water, so we get a saturated solution and when CO2 is swept away, the limestone is redeposited what we are discussing just now as the recrystallisation process. So this recrystallisation process, the steps are different from that of the rock. So the rock you have, from the rock we are getting these 2 species and these 2 species are having a beautiful structure.

So these structures are aesthetically pleasing also that you people go, the visitors go, the tourists go there to see this particular type of this has a national park in US. So is played that particular cave, they basically visit for to see this particular structure.

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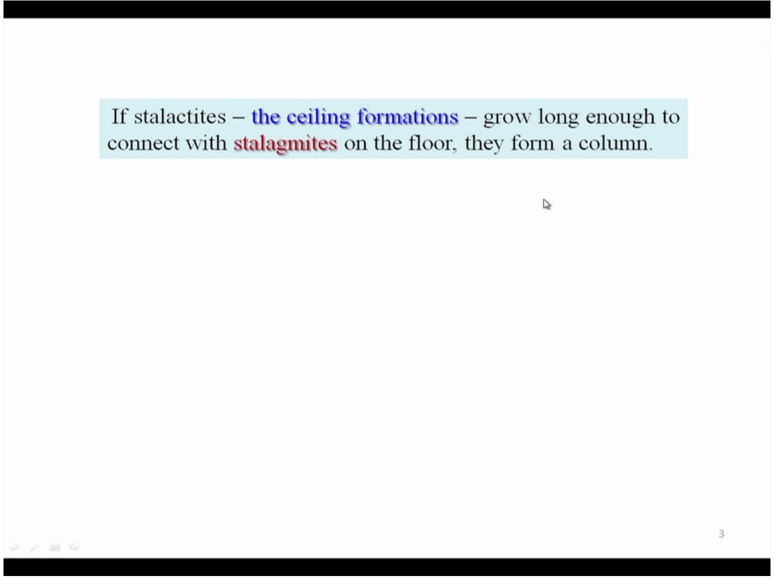

If stalactites – the ceiling formations – grow long enough to connect with stalagmites on the floor, they form a column.

So we get this so what we, the 2 forms just now I told you, what we are getting? So that stalactites what we are getting from the top of the ceiling, that means from the ceiling where water is dripping inside, so this particular dripping of water is we are getting. So grow long enough to connect the stalagmite in the floor. So if the what is forming from the top ceiling and what is getting deposited on the floor, they can have also very connections.

So if these 2 are connected, so we are having something s some very sword like thing is coming from the ceiling and something is getting deposited in the floor. So we get a column like structure. So how the column like structure is forming? Because you know, the different types of crystals we can have, the recrystal, the recrystallised form of any saturated solution such as your sugar solution, such as your sodium chloride solution, when we go for the recrystallisation process, we know they are having different forms and different structures.

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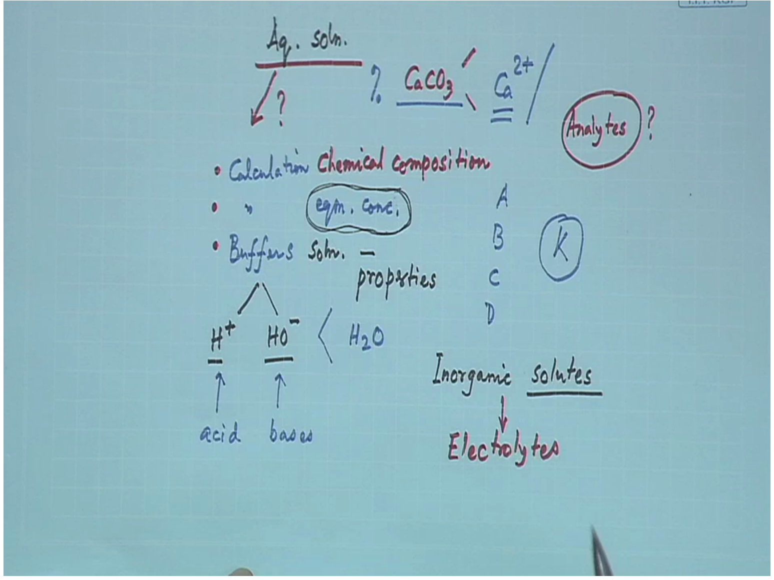

So if we talk all these things and basically we should be knowing what is there as the corresponding chemical composition and the composition of a particular aqueous solution. So so far what we were talking about is your aqueous solution, so all the time we should pay our nice attention to a aqueous solution. And what is there? Basically the composition of that particular aqueous solution is important. So this particular thing, if we know that it is only a rock sample, so not only calcium carbonate is there, but several other things are also there.

But the major constituent, say 90 percent or 80 percent of this as the corresponding calcium carbonate. So handling this aqueous solution which can be a saturated solution of your calcium carbonate, there are several things what we can think of from this aqueous solution, so we can have some idea about the chemical composition. So chemical composition if we are interested to know that is a real example of this is that just now we are discussing is your calcium carbonate.

So composition of calcium carbonate, that means the percentage of calcium carbonate present in this particular sample. So the all sorts of different calculations we can do by knowing this particular thing, that means when we quantitatively analyse that, because this analytical chemistry will be helpful to us if we determine the corresponding concentration of Ca2 + in the solution. So some model solution can be supplied to you where you can have the Ca2 + and that Ca2 + determination can be found out where we can find out that original calcium carbonate supplied.

It can be in the powder form or it can be the typical limestone rock sample. Then we can have some idea about the corresponding calculations of the equilibrium concentrations what we were just not talking about the species like A, B, C, D, for a particular type of chemical equilibrium. So what are those equilibrium concentrations depending upon the corresponding magnitude of K. So when the equilibrium is reached, we know that the A and B are consumed.

We are producing C and D. So if you have a corresponding magnitude, execution minute of K value, so concentration of A and B would be less rather than a concentration of C and D. So anything or any calculations related to your equilibrium concentrations can be found out and we will introduce something where we talk this in terms of the corresponding buffers, what are those buffers and how these buffers are formed and how we can use those buffers.

So this buffer solutions how we can use, so this buffer solution to things we will be discussing. We will discuss that the corresponding concentration of the hydrogen ion and the hydroxide ion and these concentration of hydrogen iron and the hydroxide ion in the Beaufort medium, how we can use for those calculations to find out the properties, the different properties in the corresponding pH range of those buffers solutions. So these all have some natural effect on these because we see like that of your calcium carbonate, we can find the water solution in the Lake also.

So buffers will be there and those buffers solutions can also control the corresponding chemical equilibrium and the equilibrium concentration, how the equilibrium concentrations can be affected by using those buffered solutions and the buffered medium, that we will see in our next class. So before that what we find is that this buffered solutions when we talk in terms of this H + and the hydroxide ions you know that this H + and HO - is very simple to know from you you know that this we all know that we are all coming from the water because we know that water can go for the dissociation giving this H + and HO - but apart from that, we can also get this from acids and the different bases.

So acids and different basis we can have. So this H + and HO - we can get but what we find that we are talking about something else where we are talking that Ca2 +, how a saturated solution of Ca2 + is useful so we will be discussing something where we can have this inorganic solutes. So we are introducing some terminology, so you should be very much familiar with those terminologies because these things every day or every time, we are talking about analytes what we are trying to find out?

The analytes our unknown quantity in any solution using analytical chemistry. Now the solutes which is giving you the solution, so these solutes how they can be useful for starting this particular chemical equilibrium and the corresponding this particular production of H + and HO - and the different things what we will just introduce you in your next class is about your electrolytes. So this electrolytes we will be talking from the inorganic solutes okay? Thank you very much.