Electrochemical Technology in Pollution Control

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Module IV
Lecture – 06
Properties of solution 3

We are meeting again to continue our discussion on the Electrochemical Technology. I have been trying to introduce you to solution chemistry as part of the course and we had discussed about activity and activity coefficient in the last class. We can look at the slide now.

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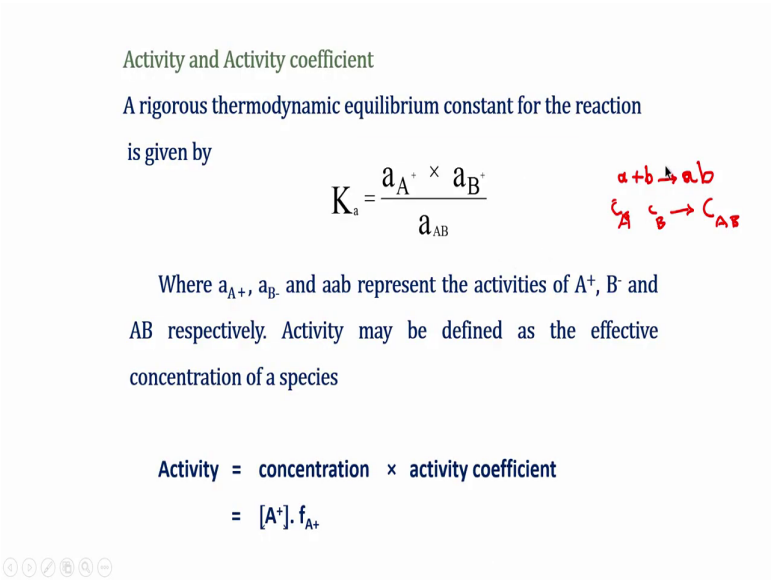

Here I have written an equation it is a plus b going to a b; I am the concentrations are here and but instead of concentrations thermodynamically to be very correct; we should write a A plus

and a into B a B plus divided by a AB. Here a represents small a, represents the activity of A a B plus represents activity of B and a A B represents the activity of AB product.

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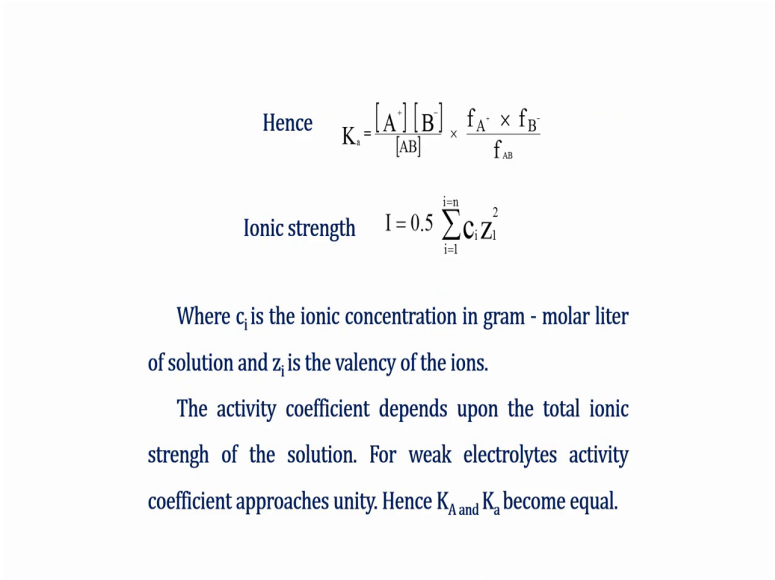

So, Activity is defined as the concentration into activity coefficient. We had also discussed about the a little bit about the ionic strength, that is the activity is nothing but co activity coefficient into concentration. So, we are defined ionic strength as the total number of ions present allow and their product of ionic concentration and valency, some of that and approximately 50 percent as the ionic strength.

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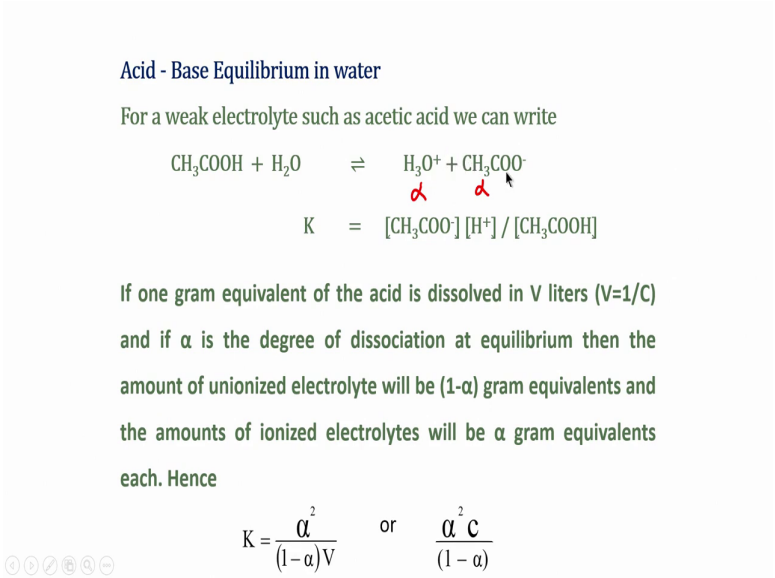

So, then we discussed about the acid base equilibrium reaction, we have written say acetic acid plus H2O going to H3O plus and CH3COO minus. We write an equilibrium reaction constant K is equal to CH3COO minus and H plus into CH3COO minus CH3COO H. And if one gram equivalent is there and a small portion that is alpha dissociates into the products. I can write undissociated product would be 1 minus alpha.

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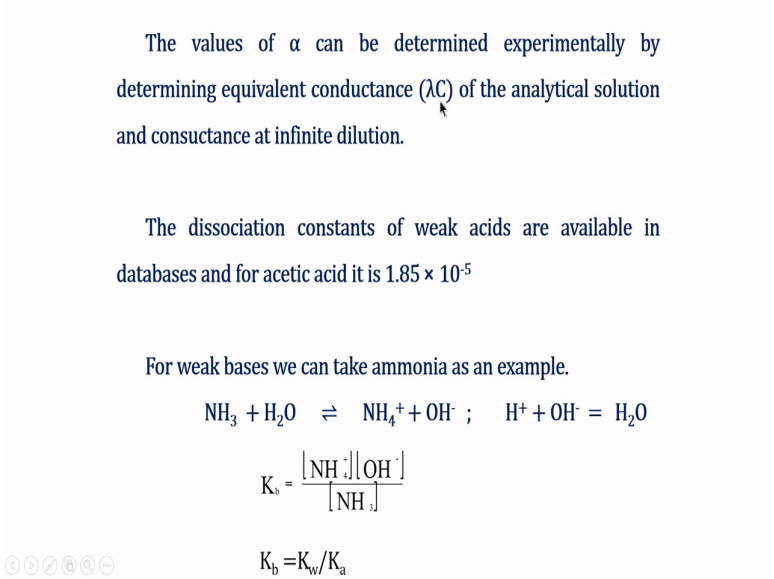

So, I can write instead of H3O plus and CH3COO minus I can write alpha alpha. So, alpha square divided by 1 minus alpha into V that is alpha square C divided by 1 minus alpha. So, this is the dissociation constant and the values of alpha can be determined experimentally by determining the equivalent conductance. Because, those things these H3O plus and CH3COO minus contribute to the conductance this will not contribute.

So, I can determine the conductance and take 50 percent has H3O plus and 50 percent as CH3COO minus of the total conductivity ok. So, that is lambda C of the analytical solutions and we assume that it is the conductance at infinite dilution. So, the dissociation constants of weak acids are available in the literature. And now up to this who had done earlier.

Now we are going to discuss about the weak basis that is dissociation of weak basis. Just like acids we also have basis, basis can be strong bases and weak basis; sodium hydroxide,

potassium hydroxide they are all strong basis, ammonia is a weak base. So, you can smell ammonia very easily you know, because it is a weak base.

So, ammonia will react with water to give you ammonium hydroxide, the reaction is represented like this NH3 plus H2O going to NH4 plus and OH minus. There is another equilibrium that is present in aqua solutions, that is water itself can dissociate as H plus and OH minus going to H2O.

So, I can write K b is nothing but NH4 plus into OH minus and divided by NH3 that is the product. We do not write the concentration of water, because it is very large compared to NH3. So, it is we assumed that it is 1 all others are very small. So, we have K b where dissociation constant of ammonia is nothing but NH4 plus into OH minus divided by NH3 plus.

And I can write an equilibrium constant there will because this is equilibrium equally available. Simultaneously going on I can write K b is equal to K w by K a; this is the equivalent concentrations of water is written as K w. I can write here similar equation H plus into OH minus divided by H2O that is K w.

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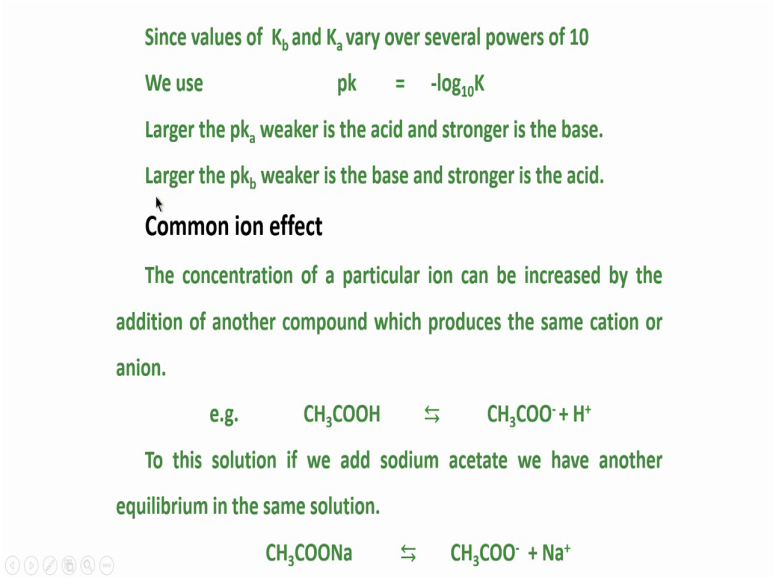

So, since values of K b and K a very over several powers of 10, that is you remember what is the value of K a that is a for acetic acid? It is 1.85 into 10 raise to minus 5 who will remember so much, you know 10 raise to minus 5 time raise to minus 6 for day to day life it does not make much sense to remember all these.

So, what we do is, we write use a value that is logarithms. So, 10 raise to minus 5 is 5 minus 5 and log of 10 raise to minus 5. So, we use pk as we defined pk has negative log of K to the power of to the base of 10. So, here if I write 10 raise to minus 5, it will be larger there it will be 5 point something; 4.87 into 10 raise minus 5 that is what it means pk.

So, larger the pk weaker is the acid and stronger is the base; this is the ultimate conclusion of the pk value. So, if you see the value of pk in it means you are seeing the value of negative log of 10 K. So, if pk is larger the acid is weak and base is strong. So, larger pkb weaker is

the base and stronger is the acid very simple to understand. And this is a about the dissociation constant.

Now, I will discuss about the common ion effect, that is concentration of a particular ion in a solution can be increased by the addition of another compound which produces the same cation anion. I want you to imagine that we are having a particular solution of acetic acid. Now acetic acid will dissolve into acetate ion and H plus ion, we have written the equation earlier, you can see the previous slides.

So, what we have written, CH3COO H going to CH3COO minus and H plus ok. Now, to this solution containing CH3COO minus and H plus and CH3COO H and dissociated acetic acid. To this if we add I want to add sodium acetate additionally from myself, then what happens we have another equilibrium means in the system is not it. So, look at the slide now, that is what I am going to explain to you.

Here I am writing CH3COO H going to CH3COO minus and H plus; to this solution we are going to add sodium acetate and we have another equilibrium for sodium acetate are separately. What is that equilibrium? Sodium acetate will decompose into CH3COO minus and N a plus.

So, if I add this there will be two equilibriums in their same solution; one is acetic acid another is sodium acetate. But, look at this; this CH3COO minus is common here in this equation and CH3COO N a is also produce going to produce CH3COO minus and N a plus. In general you have to understand that 99 percent of the salts are ionized sodium salts are ionized 100 percent. All sodium salts and potassium salts 99 percent of them are totally ionized 100 percent ionize been solution.

So, if I add sodium acetate to acetic acid, what I am going to add 100 percent ionization. So, I am going to add CH3COO minus ions to the same solution and a little bit 100 percent of sodium ions plus whatever they it can come from acetic acid in this case. So, in the solution, we have CH3COO minus coming from this reaction another CH3COO minus coming from this reaction N a plus and H plus. So, this is common so this is what we are discussing this is

what effect this edition of CH3COO N a will have on the dissociation constant of CH3COO H.

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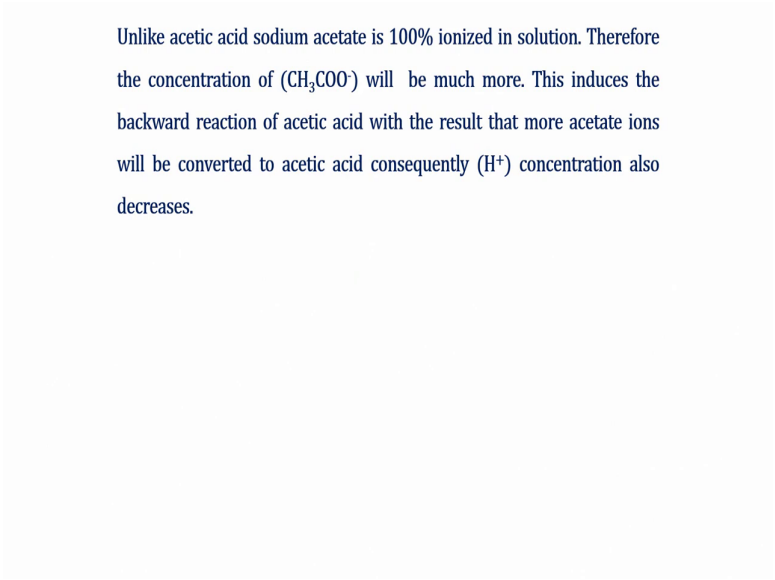

So, unlike acetic acid sodium acetate is 100 percent ionized, therefore the concentration of CH3COO minus will be much more than what is produced by the dissociation of acetic acid. So, this induces the backward reaction of the acetic acid, with a result that the acetate more acetate ions will be converted into acetic acid go back now.

Here I consider this now I have more of this and less of this more of this. So, remember Le Chatelier's principle, if I add additional CH3COO minus into this system, the system should try to remove the addition. So, how will it remove the addition of CH3COO minus it will combined more with H plus and go back to CH3COO H. That means, the dissociation of

acetic acid will become less to the extent of the effect of CH3COO minus coming from sodium acetate.

So, this effect is known as copper ion effect. So, Le Chatelier's principal is at work here and it will induced more of the acetate ions to get converted into acetic acid. So, this is the principle of common ion effect.

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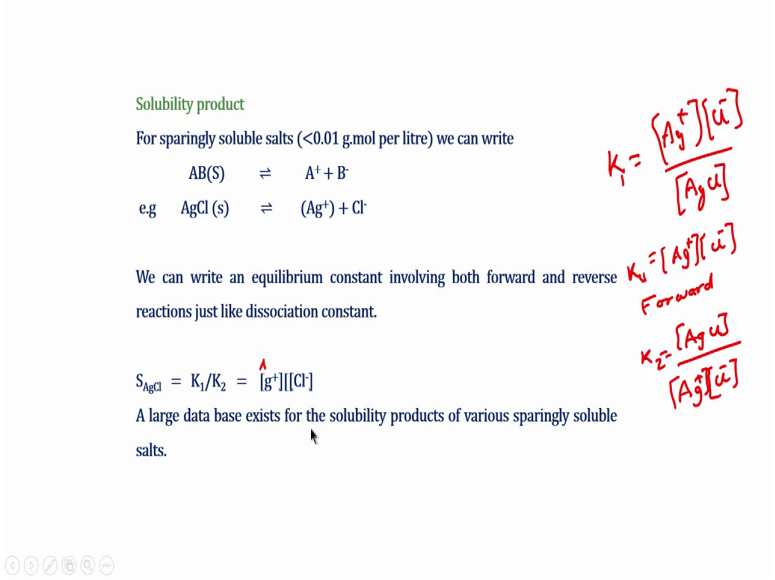

So, now we are going to talk about the solubility product ourI have so far I have been trying to introduce you to different concepts of the aqueous chemistry. So, now we have discussed about activity, concentration, dissociation and then common ion effect and all those things.

Now, I am going to introduce to you one more one more property of the aqueous solutions. That means, they contain solutes dissolved in the solvents. So, we earlier we had talked about

solubility, now I am going to talk about the solubility product. Now look at the slide now, the I have a product salt AB, it is S I have written here, it is it represents sparingly soluble salt S means salt solid it can also represent solid.

So, for sparingly soluble salts what is sparingly soluble salt mean? It means you it is very soluble very less extent that means, even if you take the solid put it in water it will remain as such but water will be saturated with the ions of the salt. So, but very little salt will be dissolved in water, their such a thing is known as sparingly soluble salt.

For example, I can choose silver chloride; all students of chemistry or high school students, PUC student's, college students use it as a chemical test for the chloride. That is, if you add silver nitrate solution to a solution silver nitrate solution to a solution containing chloride, silver chloride will precipitate.

So, why silver chloride will precipitate? Because the solubility of silver chloride is very less in water, such a substance whenever there is a precipitation reaction happening it means the solubility is very less. Such product like silver chloride is known as sparingly soluble salt. It may be of the order of few milligrams per liter, milligrams few milligrams per liter or it may be few grams per liter. But definitely not more than that ok, it may be few micrograms per liter.

So, we are going to talk about such salts which are very sparingly soluble in water. So, for earlier you also remember that I have talked to you about the dissociation; all salts dissolved salts in water they dissociate into their corresponding anion and cations. Positively charged cations and negatively charged anions, sodium chloride will give you positively charged sodium negatively charged chloride ion.

So, I am going to write an equation for the equilibrium between undissociated salt and dissociated salt in water, in the aqueous solution. So, I write here AgCl this is a specific example AgCl solid is in equilibrium with Ag plus and Cl minus ions. In water, this is the actual example this is the general example; AB solid is going to A plus B minus.

So, we can write an equilibrium constant for this reaction, involving both forward and reverse reactions just like a dissociation constant. So, I write S AgCl that is at the bottom I should write Ag plus into Cl minus divided by AgCl you know. I can write an equilibrium constant K is equal to Ag plus into Cl minus divided by AgCl, this is also concentration.

Now, you should remember that AgCl is a solid ok, because it is very sparingly soluble. The product AgCl at the bottom is a solid, so concentration of solid is always one remember that you must always remember, that they concentrations of solids in their solid form is 1. So, I do not write I can simply write K is equal to Ag plus, if the denominator is 1 I can write Ag plus into Cl minus is equal to K because of AgCl is 1.

So, here I am I am writing S AgCl is equal to Ag plus into Cl minus forward reaction. For the reverse reaction I should write, AgCl divided by Ag plus and Cl minus; this is for the forward reaction. And K 2 I can write this I can write it as K 1 K 2 will be AgCl divided by Ag plus into Cl minus.

So, this is the ratio K 1 by K 2 here also it should be K1 only no no. So, K 1 so K 1 by K 2 is nothing but the product of Ag plus and Cl minus here it should be Ag; there is an error typographical error g plus is there. So, here it should be Ag plus into Cl minus because AgCl is 1. So, a large database exists again for the solubilities of sparingly soluble salts in water and several other solvents.

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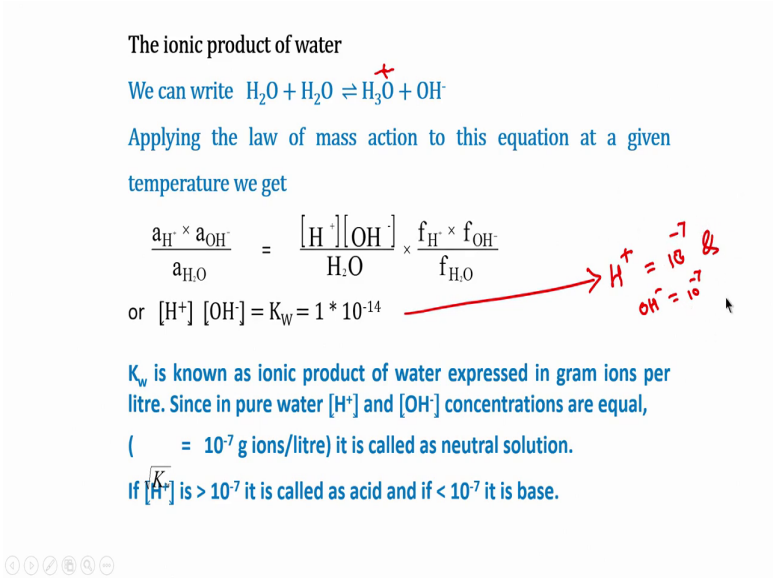

So, I will now discuss more about sparingly soluble salts but, you are introduce to the concept now is not it. Now I want to introduce you to another property of the solutions that is ionic product of water. What can do what can happened water do? One molecule of water may react with one more molecule of water to give you H3O plus and OH minus here it should be H3O plus positive charged it is a cation ok, so H3O plus into OH minus ion.

So, we can apply the same law of mass action or equilibrium constant to this reaction and I can write a H plus activity of the hydrogen ion into activity of OH minus ion divided by activity of H2O water molecules and I can write convert it into concentration because it is only pure water. So, the reaction can be written in terms of concentrations and activity products.

And activity products are one almost in all water solutions. So, I can write this is one H2O the value of H2O would be 1 and these are all 11 1 into 1 divided by 1. So, I can write the product of H plus and OH minus ion is equal to the a constant; that is it known as K w very popularly know people write this K w. Every time you write our dissociation of water is simply write K w.

So, the this value you should always remember that it is 1 into 10 raise to minus 14 sorry 10 raise to minus 14. So, what would be the value of H plus? H plus would be 10 raise to minus 7 and OH minus also should be equal to 10 raise to minus 7. Then only K w would be 1 into 10 raise to minus 14.

So, this K w is known as ionic product of water because it is the multi product two values are two values are there which is 10 raise to minus 7 and 10 raise to minus 7. So, H plus is equal to 10 raise to minus 7 OH minus ion concentration is equal to 10 raise to minus 7. So, it is called as neutral solution. So, H plus is greater than 10 raise to minus 7 we call is as acidic and if H plus K w H plus is less than 10 raise to minus 7 then it is called as basic solution base solution. So, this concept of ionic product of water is a very important concept.

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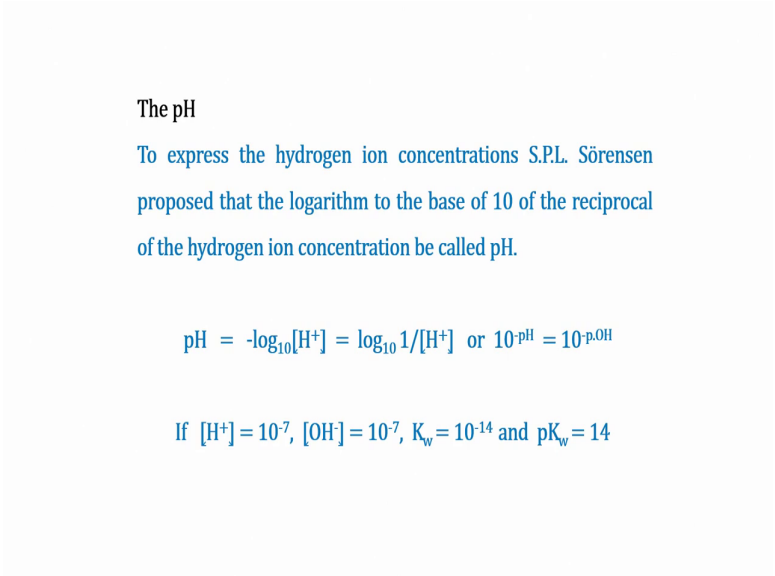

So, that brings us to the discussion of what is a p H. So, you should remember that we are writing almost all things in the negative log domain. So, the to express the hydrogen ion concentration again, in pure water it is H plus is 10 raise to minus 7 and then in acidic solutions it maybe 10 raise to minus 2 10 raise to minus 5, it may be 10 raise to minus 1 it can be anything.

So, again this 10 raise to minus 7 exponential terms are difficult to handle difficult to remember. So, the concept of log value has been introduced and even to write the H plus concentration. We this gentlemen he is a great scientist actually S.P.L Sorensen proposed that the instead of writing 10 raise to minus so much so much so much etcetera, he simply used write it has negative log of concentration that will be very simple number.

So, he is suggested that use logarithm to the base of 10. So, according this is very widely accepted all over the world. So, p H it is called as p H is negative log of H plus ion that is log of one plus 1 divided by H plus; this is nothing this expression can also be written like this or 10 raise to minus p H or 10 raise to minus p OH.

So, if H plus is 10 raise to minus 7, OH is 10 raise to minus 7, K w 10 raise to minus 14 p K w is 14. It becomes instead of 10 raise to minus 14, it becomes 10 raise to 14 this is this becomes 10 raise to minus 7. But in pH scale it becomes 7 this becomes this is concentration is 7. And if there is no OH plus, it becomes 10 raise to minus 7.

So, K w is 10 raise to minus 7. So, there are 7 regions of OH minus 7 numbers up to 7 and 7 numbers for hydrogen. So, we say p H 7 do we divide p Kw 14 exactly so half of this is 7. So, pH 7 is a neutral solution anything above that 8, 9, 10, 11 etcetera. Then it is a basic solution and if it is less than that it is acidic solutions.

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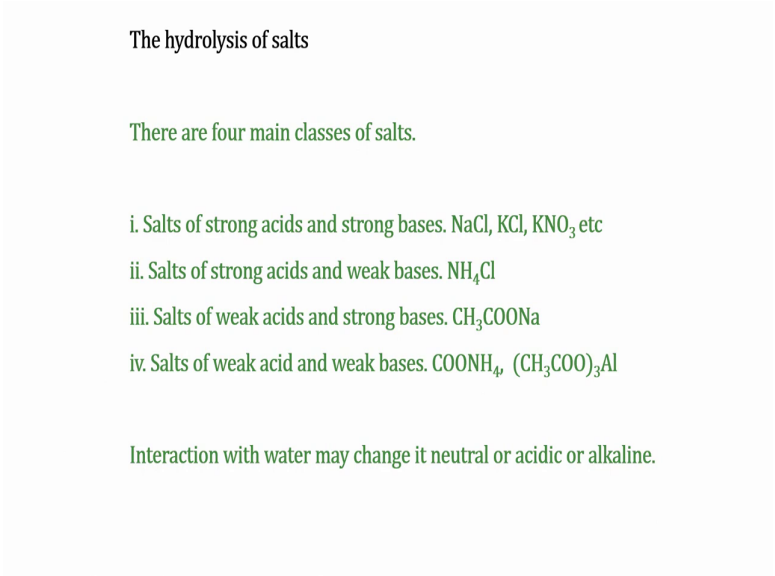

So, we have this expression, the next thing we want to discuss is about the hydrolysis of the salts. So, what kind how many salts are there? There are n number of salts thousands of salts. But many of the salts dissolve in water and that process is known as hydrolysis. So, I can have there are four kinds of salts, salts of strong acid hydrochloric acid you all know.

So, a salt of strong acid like sodium chloride, potassium chloride, potassium nitrate etcetera. And, that is sodium chloride they are all salts of strong acid and strong basis ok. And then salts of strong acids and weak basis are there ammonium chloride, ammonia is a weak base chloride is a salt of strong base. So, I have here salt of strong acid and weak base ammonia is a weak base.

So, sodium chloride weak base and strong acid strong base sodium sodium hydroxide is a strong base, hydrochloric acid is a strong base. So, NaCl is a strong base salt of strong acid

and strong base. So, KCL also dittoKNO3 it is salt of nitric acid here I have salt of strong acid and weak base you remember like this. And then, salt I can have salt of weak acid and strong base CH3COONa; this is a strong base if I make a base out of this add a OH it becomes a very strong base, CH3COO minus is a weak base weak acid.

Then I can have salts of weak acid and strong base weak acid and weak base, ammonium acetate CH3 COONH4 or CH3COO thrice aluminum acetate; these are all aluminum is also very weak base acetic acid is also a weak acid. So, I have salt of weak acid and weak base. So, interaction with water of all such salts of all the salts may change it to neutral or acidic or alkaline any of these things is not it. Because, they all they are all going to dissociate in water.

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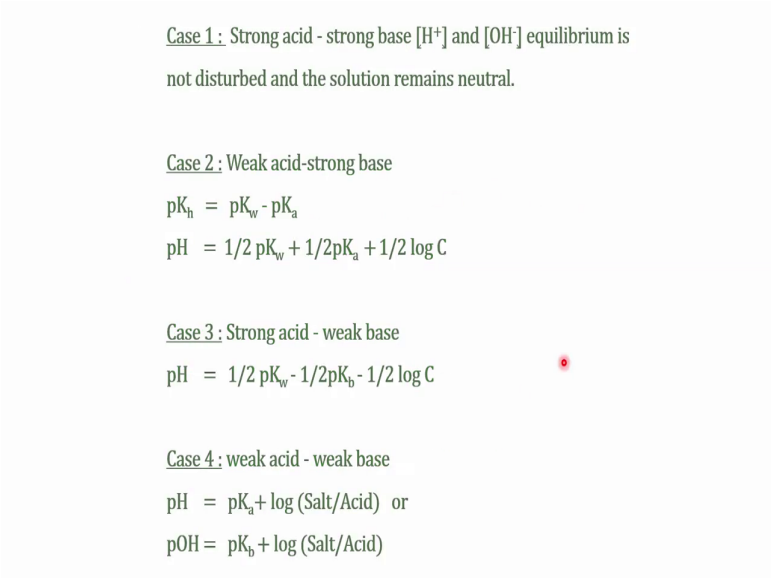

So, I have a case 1 here strong acid and strong base, that is H plus and OH minus ion equilibrium is not disturbed and the solution remains neutral. If I take a strong acid and strong

base salt of a strong acid and strong base, I have only H plus and OH minus ions are not disturbed.

So, NaCl where is H plus and where is OH minus in NaCl? Nothing so, N a plus and Cl minus will be there so, the p H will remain constant it will not change if I put it in water. So, but if I take weak acid and strong base salt then what happens? p H would be the half of this p K w that is dissociation constant of the water and dissociation constant of the acid plus 1 by 2 log of concentration of the salt. So, there is a certain amount of derivation of this equation in the book by Vogel third edition quantitative inorganic chemistry. And this expression is usually used to determine the pH of a solution containing a salt of a weak acid and strong base.

Here if I know the concentration of the salt, I can this is the this data p K w and p K a are available from database, p K w is always 14 you know, so half of p K w is 7. So, I can always calculate what is the p H. p H measurement is a day to day affair in all chemistry labs and pollution control labs.

So, it is in whatever you do you whatever salts you have the one of the activities to find out the p H of the solutions. So, if I have a salt of strong acid and weak base, I can write an equation expression like this 1 by 2 p K w minus 1 by 2 p K b minus 1 by 2 log C that will give me the p H. That is if I know the concentration of the salt I can simply calculate the p H and check whether it is correct or wrong.

So, I do not have to go to a laboratory to check the p H, if you are tell me that you have dissolved so much salt, we a salt of strong acid and weak base. So, it is a another way of putting it, then I have case the 3; that is weak acid and weak base, here also I can write p H is nothing but p K a logarithm of the ratio of salt to acid. Weak acid weak base you know or salt to acid that will give me p OH. That is just like p H we can write p OH and p K b, if I know I can write poo find out what is p OH whether it is 9 or 8 or something like that.

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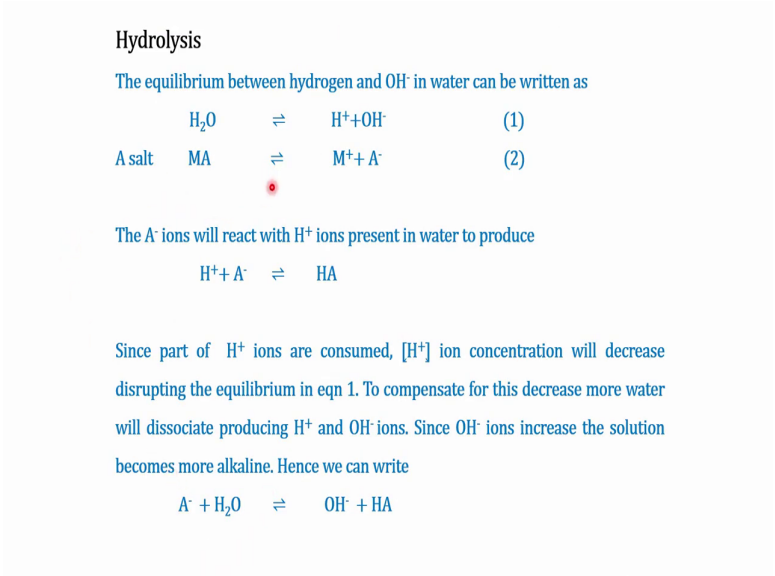

So, we are going to discuss about Hydrolysis. What is Hydrolysis? I am writing H2O plus has H plus and OH minus and I can write a salt MA as M plus and A minus M represents metal, it maybe sodium potassium or anything A maybe acetic acid or any other salt. So, the A minus ions will react with H plus to give me H A, since part of H plus ions are consumed H plus ion concentration will decrease, part of H plus is consumed so, HA is 1 this is undissociated so, the pH should degrees.

So, disrupting the equilibrium in equation 1; so, to compensate for this decrease more water will dissociate producing H plus and OH minus ions. Since that Le Chatelier principle again since OH minus ions decrease the solution increase the solution, solution becomes more alkaline. Hence we can write A minus plus H2O going to OH minus plus HA. The reverse reaction in this case is more predominant that is what I am trying to drive.

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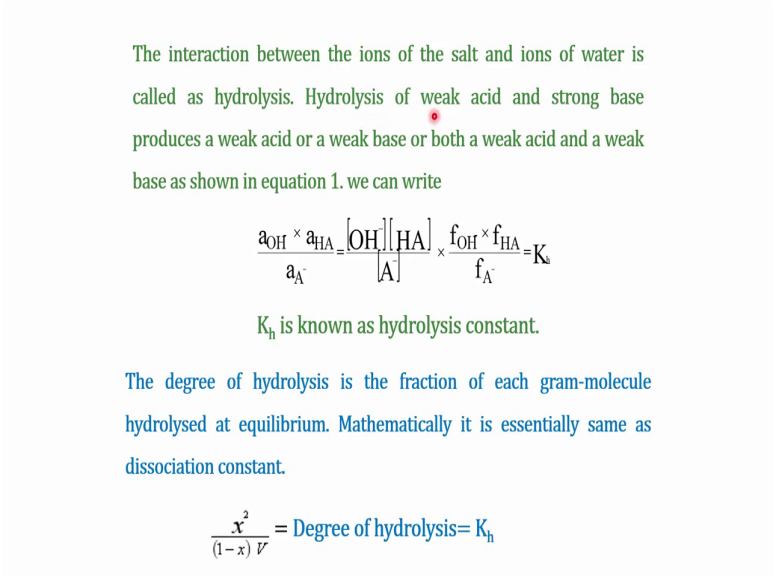

So, the interaction between the ions of the salt and ions of water is known as hydrolysis. So, the hydrolysis of weak acid and strong base produces a weak acid and or a weak base and or both a weak acid and weak base we can write a OH into a HA divided by a A minus that is concentration term this is f OH into f HA that is a activity coefficient, all these we had discussed earlier.

So, the degree of hydrolysis is the fraction of each gram molecule hydrolyzed at equilibrium this is the definition. The degree of hydrolysis is the fraction of each gram molecule hydrolyzed at equilibrium, mathematically I can write a similar expression like a dissociation constant; that is x square divided by 1 minus x or into V that is the degree of hydrolysis that is symbol is K h.

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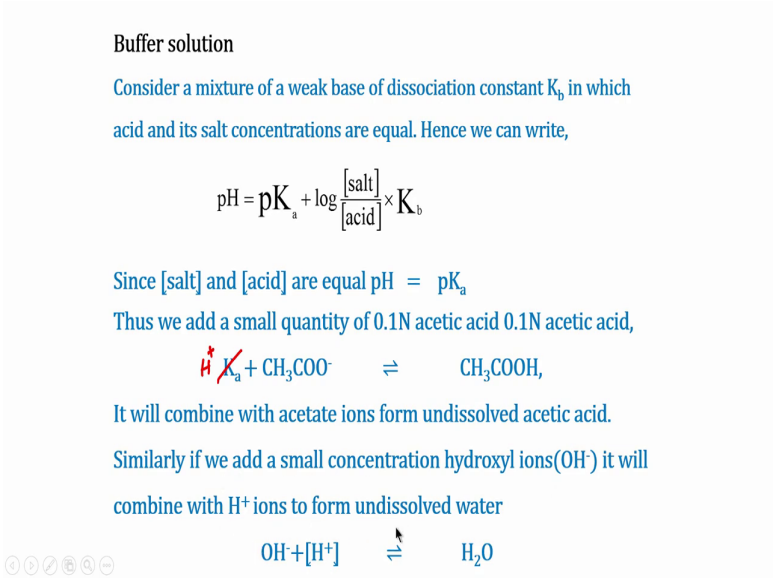

So, degree of hydrolysis leads us to the situation of Buffer solutions. So, what is a buffer solution? We consider a mixture of weak acid or a weak base dissociation constant p H is equal to p K a plus log of salt or acid into K b. So, salt and acids are equal p H is equal to p K a. So, we add a small quantity of 0.1 normal acetic acid, then K a plus CH3COO minus will become CH3COO H here it should be H plus please correct this. Here it should be H plus.

So, it will combined with acetate ions from undissolved acetic acid. Similarly, if I add a small concentration OH minus ions it will combined with H plus to form undissolved water. So, in affect the p H remains unaffected.

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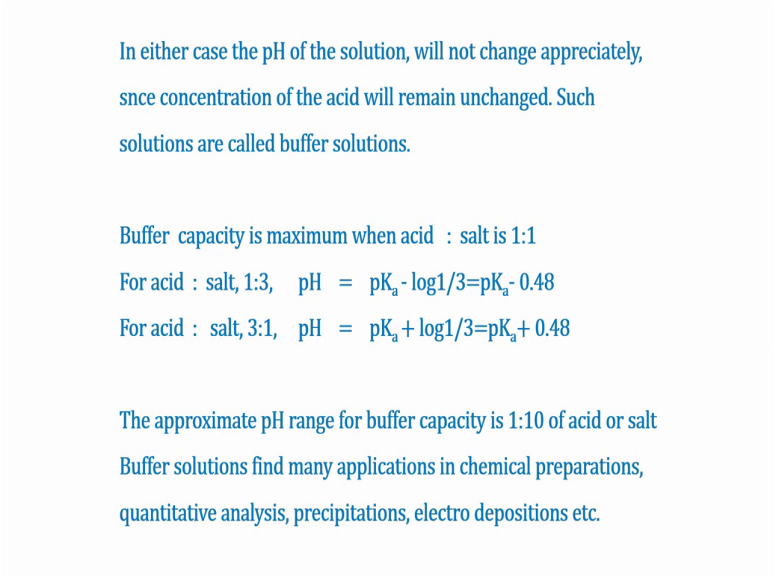

So, in either case the p H of the solution will not change appreciably, since the concentration of the acid will remain unchanged such solutions are called buffer solutions.So, buffer capacity is maximum when acid to salt is 1 is to 1 ratio; for acid to salt 1 is to 3 p H is given by this expression p K a log of minus log of one third for acids it is p K a plus 0.48.

And the appropriate approximate p H range for buffer capacity is if you add 10 times acid or salt buffer solutions find the p H will not change appreciably. The buffer solutions find many applications in chemical preparations, quantitative analysis, precipitations, electro deposition etcetera.So, here we we come to the end of our general chemistry introduction to electrochemical techniques. And from the next class we will start looking at the electrochemical techniques in particular.

So thank you very much. We will continue our discussion in the next class.