Course on Analytical Chemistry Professor Debashis Ray Department of Chemistry Indian Institute of Technology Kharagpur Module No 03 Lecture 12: Chemical Equilibria (Contd.)

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Hello, welcome back to this class. So in the previous class what we have seen that we are producing electrolytes. Okay? Electrolytes. So we all know that it has some relationship with electrolysis and how the inorganic samples, that's why we are very much interested to know that what are the different inorganic samples, or inorganic solutes because most of them are producing these ions. So if you have, we all know that NaCl is there. So this NaCl Na plus and Cl minus it will give.

And even in the solid state, we all know that they are present as Na plus and Cl minus. And when we put water, they will be separated by Na plus or read by so many water molecules. Similarly this Na plus is also surrounded by so many molecules. Similarly, this Cl minus is also surrounded by many water molecules which is unlike from that of our any other organic samples such as glucose, that means C6H12O6. If we write, from our schooldays we are knowing all these things.

Even if we write the simple benzene molecule, Uhh so even if we write the corresponding phenol molecule, so there will be some amount of this corresponding dissociation because this we all

know that this can be dissociated by phenoxide ion and H plus. Similarly, some salts, that means the organic salts are there and we know from our schooldays the the typical definition of these salts. So that is why something will come again and the picture that H plus and HO minus will be there.

So from this thing, that means this is your medium, this is your water medium and if something is giving you H plus, and something is giving you HO minus, so acid and the corresponding base, if they are forming or reacting together like that of our H plus B forming C plus D, similarly acid plus base can react, giving rise to salt plus water. So in the same fashion, you see they are also the product of those reactions.

That means when acid and base is reacting, so if we go for, how to determine this thing from the very base this point from this very point, what you can understand is that if these 2 are reacting, some acid is reacting, some base is reacting giving salt plus water, so that is the thing that you can have the corresponding reaction what we call as the neutralisation reaction. So if we have the stoichometric amount of A plus B is reacting giving C plus D. So salt plus water is there.

So one acid and one base is giving rise to the corresponding salt. And the same salt what we're talking about, whether you have the inorganic salt like NaCl or some organic salts like that of our sodium acetate what we all know, CH3CO2Na. So is that corresponding sodium acetate. So this is also a organic salt. So how they are going to react basically when you have sufficient amount of water? So this NaCl is giving in the water.

This we are putting inside this particular water. So whether all of them produce ions and how many of those files are forming over there, so that is very interesting observation to know. So when we have these electrolytes are there, so they produce basically ions. So that is why we are all very much interested to know if some white powder is given to you and you are asked to analyse both of them for this white powder of sodium chloride, our common table salt what we get in our home also, in our kitchen and everyday, we consume it.

But if a white powder is given to you and you are asked to go for the corresponding analysis, so this when we dissolve in this water, so this is water you have, so these are there, that means if we know that the sodium chloride is a very good electrolyte which can conduct electricity and also it can produce ions. I saw what? Ions are nothing but Na plus and Cl minus. So these electrolytes basically, so you can have these electrolytes.

So these electrolytes, they are basically producing ions. So how many of those ions are forming and what are those typically ions? So that basically in this particular process is known as the corresponding, one will be strong and another will be weak. How do we know that? So this is the thing. That means when we put water. That means the complete dissociation of this Na plus aqueous plus Cl minus aqueous.

So basically is going towards the right-hand side and almost 100 percent. So these organisation, that means is definitely a strong electrolyte and this giving Na plus and Cl minus. Similarly, there is also not only this NaCl because we are getting this NaCl from the reaction of HCL which is your aqueous hydrochloric acid. So aqueous hydrochloric acid, when we react this particular one, this same thing we are trying to get, that means acid plus base giving rise to salt plus water.

So when this reaction is taking place and this basically gives us the corresponding species. So we get salt and water. So this should also be a strong electrolyte. So HCL is also a strong electrolyte and when both of them are very strong, we know that this particular one, if HCL is strong, so several inorganic acids we can have. We can have a big list in any book, any of the books. So I can give you one example of the book.

Again, the only textbook I am following everyday and giving the reference, you can have that book also. That scoops analytical chemistry book. So that basically give us some idea that if this is strong, this is also strong reacting a salt. So salt will also be a very good electrolyte. So salt what was there, salt will also a very good electrolyte and they completely dissociate and we can test for Na plus and we can test for Cl minus.

So what we get as the strong electrolytes? All inorganic salts or the most of the salts are basically will fall under this category. So this is under this category, NaCl is under this particular category. So they are basically strong salts, strong electrolytes and the salts. So basically, that gives us that particular information what we do, our inorganic lab classes. So inorganic lab classes we all know that the qualitative analysis what we call also, the salt analysis.

So this particular thing is the salt analysis and all these things. So if the salt is not so weak Uhh strong, so what will happen? So initially, by looking at those salts, if we get a white powder, you try to expect or you try to suspect that is a sodium chloride but it may not be sodium chloride. It can be simple mercury chloride. So whether that mercury chloride or any other form of mercury chloride we all know that is a mercurous chloride which can also be a strong salt.

Similarly, there will be a weak one. So there will be some weak acid. So if we just simply because we are since we are talking about the inorganic lab, we are having these acids because we are talking all these acid and the base. So in a particular inorganic chemistry lab which we are basically dealing with the qualitative analysis and qualitative analysis very smartly coming under the category of analytical chemistry. So the salt analysis of this inorganic lab is that whether we can have this strong acid like that we can have the also the inorganic acids as the weak acids.

So inorganic acids, so what are those inorganic acids which can be your weak acids? So these weak acids and several other categories what we will be looking for, so that gives us a very simple idea or are very basic idea that what are the salts we are handling. So if we are handling sodium chloride and at the other point, if we are handling sodium acetate, so if we can have a very good taste or the qualitative taste to identify these as the sodium, so if we have in the medium, that means if this is a salt, so is our weak acid and strong base salt as we now it is forming from acetic acid and sodium hydroxide.

So that particular salt also is very nicely dissociated in water. So giving rise to the corresponding test of Na plus and acetate ions. So if we selectively go for the test of sodium ion, so sodium iron from sodium acetate or sodium ion from sodium chloride we all know that we can have a flame test like that, a golden yellow flame can be developed if we directly introduce a sodium salt which is a strong electrolyte, that means which can be either a salt of inorganic acid or a salt of organic acid or rather we can say that it is a sodium salt of an inorganic acid of HCl or a sodium salt of acetic acid.

So they can respond to the corresponding flame test. And if they are also present in the solution and the solution test we can have, a wet test. So this we all know, which we call as a dry test. And if we can have something where we can go for the wet test also. So both are dry test and wet test, so the initially or the preliminary investigation tell us that we can identify initially the Na plus as through this particular dry test because the flame test is a dry test is there is no solution preparation, no other techniques, and other reagents, you directly insert that from the tip of the platinum wire or the nichrome wire to the clue to the Bunsen burner flame.

So this basically is the true sense that whether we are able to detect it in this particular form and how the different electrolytes we can have and what are the different salts we can have.

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So this composition of these aqueous solutions tells us that particular thing once again that if you have a solution of sodium chloride we should know that there are ions of Na plus and ions of Cl minus. Similarly if we have a solution of sodium acetate, we can have the corresponding ions of Na plus and acetate ions. So electrolytes are nothing but the solutes which form ions when dissolved in solvent which is our water and hence conducts electricity.

So this is the sample definition for all these things and we are looking for those electrolytes and life sodium chloride, like hydrochloric acid, they ionised completely in solution almost completely, 98 percent or 99 percent ionisation can take place which we will consider as the strong electrolyte. So the reverse of that, that means the corresponding weak electrolytes, they ionize partially in the solution. That means what is happening for the A plus B reaction giving rise to C plus D, so most of thing is going towards the right and in case of weak electrolyte, everything is in the left.

So only some part is getting solubilised. So weak electrolyte, we should also be very much careful to handle that particular thing that how we can test those things. So the concentration of those ions which can come from those electrolytes will be less. So this concentration would be different. So for those electrolytes, we can have some other technique to identify all these.

Strong	Weak
1. Inorganic acids such as HNO ₃ , HClO ₄ , H ₂ SO ₄ , HCl, HI, HBr, HClO ₃ , HBrO ₃	1. Many inorganic acids, including H_2CO_3 , H_3BO_3 , H_3PO_4 , H_2S , H_2SO_3
2. Alkali and alkaline- earth hydroxides	2. Most organic acids
3. Most salts	3. Ammonia and most organic bases
	4. Halides, cyanides, and thiocyanates of Hg, Zn, and Cd

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So classification, that is why we have the classification of those electrolytes, the strong and weak. So these we are talking. So is a big list from the textbooks that you have inorganic acid. So all this inorganic acids you can have this idea that most of you all know that this starting from your nitric acid, hydrochloric acid and all this to corresponding HClO3 and the chloride acid and the bromide acid and the perchlorate acid as well. They are inorganic acids which strong enough.

Then in terms of those as the week acids in this particular category, so they are also weak acids, as well as they are weak electrolytes. They are not dissociated much. So many inorganic acids including the simple carbonic acid, just now what we are discussing about the mammoth cave incident of the mammoth what is happening there. For the recrystallisation of calcium carbonate, rather dissolved carbon dioxide is forming nothing but your carbonic acid.

So this H2CO3 is there. So this carbonic acid is unlike your sulphuric acid. So this carbonic acid is not dissociated much. So you can have more and more amount of this bicarbonate ion. So though is giving H plus but most of these things are converting in the form of HCO3 minus. So

in presence of carbon dioxide and water, what is forming? Some amount of H2CO3 is forming but in presence of that corresponding due to that dissociation, we have only some ions only.

So this is the thing. That means we can have this, the weak dissociated form. Then we can get this that the corresponding H3BO4, the boric acid, then phosphoric acid, then H2S. But wherever we have H which can give rise to H plus when bound to sulphur, when bound to phosphorus oxygen and bound to carbon and when to boron and when bound to sulphur. So when this is not sulphuric acid, this is sulphurous acid. When sulphurous acid is there, when SO2 is dissolved in water, we get H2SO3 and which is a weak acid.

So why this H2SO4 and H2CO3 we are talking differently and how we can find them in the form of this reactivity pattern?



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So what we find that if we have H2SO4 and we consider this H2SO4 as the strong electrolyte, so this definitely can go for H plus and HSO4 minus. So this particular one, so this is a strong acid. So the 1st type of dissociation, that means removal of 1st proton from sulphuric acid is 1st and it is going towards on the right-hand side so is a strong electrolyte. But this one if you the see that this is not so easily can dissociate between H plus and SO42 minus then this can be a weak electrolyte.

So in actual practice also, this is also a weak electrolyte because the dissociation of this HSO4 minus to H plus and SO42 minus is not so easy, is a difficult process. So this H2SO4 minus HSO4 minus is a weak electrolyte. But in case of your H2CO3 if we get, that means this is not so big. So this is a very big one. Here also, since this is going, so this is on the right-hand side the left-hand side is a small one.

So the rate of the forward process or the rate of the forward reaction is very high. So here rate of the backward reaction is very high. So we can have the corresponding rate processes or the rate of the reactions which is ultimately controlling the corresponding K value, the equilibrium constant which is a ratio of these 2 rates, the rate of forward reaction and the rate of backward reaction. So when this is giving us H plus and HCO 3 minus, so this is already weak, so this is further species.

So it is only remain as HCO3 minus. So most of the cases, is very difficult to get H plus and CO32 minus from here. But the reaction what is happening over there, we all know that we also produce some our body, carbon dioxide and we exhale out that particular carbon dioxide also for this particular hydration reaction of carbon dioxide giving rise to this bicarbonate anion. So this particular one, so this is a weak one, this is also weak. So this is a weak acid.

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Strong	Weak
 Inorganic acids such as HNO₃, HClO₄, H₂SO₄, HCl, HI, HBr, HClO₃, HBrO₃ Alkali and alkaline- earth hydroxides 	 Many inorganic acids, including H₂CO₃, H₃BO₃, H₃PO₄, H₂S, H₂SO₃ Most organic acids
3. Most salts	3. Ammonia and most organic bases
	4. Halides, cyanides, and thiocyanates of Hg, Zn, and Cd

So this polypretic acids, therefore give rise some idea about this thing, that means if your phosphoric acid is not so strong like your nitric acid or hydrochloric acid, so again you can have the different steps or the different stages of the dissociation. So one proton will come out and the next proton can come out also from this. So these acids basically can compare.

So comparison of these acids will tell as something that if we are talking about in terms of the corresponding estimation of phosphorus, estimation of boron and estimation of sulphur through the involvement of these acids, either you consume those acids, or reproduce those assets from there. Similarly in terms of the corresponding hydroxides, all of the alkali and alkaline earth hydroxides are strong enough like that of your sodium hydroxide and calcium hydroxide.

But the corresponding one, that means weak electrolytes of this category will be the most organic acids as I just told you that the corresponding acetic acid and all other organic acids, similarly the benzoic acid and all other, so they are of that particular weak category. So these most salts whether you have inorganic salts or whether you have a organic salt, the most salts will be of this category. They are strong electrolytes compared to your ammonia and most organic bases like triethylamine or trimethylamine, they are weak.

Then the this category basically will be very much careful about knowing this particular category when we talk about something which are not so ionic in nature. That means the 3D, 4D and 5D

ten series which is zinc, cadmium and mercury. And their corresponding source, that means the halide, that means zinc chloride, cadmium chloride and mercury chloride mercurous as well as mercuric, they are cyanides and thyocyanides. When they are dissolved in water, I did not that they will be dissociating like sodium chloride or calcium chloride. They are not dissociating much. So they are basically a very weak sample. So that is why your corresponding sample of zinc chloride or corresponding sample of mercury chloride we are not handing in most of the time for getting the corresponding estimation of chloride from these salts. Okay?





So what we are talking? We are just discussing about the typically acids and the bases what we can have. So quickly, we should go through, this is some process of recapitalulation but we are talking all these things very easily and very nicely that what is basically your acid, a substance acts as acid and when it can act as a acid? Because you can have the also the presence of the corresponding base. Even if you have the solution water which is giving us H plus as acid and which is also giving rise to HO minus which is also a base.

So in presence of the corresponding base, a particular species or particular compound or a particular acid can sow its acidity. So this concept we know that the Bronstead-Lowry definition or the concept is based on the corresponding proton donation and the proton acceptance. So if we talk in terms of the corresponding titration, that means if we talk in terms of the corresponding

reaction between hydrochloric acid and the sodium hydroxide, that means the neutralisation reaction what we can study by neutralisation or the neutralising titration reaction.

In presence of some indicator we can do very nicely because your hydrochloric acid say can give the proton for the reaction and your sodium hydroxide or any other base, it can be definitely a strong base which can accept the corresponding proton. So when this particular thing is happening, we basically get the corresponding other thing, that means we know that those now we have considered this is the ammonia and most other organic bases as the weak base.

So if you have a weak base which is your base 1, and this is base, that means when it reacts with some water, it definitely give rise to the corresponding conjugate acids. So like that of our thing what we are discussing so far is the formation of A plus B giving rise to C plus D, similarly the proton donation or the proton acceptance is also a similar type of equilibrium process. So acid-based reactions are all of that equilibrium type. Only difference is that which particular species is accepting what.

So when ammonia, that means ammonium hydroxide we are not talking anything else. We are just talking ammonium hydroxide. So base, so in presence of that particular base, so definition is that if substance acts as a acid only in presence of a base. So similarly this particular substance, that means ammonia NH3 can act as a base if the acid is present. So in presence of water, ammonia is a gas, we all know. So the ammonia, the ammonia solution which is nothing but your ammonium hydroxide we call or the aqueous ammonious in presence of water.

This water molecule can function as a acid. That means it is the proton donor which can donate the proton to ammonia, forming ammonium ion and the hydroxide ion. So if we know, that means the starting point that what sort of base and what sort of acid we can have, so the corresponding strength of this conjugate form, that means the conjugate acid and the conjugate base we can talk about, we can think about and we can to realise about and we can plan accordingly for the corresponding neutralisation reaction or the titration based on acid and base.

So base 1 is giving rise to the corresponding conjugate acid 1, similarly acid which is 2 is giving rise to the corresponding base 2. So the identity is 1 and 2. The subscript written below base and subscript written below acid, they are one type. So if we do not write the top of these things, so

from these we can write, so these 2 are related one one related, and two two are related in terms of the corresponding proton transfer reaction.

Similarly, in a similar fashion, that means at the same time that when your water can also function as a base also because it can function a dual role. It has a typical name for that also that this water is your acid but now we are using something else which is a stronger acid compared to water molecule. So this acid 2 now what we can have, this acid2 is nothing but your nitrous acid. So this nitrous acid can now react with your water. That means water is functioning as our base forming H3O plus.

So water is your now proton acceptor. In our previous example, this water was your proton donor, now you have a proton acceptor giving rise to Hydronium ion which is your conjugate acid. I am giving the nitrate ion as your conjugate base. So in solution, if we are able to produce all these things because we all know that the ammonium hydroxide is a reagent and insitu in some of the reactions in the test to be know that we can produce nitrous acid from the reaction of the nitrate ion.

So these all 4 on the left-hand side you can identify nicely by the help of the analytical chemistry knowledge. Similarly all these ions on the right-hand side, you can have and these are related to the corresponding chemical equilibrium process or acid-based equilibrium process. So acid by definition can give up the proton and conjugate base can accept the proton. So how you get the corresponding conjugate version of the acid and the conjugate version of the corresponding base.

So the base accepts proton to form the conjugate acid capable of giving proton. So this is the statement which is useful also. Your ammonia is a base. So when it accepts proton it is the ammonium ion. So it has become an acid. So how readily we can get the corresponding proton from the ammonium ion or say hydronium ion, that we also can see depending upon the relative acidity. So the corresponding pair, that means the conjugate pair of the acid, or the conjugate base pair also we can have some knowledge.

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If one is weak on the left-hand side, the other one, its conjugate version on the right-hand side would be strong because in one way you can have some ability to transfer that particular proton. So we get now the nice example, the water just now we are talking that we are putting water in both the 2 reactions. In one way, we are it is utilised as the proton acceptor, in another way, it is utilised for the proton donor. So it is a amphiprotic species. So amphiprotic species is such that it can have some dual role.

It can accept the corresponding proton or it can donate the proton. So you see what is your anion, what we are taking is H2 PO 4 minus. So this H2 PO 4 minus which has been derived from the phosphoric acid, so this phosphoric acid derived anion is now reacting with this which is again derived from your water. So hydronium ion is derived from water and this H2 PO 4 minus is also derived from the phosphoric acid giving rise back to these 2 things. That means when these 2 are reacting, we are getting back acid 1 and base 2. So this is base 1 acid 2 and acid 1 base 2.

So if this is reacting with the base, is giving rise to something else. So what is this? So this we are looking at, the species. This H2 PO 4 minus, so H2 PO 4 minus, it can react with something as it is reacting with the hydronium ion. So there it is functioning as the base like that of our water molecule itself and in the other case when you have this base as the hydroxide ion, the hydroxide ion is a strong base.

So this cannot function as a base. So it will function as a base because you have something where you can get or remove the proton because the species formula, the species the nature of the species which is H2 PO 4 minus is telling you that you can remove further, some amount of this H plus which is directly attached to this O. So this OH bond is there and we are able to dissociate that giving rise to HPO42 minus and water back.

So if it has both acidic and basic properties, you get a amphiprotic species like that of water, like that of H2 PO 4 minus. So these are the examples. So another example what we find that ammonia is reacting with methanol and methanol is reacting with the corresponding nitrous acid. So these 2 are the common things. Here also, these 2 were common. So in one case, it is functioning as a base, in another case, it is functioning as an acid.

Similarly here also, one is functioning as an acid and another is functioning as the base. So all these cases, that means whenever we write some reaction, we should be very much aware of the fact that what are the other species we are producing in the medium. That means when we do some chemical reaction, we should all know that suppose somebody reaction we are doing, some complexation reaction we are performing in methanol medium and that methanol medium in presence of some other base, not only your ammonium base but also some other organic base, like that of our triethylamine.

So these reaction is taking place definitely. So without talking in terms of the metal ion and the ligand, we all know that they are giving you the corresponding complexation reaction. What is happening that this particular ammonium ion, availability of this ammonium ion and this methoxide ion, CH3O minus is there. So these can bind to the metal ion itself and if more number of this is bound to the corresponding metal ion centre because we all know, the metal ion alcoxides are forming, this is methoxide.

So some methoxides will be forming and the more number of methoxides are accumulating around the metal ion, you have overall a negatively charged species. And that can be counterbalanced by the corresponding positive charge of the ammonium ion. So this simple reaction that any organic base in presence of this methanol can give rise to something else, that the the production of other cationic form and the anionic form. Similarly when acid is your nitrous acid, we get just now this example of this nitrous acid reaction with water. So this particular one also like that of your water molecule, your methanol is also can be protonated and you have the corresponding nitrate ion. So what are the methanol like species? Then what are the water like solvents? So it is a very good solvent. So solvents, water is you have, solvent methanol you can have.

So this also give rise to some idea that what are the medium you would be choosing for a particular type of reaction and what we are doing because in most of all these cases because mostly we will be Uhh considering the corresponding medium where we are talking in terms of the corresponding aqueous medium. But alcoholic medium also we should know because in some interesting organic reactions we know that they are only going in some medium which is alkaline medium and the corresponding alcoholic mediums, the alcoholic KOH is a reagent we all know for any organic transformation.

Similarly alcoholic KOH and aqueous KOH, so they both can be functioning in a different way but what are the ions and what are the species present in this particular reaction for the all these things, that we should know. So we get water, we get methanol. Similarly other alcohol, ethanol they are common amphiprotic solvents.

So when we choose that particular amphiprotic solvent for this, getting this particular type of anions, we should also be very much careful that what are the corresponding species or the ions because depending upon the nature of these, you see that with respect to your methanol molecule, you have this particular one, so with respect to your methanol molecule, if we consider that both these 2 methanol methanols are your solvents. So in one case, it is functioning as acid, in another case, it is functioning as base because the presence of these 2, that means you have ammonia which is a strong base compared to your methanol, so that is why it is your base.

And your nitrous acid which is functioning as a acid, so presence of these things because ammonia, it can be liberated from any other source or the nitrous acid insitu can be prepared from the solution. So the nature or the characters of this methanol which can be a solvent also can change very quickly from form to the other. (Refer Slide Time: 34:16)



So all these things just now we can summarise these things that you can have is one form that means if we have the self reactions, that means water is reacting with water and the methanol is reacting with methanol,, we get these 2. So what we find is that you have a amphiprotic solvent which can go for auto protolysis, that means self ionisation to form a pair of ions. So this you cannot stop basically.

So you can have the self ionisation process that if you have a mixture of these things, that means within this some part, some dissociation can take place. They are weak electrolytes, as per our definition, they are weak electrolytes but you cannot stop this particular one, they all are in equilibrium form. So a very few amount of this, that means a very small concentration of this automated form of water and the protonated form of methanol is present.

So depending upon this concentration of this protonated form of these 2, you can have the corresponding bases, that means some amount of this hydroxides and some amount of this methoxides I will be there. So that is the typical definition for the corresponding amphiprotic solvent. So what are the amphiprotic solvents and what we should know about the corresponding auto protolysis. Since we are talking about the transfer of the proton, similarly can be a very good solvent for a chemical reaction. Okay, thank you very much.