Chemical and Biological Thermodynamics: Principles to Applications

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Lecture - 33
Acids and bases and equilibrium concepts

Last few lectures, we have dedicated to the discussion of equilibrium, equilibrium constant and effect of various factors on the value of equilibrium constant. Being a very important topic because it not only allows us to answer many questions qualitatively, but makes the process quantitatively; this concept is very important.

From chemical systems to biological systems, the concept of equilibrium and equilibrium constant is required. For example, when we talk about the biologically important systems maintaining the p H becomes very very important and therefore, the concept of p H also becomes very very important.

In today's lecture, we will focus our discussion on acids and bases and equilibrium concepts; as well as we will discuss a little bit about p H and how p H is related to activity of the hydronium ion or can p H be related to the concentration of the hydronium ion; let us discuss about these matters.

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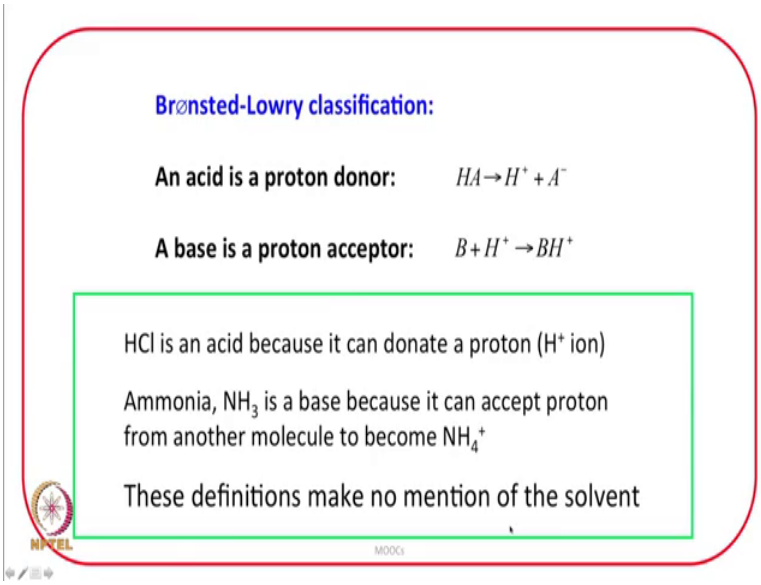

First of all, let us talk about the Bronsted-Lowry classification of an acid. Let us take a look at the slide; according to Bronsted-Lowry classification, an acid is a proton donor; a

substance which can donate a proton to another molecule will be classified as an acid according to Bronsted-Lowry classification.

As seen in this slide in this equation HA is an acid because it is a proton donor and a base is a proton acceptor; that is a substance which can accept proton from another molecule is a proton acceptor and it acts like a base. So, in the first reaction HA going to H plus; plus A minus it is donating proton. So, therefore HA is an acid and B is accepting a proton therefore, B is a base.

Let us discuss a little more about this HCL according to this classification is an acid because it can donate a proton that is hydrogen ion. We know that when HCL is dissolved in water, it dissociate into H ions and chloride ions. So, therefore, HCL is capable of donating a proton to another molecule and that is why let us take a look at slide.

The statement that HCL is an acid because it can donate a proton H ion is called as a proton. If we take another example that is of Ammonia; ammonia is base because it can accept proton from another molecule and it can form ammonium ion. So, these examples justify the definition of Bronsted-Lowry classification that an acid is a substance which can donate proton like an HCL; HCL is donating a proton. So, HCL is an acid and ammonia can accept a proton; therefore, it is a base.

In the Bronsted-Lowry classification there is no mention of the solvent. The solvent can be any and if we are talking about the biological systems. The biological systems are mostly in aqueous media; therefore, the discussion of water as a solvent becomes very very important. In most of the examples which I am going to take in further discussion we will take water as the solvent because many reactions take place in aqueous media especially the biologically important reactions take place in aqueous media.

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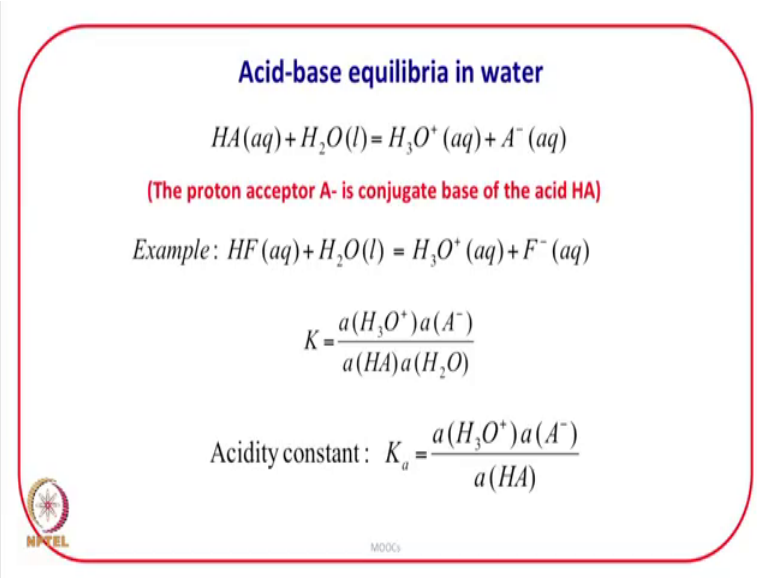

So, let us talk about Acid-base equilibria in water; let us consider this equation or this reaction; in which HA is interacting with water and donating a proton to water forming H 3O plus and A minus all are in aqueous solution and this H 3O plus is called hydronium ion; what HA has done? It has donated a proton to water and water has become hydronium ion, it has become charged and left over is A minus. So, we say that HA is an acid and A minus becomes the conjugate base of the acid HA; acid is HA and its conjugate base is A minus; this is how we will classify these.

An example of this type of reaction is dissolution of H F in water H will donate its proton to water and it will form H3O plus and F minus. Here H F is an acid and F minus that is fluoride minus is its conjugate base. So, this dissolution of H F into water what it has produced, it has left to the formation of hydronium ion and it has formed fluoride ion.

Now, we have thoroughly discussed in previous lectures; how to write an expression for equilibrium constant. We will apply that concept over here and write an expression for equilibrium constant. How do we write equilibrium constant? Is equilibrium constant is equal to the product of activities of the products raised to the power by their stoichiometric number, divided by the product of the activities of the reactants raised to the power by their stoichiometric numbers.

Keeping that in mind; let us go to slide and write an expression for the equilibrium constant for this process; this reaction. The equilibrium constant for this reaction is equal to K is equal to activity of hydronium ion into activity of or let us say we write for this upper reaction. K is activity of hydronium ion into activity of A minus divided by activity of HA into activity of water. This is an expression for equilibrium constant for this reaction; this reaction corresponds to the dissolution of an acid into water and also it is worth noticing again that equilibrium constant is expressed in terms of the activities water is an excess over here.

Mostly when the solution is very very dilute; generally we deal in aqueous solution we deal with dilute solutions. And the activity of water is taken as 1 unity. So, by taking the activity of water as unity and consuming it with along with K equilibrium constant, I can write another constant which is called the acidity constant. When I convert this expression into acidity constant this A activity of water is consumed into this by treating activity of water to be equal to 1.

So, the acidity constant K A becomes activity of hydronium ion, into activity of A minus which is the conjugate base of the acid HA; divided by the activity of HA, we have taken activity of water to be 1. Acidity constant is a very important quantity because this acidity constant; as we will realize later on gives us an information on the proton donating power of a molecule, let us discuss further how it gives information.

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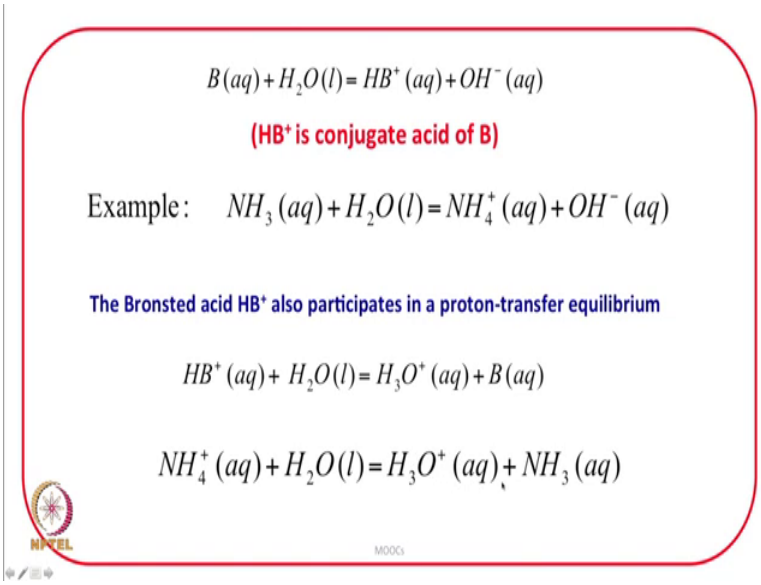

But before that; now let us consider a base; a base when dissolved in water, it will accept a proton from water and will form hydroxide ion. In the same manner, if B is a base then its conjugate acid is H B plus. So, once again it is worth noticing over here that when this base is dissolved in water then after accepting the proton H B plus; H B plus becomes the conjugate acid of the base b.

Let us take an example of this kind ammonia on dissolution with water, it will accept a proton from water; form ammonium ion and hydroxide ion and; obviously, here if N H 3 is a base, NH 4 plus is its conjugate acid. Ammonia acts as a base, ammonium ion acts as an acid and we will soon discuss whether this acts as a weak acid or it acts as a strong acid that we will discuss a bit later.

Now, what happens is since this NH 4 plus itself is an acid, so the Bronsted acid H B plus NH 4 plus is a type of an acid H B plus and H B plus itself can participate in a proton transfer equilibrium. Because as we discussed earlier H B plus or any molecule which can donate proton to another molecule will act as an acid. Therefore, if we have H B plus type of species in solution, which is bronsted acid can also participate in proton transfer equilibrium; as we can see in the next example.

H B plus aqueous plus water is forming H 3O plus plus b. So, you see what we have here is H B plus is donating proton to water and what we are getting is H 3O plus plus B which in the example that we took over here, the ammonium ion can lose the proton to water resulting into hydronium ion and ammonia.

So, the point to be noted from this slide is that when you dissolve a base into water; it forms its conjugate acid and that conjugate acid can further participate into a transfer of proton; proton transfer equilibrium and setup another equilibrium. That is you see that the Bronsted-Acid; whether you talk about H B plus or NH 4 plus, it will donate proton to water and will form hydronium ion; we need to keep all these kind of equilibria in the mind; let us take a look at the slide.

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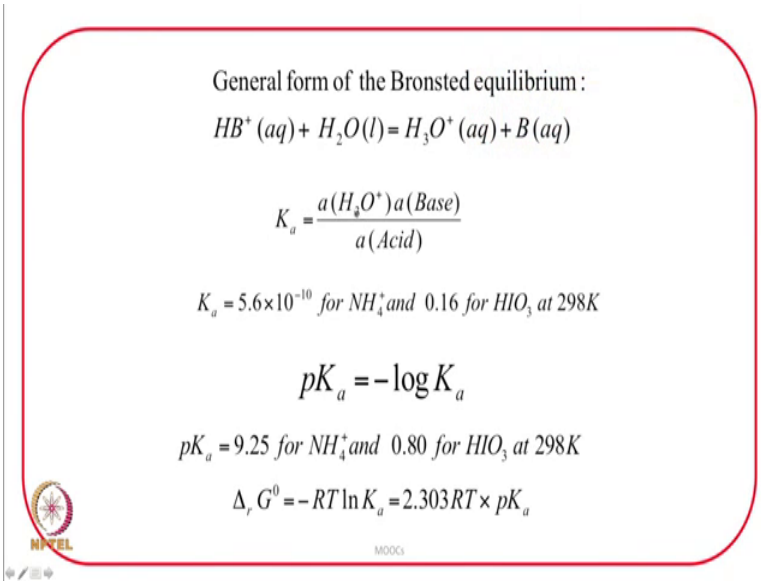

The general form of bronsted equilibrium is that you have an acid and you add water and bronsted acid will donate proton and you have this kind of expression, reaction. When we write an expression for acidity constant, it will be activity of hydronium ion into activity of the base, divided by the activity of the acid and we are taking the activity of water to be 1 because water is in excess.

K a is the acidity constant depending upon the type of acid, the value of K a is going to be different whether we are talking about NH 4 plus or we talking about H F or H I O 3; the value of K a is going to be different. Let us take a look at the slide.

The value of acidity constant for ammonium ion is 5.6 into 10 raised to the power minus 10 and the value of K a for H I O 3 is 0.16 at 298 Kelvin. Please note that K a; which we are calling as acidity constant is an equilibrium constant and the value of equilibrium constant does depend upon temperature. Please recall the Van t hoff equation; that whether the equilibrium constant will go up or go down in its value with increase in temperature; is decided by the exothermicity or endothermicity of the process.

So, going back to the slide; the values of K a have to be given at a specific at a particular temperature because as I said this K a is actually an equilibrium constant and therefore, it is temperature dependent. K a is very small you see 5.6 into 10 raised to the power minus 10 for ammonium ion and it is high compared to this 0.6 is very high. For H I O 3 at 298 Kelvin and since K a has been introduced, it makes a sense to introduce another simpler

quantity which is based upon K a and that is p K a; p K a is negative logarithm of K a this is log base 10 and when you substitute these K a values for NH 4 plus and H I O 3; what do you get? We get p K a is 9.25 for ammonium ion and 0.80 for H I O 3; you see there is a negative sign here and that takes care of the very small value of K a and since K a for ammonium ion was very very small; you see the p K a value is terming out to be very high.

So, we can make a general statement here if p K a is very high; the corresponding K a is going to be small. In other words, if p K a is very high or K a is very small; it is a poor proton donor, it is its proton donating capacity or ability to other molecule is not very good, not very high. So, you see here p K a for H I O 3 is small; very small compared to the p K a for NH 4 plus and that is why the K a value for H I O three is very high when you compare this value with the K a value for ammonium ion.

And since K a is an equilibrium constant and therefore, these values can also be manifested in delta G naught. Delta G naught is minus R T log K and if you convert this natural log into log base 10 and put minus log K a as p K a; do this transformation and substitute over here. We end up with this relation 2.303 RT; p K a. So, form p K a; we can also talk about the reaction standard reaction gives arising.

So, the concept of p K a or K a is very very important because essentially K a defines how much hydronium ion is present in the solution and how much of course, is the amount of base and acid also present at the solution.

Now, let us discuss autoprotolysis and p H water is a very important solvent. I have been highlighting the significance of water again and again; this is because although water appears to be simple, but when we try to look at the structure of water and see how the structure of water is altered when the solute is added to it; it brings complications and water is a very important solvent when we talk about biological systems; let us take a look at slide.

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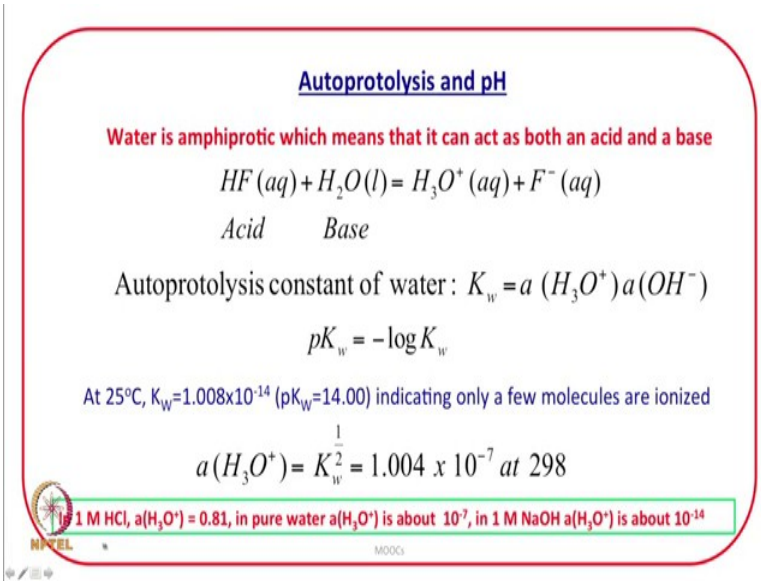

Water is amphiprotic solvent or amphiprotic molecule which means that it can act as both an acid and a base water.

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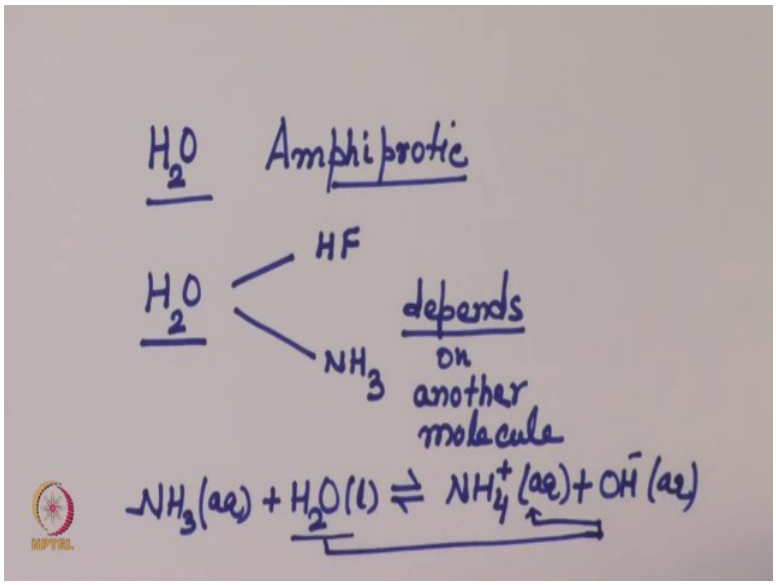

Let us take a look at; water it can accept a proton, it can also donate a proton. Therefore, it is amphiprotic that is what we are talking about; what this means is; if I take two water molecules or if I mix water with another molecule; depending upon the type of the molecule, it may accept proton or it may donate proton. Like I can take its example with

H F and I can take its example with ammonia. So, therefore whether it will accept proton or it will donate proton, it depends on type of molecule on type of another molecule.

Let us go to the slide; we take an example of H F dissolution in water, what we have is H 3O plus and forming fluoride ion. Water has accepted a proton therefore, it has acted as a base over here. On the other hand, if I choose another example; for example, if I take N H 3 aqueous and take water liquid; what I get is NH 4 aqueous plus O H minus aqueous. In this case water has donated a proton, you see here when you see it has donated a proton to ammonia and formed ammonium ion. Therefore, it has acted like an acid over here and that is what I was talking to you that water is amphiprotic, it can act as an acid or it can act as a base.

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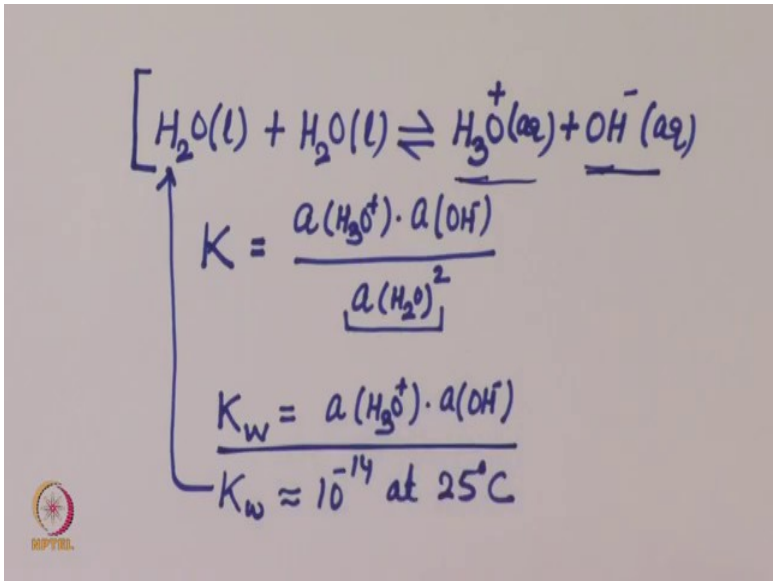

Let us take water liquid plus water liquid; water itself can act as an acid or it can act as a base because water can accept a proton or water can donate a proton. If it accepts a proton what I have is this hydronium ion and if it donates a proton, I have the hydroxide ion this is called autoprotolysis of water; water itself is acting as an acid it is acting as a base.

And autoprotolysis constant; if I write actually K for this, it will be activity of H 3O plus into activity of O H minus over activity of water square. Now, if I take activity of water to be 1 and consume it along with K; I will write another constant which is called K W and this is activity of H 3O plus into activity of O H minus.

Let me now go back to the slide and this constant K W is called autoprotolysis constant of water which is activity of hydronium ion into activity of hydroxide ion. And similarly I can write p K W; which is minus logarithm of K W at 25 degree centigrade the value of the autoprotolysis constant of water is 1.008 into 10 raised to the power minus 14 so; that means, p K w comes out to about 14 and since K is so small 10 raised to the power minus 14.

Let me write here K W is 10 raised to the power minus 14 at 25 degree centigrade for this reaction; that means, the extent of ionization is very very small that is what is commented over here at 25 degree centigrade, the autoprotolysis constant of water is 1.008 into 10 raised to power minus 14 indicating only a few molecules are ionized

And since in water; the activity of hydrogen ion and activity of hydronium ion are same; if we look at this equation the 1 is to 1 ratio; they are produced activities are same and therefore, I can use this equation to calculate the activity of hydronium ion. Since, they are same I can let us look at the slide activity of hydronium will be just K W square root which will come out to be 1.004 into 10 raised to power minus 7 at 298 Kelvin.

If we note down the activities of hydronium ion in 1 molar HCL; it is 0.81 and pure water it is 10 raised to power minus 7 we just discussed and in 1 molar activity of hydronium ion is about 10 raised to the power minus 14. See the activities, if I say 1 molar concentration activity is different because activity coefficient has to be included. And here activity is 10 raised to power minus of 7 here activity of hydronium ion is 10 raised to power minus 14. Therefore, there is a need to develop a new simpler scale which should depict the value of activity of hydronium ion in a simpler manner and that is p h scale; p h scale is very important and that p h scale we will discuss in the next lecture.

So, the discussion in this lecture on the weak acids, strong acids, autoprotolysis and p h we will continue and again use the concept of equilibrium in getting more insights into these kind of reactions in the next lecture.

Thank you very much.