Chemical and Biological Thermodynamics: Principles to Applications

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Lecture - 34
PH scale Strong and weak acids and bases

In the previous lecture we discussed the bronsted Lowry concept of acids and bases. And we extended our discussion till the autoprotolysis of water. Let me recall that slide, in autoprotolysis of water.

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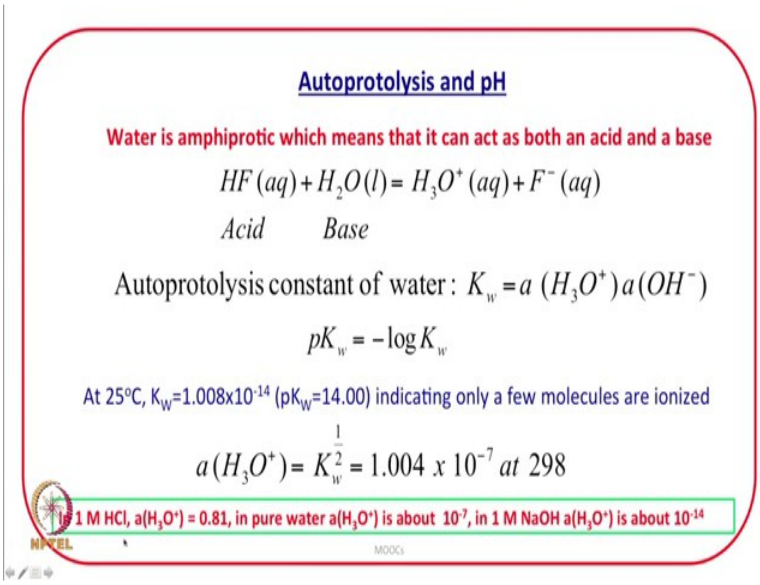

Autoprotolysis and pH

Water is amphiprotic which means that it can act as both an acid and a base

$$HF\,(aq) + H_2O\,(l) = H_3O^+\,(aq) + F^-\,(aq)$$

Acid Base

$$\text{Autoprotolysis constant of water: } K_w = a\,(H_3O^+)\,a(OH^-)$$

$$pK_w = -\log K_w$$

At 25°C, K_W=1.008x10^{-14} (pK_W=14.00) indicating only a few molecules are ionized

$$a(H_3O^+) = K_w^{\frac{1}{2}} = 1.004\ x\ 10^{-7}\ at\ 298$$

In 1 M HCl, $a(H_3O^+)$ = 0.81, in pure water $a(H_3O^+)$ is about 10^{-7}, in 1 M NaOH $a(H_3O^+)$ is about 10^{-14}

We discussed about the amphiprotic nature of water, that is water can act as both an acid and a base. We also introduced the autoprotolysis constant of water, and discussed that pKw for water at 25 degree centigrade is 14. And we also showed that the activity of hydronium ion, at 25 degree centigrade is given by the square root of the autoprotolysis constant of water which comes out to 1.004 into 10 raised to the power minus 7 at 2 98 kelvin

And then we further discussed, that for one molar hydrochloric acid the activity of hydronium ion is 0.81. And this 0.81 as I was discussing it is less than 1, because you have to account for the activity coefficient. For pure water we just discussed it is 10 raised to power minus 7, and for one molar sodium hydroxide it is about 10 raised to power minus 14.

And then we discussed that there has to be a simpler method of expressing these activities of the hydronium ion, there has to be a scale we should capture these activities of hydronium ion. And that scale is pH scale pH scale is very, very important. Especially when we talk about the biological importance system pH becomes very, very important. Because as we will discuss later on, the biological molecules whether we talk about the proteins or we talk about the nucleic acids pH becomes very, very important towards their conformational and thermal stability. We will discuss more later on about the conformational and thermal stability of biological macromolecules. But at present we are talking about the concept of pH.

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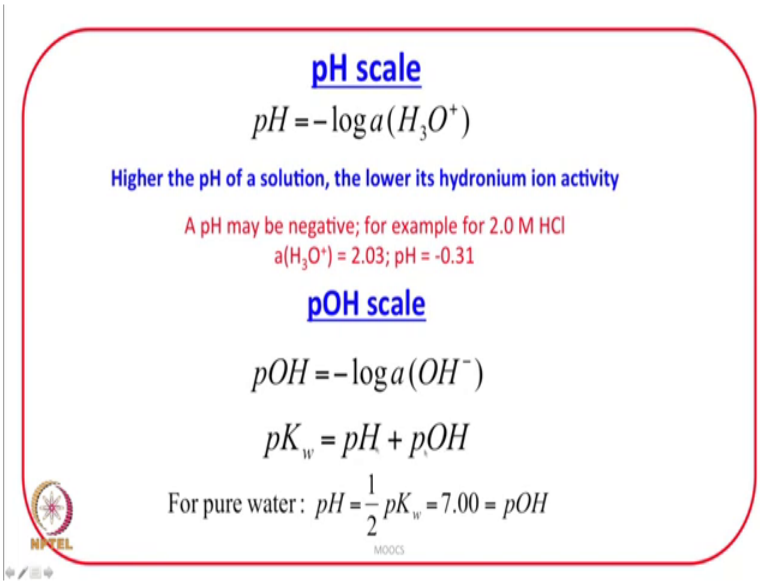

pH scale

$$pH = -\log a(H_3O^+)$$

Higher the pH of a solution, the lower its hydronium ion activity

A pH may be negative; for example for 2.0 M HCl
$a(H_3O^+) = 2.03$; pH = -0.31

pOH scale

$$pOH = -\log a(OH^-)$$

$$pK_w = pH + pOH$$

For pure water: $pH = \frac{1}{2} pK_w = 7.00 = pOH$

So, let us discuss pH scale, how do we define pH? PH is defined as negative logarithm of activity of hydronium ion. Please note it is l o g; that means, it is log base 10. And the correct definition of pH is minus logarithm of activity of hydronium ion. Please note I am not saying concentration, I am not saying molality, I am not saying mole fraction. I am saying that pH is equal to minus log activity of hydronium ion. According to this definition higher the pH of a solution, the lower it is hydronium hydronium ion activity because there is a negative sign over here; that means, if the amount of hydronium ion or the activity of hydronium ion is very, very small the pH is going to be high

Let us take an example. Can the pH be negative? Yes the pH can be negative for example, as shown over here if we calculate pH 4 2 molar hydrochloric acid 2 molar, for which the activity is 2.03 the pH comes out to be minus 0.31. That is what I said earlier, if the concentration of hydronium ion or the activity of hydronium ion is very high the pH is going to be very low and vice versa. We can also define pOH scale. How do we define pOH? In the same, way pOH is equal to minus logarithm of activity of hydroxide ion. Here again this log is log base 10. PH and pOH are related to each other.

For example let us take an example of water.

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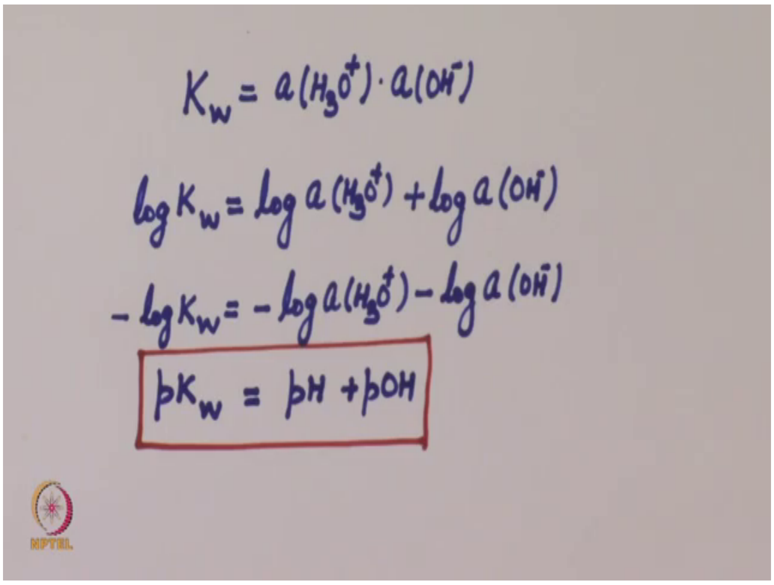

$$K_w = a(H_3O^+) \cdot a(OH^-)$$

$$\log K_w = \log a(H_3O^+) + \log a(OH^-)$$

$$-\log K_w = -\log a(H_3O^+) - \log a(OH^-)$$

$$\boxed{pK_w = pH + pOH}$$

We defined the Kw autoprotolysis constant of water as activity of H3O plus hydronium ion into activity of OH minus. Let me take log base 10 log Kw is equal to log activity of H3O plus, plus log activity of OH minus. And let me introduce a negative multiply both sides by negative sign, minus log Kw is equal to minus log activity of H3O plus minus log activity of OH minus. And this is pKw is equal to this is equal to pH and this is equal to pOH.

So, you see we develop a very important relation, pKw is equal to pH plus pOH. Let us go to the slide. Since Kw at a given temperature is constant; that means, pKw is constant; if the left hand side is constant; that means, if the pH of a solution goes up the pOH has to go down to k to keep the sum constant. Since Kw is constant, pKw is a constant quantity at a given temperature. Therefore, pH and pOH have to adjust in such a way that the sum remains constant. In other words if one goes down other has to go up the value of if the value of one goes down the value of the other must go up to keep the sum constant. For pure water pH is equal to half pKw because pH plus pOH are same.

Therefore pH will be equal to just half of pKw. Once again because pOH, pH and pOH are same for water, why I am saying is because the activity we just discussed in the previous slide that the activity of hydronium ion and activity of hydroxide ion are same for pure water therefore, pH and pOH will also be same which is equal to half the value of pKw is pOH. PH is equal pOH. Next question is does pH depend upon on temperature. When we do experiments in the laboratory is it important to mention temperature at which the pH is measured?

Let us try to get an answer to this question from the next discussion. Let us go to the slide. The question is does pH depend upon temperature.

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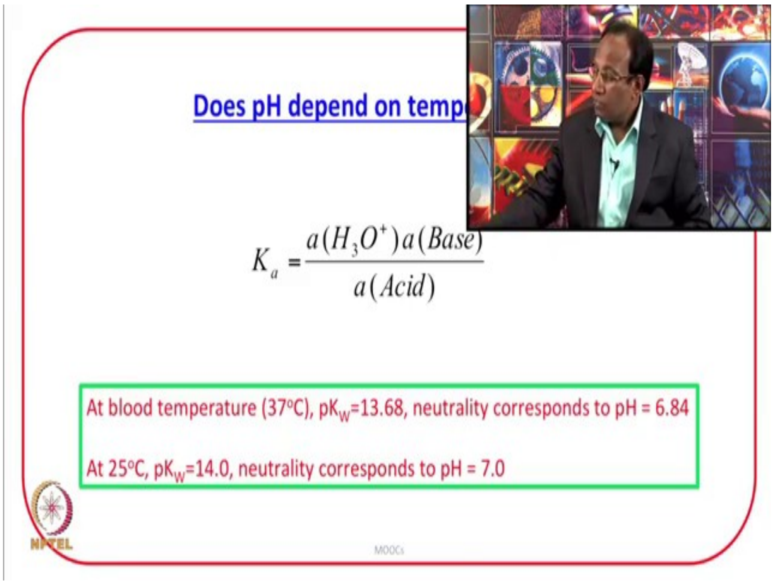

Does pH depend on temp

$$K_a = \frac{a(H_3O^+)a(Base)}{a(Acid)}$$

At blood temperature (37°C), pK_W=13.68, neutrality corresponds to pH = 6.84

At 25°C, pK_W=14.0, neutrality corresponds to pH = 7.0

For this We need to take a look at the expression for acidity constant which we defined as activity of hydronium ion into activity of base divided by the activity of the acid. And as I discussed earlier the activity the acidity constant is actually an equilibrium constant and the value of equilibrium constant is temperature dependent if delta H is either positive or delta H is negative.

So, when the reaction is endothermic the Ka value will go up with temperature when the reaction is exothermic the value of Ka will go down with temperature. So therefore, if Ka depends upon temperature the activity of hydronium ion will also depend upon temperature. If activity of hydronium ion depends on temperature the pH will also depend upon temperature. So, let us take a look at the comments at blood temperature 37 degree centigrade PKw is not 14 it is 13.68. And there if you calculate the pH it will turn out to be 6.84 naught 7.

That means when we talk about the neutrality concept at blood temperature the neutrality will correspond to pH equal to 6.84. And since pKw is 14 at 25 degree centigrade, at 25 degree centigrade the neutrality corresponds to p equal to 7. Use this value of pKw and set this equal to activity you know Kw you calculate Kw and Kw is equal to activity of hydronium ion into activity of hydroxide ion and when you calculate the activity of hydronium ion and hence the pH it will come out to be 6.84. So, at blood temperature 37 degree centigrade neutrality corresponds to pH 6.84. At 25 degree centigrade neutrality correspond to pH 7. So, this discussion clearly establishes that the pH does depend upon temperature. How do we calculate pH?

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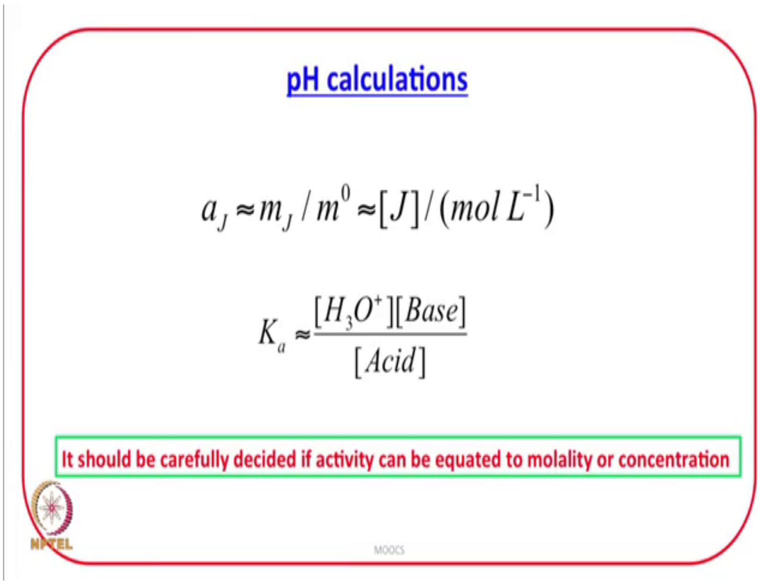

pH calculations

$$a_J \approx m_J / m^0 \approx [J]/(mol\,L^{-1})$$

$$K_a \approx \frac{[H_3O^+][Base]}{[Acid]}$$

It should be carefully decided if activity can be equated to molality or concentration

Let us discuss about that. PH determination in laboratory requires the use of a pH meter. PH meter what is the pH meter and how it determines the hydronium ion activity or concentration? It is a matter of a different discussion you will learn it somewhere else about the pH electrodes.

But let us here talk about the calculations. When we prepare solutions in laboratory this I have discussed earlier also, the amount of different species in the mixture we usually calculate as molality or molarity or mole fractions. But the definition of pH is minus logarithm of activity of hydronium ion. Let us take a look at the slide. Since the definition of pH is minus logarithm of activity of hydronium ion, we need to talk about the activity. And when the solution is very, very dilute then the activity coefficient can be taken as one and we can express or equate approximately the activity by the molarity or molality whatever way you want to express mole per liter is molarity. And in that case the acidity constant can be written in the form of concentrations, since for very dilute solutions we assume activity coefficient to be one. And if that assumption is valid then activities can be replaced by the concentrations, and Ka can be expressed in the form of concentrations and that is what is commented over there.

It should be carefully decided if activity can be equated to molality or concentration or not. We need a small discussion over here, when I was discussing about the activity and activity coefficient I mentioned that the concept of activity or activity coefficient is very, very important, because when we talk about the experimental measurements especially in the solutions which contain ion selectrolytic solutions ionic solutions. Even under very, very dilute conditions the values of activity coefficients are quite different from one.

And therefore, activity coefficients cannot be ignored in ionic solution. And when we talk about the pH the definition of pH itself is negative logarithm of activity of hydronium ion here we itself for talking about an ion. Therefore, the value of activity coefficient in these calculations becomes very, very important. And if we are absolutely sure if we are sure that the conditions are So dilute the solution is So dilute that we can treat activity coefficient to be approximately one, then we can make the assumption as seen in the slide, that is we are expressing the acidity constant in terms of the concentration.

Soinelementary text books what we see is the acidity constant is return as the ratio of the concentrations. And in advance text books what you see is the acidity constant is written as the ratio of activities. Therefore, please make a suitable judgment when activities can be replaced by molality or by concentration.

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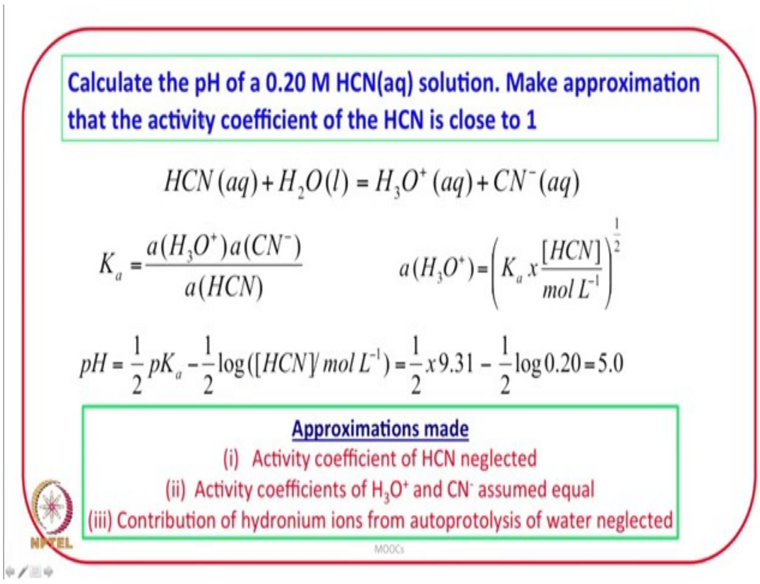

Calculate the pH of a 0.20 M HCN(aq) solution. Make approximation that the activity coefficient of the HCN is close to 1

$$HCN(aq) + H_2O(l) = H_3O^+(aq) + CN^-(aq)$$

$$K_a = \frac{a(H_3O^+)a(CN^-)}{a(HCN)} \qquad a(H_3O^+) = \left(K_a x \frac{[HCN]}{mol\,L^{-1}}\right)^{\frac{1}{2}}$$

$$pH = \frac{1}{2}pK_a - \frac{1}{2}\log([HCN]/mol\,L^{-1}) = \frac{1}{2}x9.31 - \frac{1}{2}\log 0.20 = 5.0$$

Approximations made

(i) Activity coefficient of HCN neglected

(ii) Activity coefficients of H_3O^+ and CN^- assumed equal

(iii) Contribution of hydronium ions from autoprotolysis of water neglected

Let us take an example. Calculate the pH of 0.2 molar HCN solution make approximation that activity coefficient of HCN is close to 1. So, we have been asked to calculate the pH of 0.2 molar HCN aqua solutions. Let us see how to approach this.

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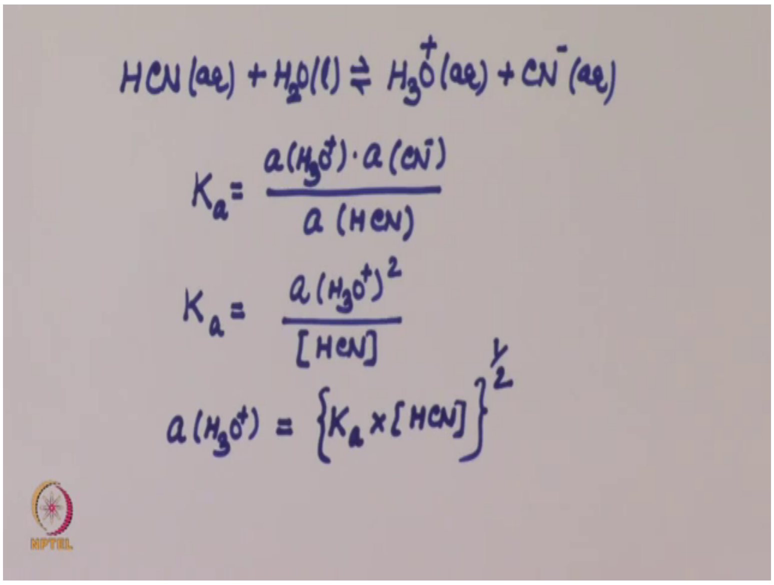

$$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$$

$$K_a = \frac{a(H_3O^+)\cdot a(CN^-)}{a(HCN)}$$

$$K_a = \frac{a(H_3O^+)^2}{[HCN]}$$

$$a(H_3O^+) = \{K_a \times [HCN]\}^{1/2}$$

We have HCN aqueous plus water liquid and this is an equilibrium with H3O aqueous plus CN minus aqueous. That is what is the ionization reaction over here. When HCN is added to water you have this equilibrium. And we will write an expression for the acidity constant, which will be activity of H3O into activity of cyanide over activity of HCN.

And we are given in the statement that the activity coefficient of HCN is close to 1. So, that allows me to replace this activity by the concentration.

And if you look at into the into this equation the activities or see the activity of H3O plus and activity of CN minus we can assume to be same over here it is 1 is to 1 ionization over here. So, I can write Ka is equal to activity of H3O plus square over I am writing here concentration of HCN. Because I am making use of the fact or making use of the statement that I can treat activity coefficient to be close to one for HCN.

So, this therefore, activity of H3O plus if I rearrange this is going to be Ka into concentration of HCN whole raised to the power 1 by 2. In order to calculate pH I need the activity of hydronium ion that is what I need, and you see how I have done. Wherever the information about activity coefficient was given to be almost one I have used that otherwise I have retained activity.

Now, let us go back to the slide. We were talking about disequilibrium in aqua solution HCN plus water forming H3O plus CN minus allin aquas media. And we also wrote the value the expression for Ka and we came up with this expression, that activity of H3O plus is equal to the value of acidity constant into concentration of HCN of course, that is in mole per liter raised to the power 1 by 2.

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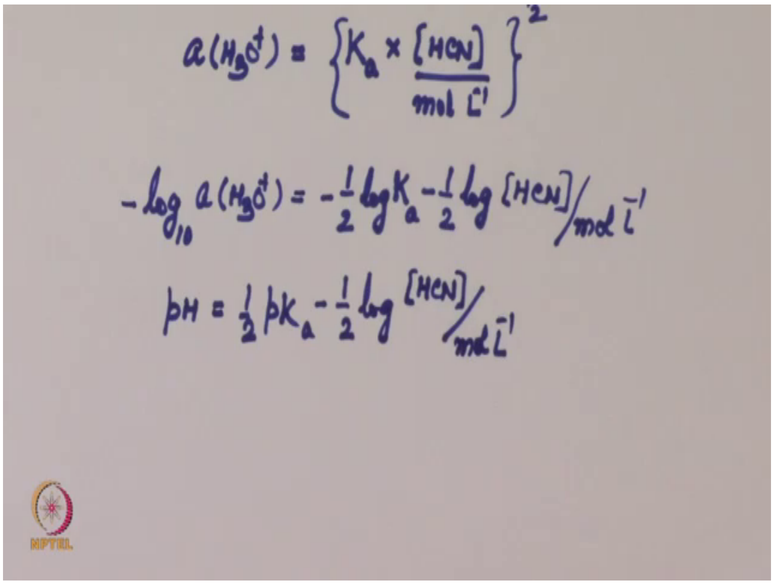

$$a(H_3O^+) = \left\{K_a \times \frac{[HCN]}{mol\ L^{-1}}\right\}^{2}$$

$$-\log_{10} a(H_3O^+) = -\frac{1}{2}\log K_a - \frac{1}{2}\log [HCN]/mol\ L^{-1}$$

$$pH = \frac{1}{2}pK_a - \frac{1}{2}\log [HCN]/mol\ L^{-1}$$

So, now what we do is, we have derived this expression activity of H3O plus is equal to Ka into concentration of HCN and in order to make it dimensionless, I will put mole per liter and this is 1 by 2 and pH will be minus logarithm of hydrogen ion activity or hydronium ion activity.

So, let me directly use that minus log 10 activity of H3O will be equal to minus 1 by 2 log Ka minus 1 by 2 log concentration of HCN and of course, you divide by mole per liter. So therefore, I can write this as pH is equal to half pk minus 1 by 2 log concentration of HCN and I divide by mole per liter to make it dimensionless quantity. And let us take a look at the slide. Now that is what I just derived that pH is equal to half pKa minus half log of HCN concentration and pKa of HCN is 9.31. And this concentration of HCN given to us is 0.2 molar and after calculation you see the pH turns out to be 5.

Now, in this example, we discussed how to do the calculations for pH. As I said that for elementary chemistry these calculations may be. Because in these calculations we have made assumptions and what are those assumptions let us take a look at what are the assumptions made. The given information was make approximation that activity coefficient of HCN is close to 1. So, first activity coefficient of HCN neglected; that means, if we want to really get very, very accurate number we cannot ignore the activity coefficient of HCN. Secondly, we have assumed that the activity coefficients of H3O plus and CN minus are equal that is what we did we equated the 2 and took the square. In fact, this may not be equal this is another assumption that we have made.

The third one is as I discussed in the previous lecture that H3O plus this itself know, the contribution to this concentration that is the amount of H3O plus form from autoprotolysis of water we have neglected. Because water itself as we say if it is we discussed earlier to autoprotolysis may contribute to some amount of H3O plus. So, we have ignored those; although, if you calculate these 3 contributions this may not be very, very high, but it may be still significant to be expressed as a very, very accurate value of the pH. So, it is important to recognize that here in doing these type of calculations we have made some assumptions especially when we equate activities with the concentration like a HCN is taken as the concentration and that we did because the statement asked us to use that information that that approximation that the activity coefficient of HCN is close to 1.

So, that is why it is important to keep in mind the approximations made, because if we are interested in doing very, very accurate calculations, we cannot ignore the values of activity coefficients, because after all we are dealing with the ionic solutions over here. So, in this lecture we discussed a very important concept of pH. PH is defined as negative logarithm of hydronium ion activity. And this definition must be remembered. And then we must be careful when we equate activity with the molarity molality or mole fraction. And with reference to pH one will have to put the concentration.

So therefore, we have to be very, very careful, when we equate activity to concentration or activity due to molality. And as we will realize later on that when we discuss the biologically important system, how important the role of pH is in maintaining the conformational and thermal stability of the biological systems, as well as the various processes which are biologically important.

So, I hope that the concept of the pH is very, very clear. And it is also very clear that how to obtain or how to calculate pH by making some assumption and also to recognize that when those assumptions can be made or when we need to really include the values of activity coefficient.

Thank you very much.