Chemical and Biological Thermodynamics: Principles to Applications

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Lecture - 35
Strong and weak acids and bases

In the previous lecture, we discussed about the Bronsted Lowry classification of acids and bases. We talked about what is an acid and what is classified as a base based upon the proton transfer or proton accepting abilities of a molecule. We also introduced P H and now we will extend that discussion and discuss strong and weak acids and bases.

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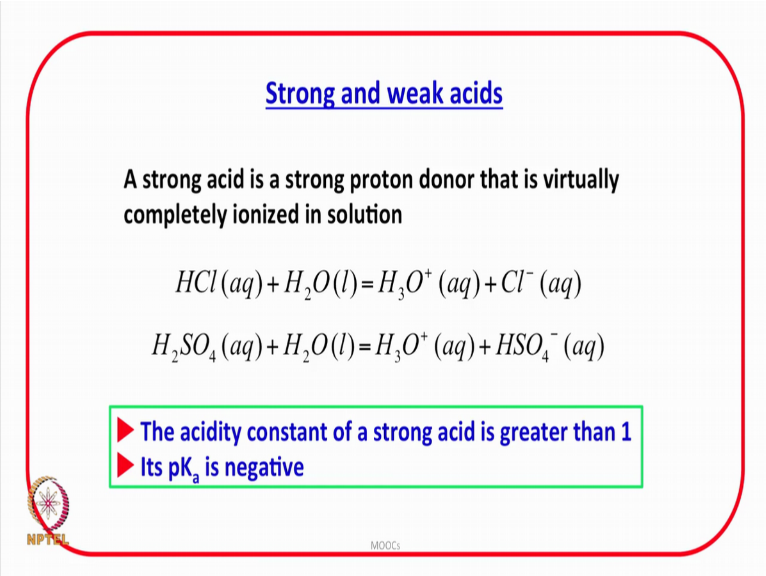

Strong and weak acids

A strong acid is a strong proton donor that is virtually completely ionized in solution

$$HCl(aq) + H_2O(l) = H_3O^+(aq) + Cl^-(aq)$$

$$H_2SO_4(aq) + H_2O(l) = H_3O^+(aq) + HSO_4^-(aq)$$

- The acidity constant of a strong acid is greater than 1
- Its pK_a is negative

So, what is a strong acid? A strong acid is a strong proton donor that is virtually completely ionized in solution. So, a strong acid will be a molecule which can easily donate proton to another molecule and in the solution, it is virtually completely highest. So, this strong proton donating ability makes a molecule as a strong acid. For example, if we take HCl, HCl in water easily donates proton, HCl easily donate donates proton to water and forming hydronium ion plus chloride ion and in such a reaction, we say that HCl is virtually completely ionized in solution in the form of hydronium ion and chloride ion.

So, therefore, we call HCl as a strong acid. Similarly if we consider sulfuric acid, sulfuric acid in water donates a proton to water very easily and forms H3O plus HSO4 minus this is also; we treat as virtually complete ionization and that is why sulfuric acid is a strong acid and there are certain parameters which will classify about a particular molecule be a strong acid and that parameter we discussed in the previous lecture also is acidity constant.

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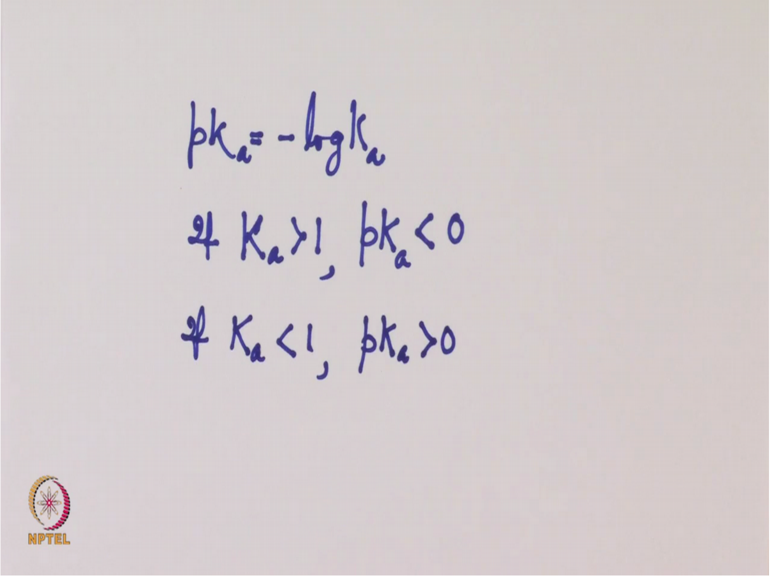

$pK_a = -\log K_a$

if $K_a > 1$, $pK_a < 0$

if $K_a < 1$, $pK_a > 0$

Let us take a look at this comment, the acidity constant of a strong acid is greater than 1, this is true for strong acids that if the acidity constant is greater than 1 then p K is equal to minus logarithm of K a. So, if K a is greater than 1 then p K a will be less than 0. It will be negative and that is what is commented over here that acidity constant of a strong acid is greater than 1 and the p K a of a strong acid is negative.

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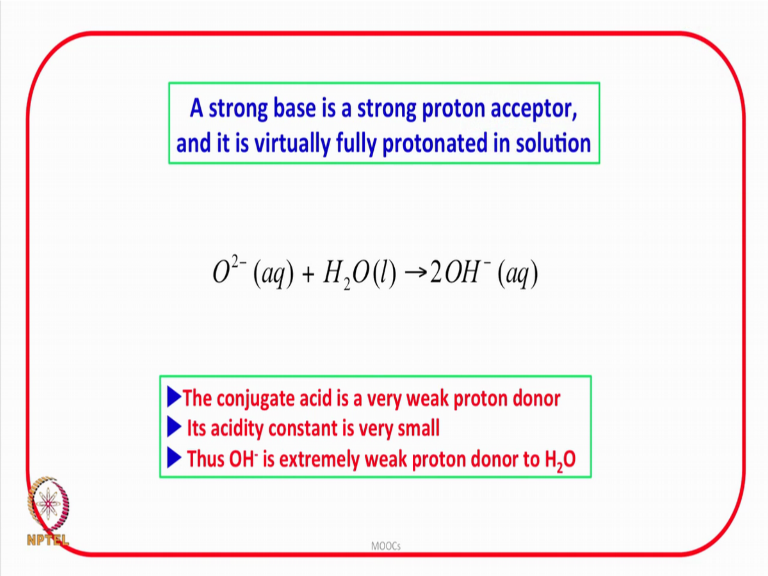

A strong base is a strong proton acceptor, and it is virtually fully protonated in solution

$$O^{2-}(aq) + H_2O(l) \rightarrow 2OH^{-}(aq)$$

- The conjugate acid is a very weak proton donor
- Its acidity constant is very small
- Thus OH^- is extremely weak proton donor to H_2O

Now, what about a strong base? A strong base is a strong proton acceptor and it is virtually fully protonated in solution. When we discussed about strong acids, we said there is a virtually complete ionization in solution of the acid and now when we are talking about a strong base, a strong base is the one which is a strong proton acceptor and it is virtually fully protonated in solution.

Let us take one example O2 minus in aqueous form plus H2O forms 2OH minus this oxygen 2 negative itself will not exist in solution as such, it is virtually protonated, you see over here, it immediately interacts with water and forms hydroxide ion that is what is the meaning of that O2 minus is a strong base and it is a strong proton acceptor. It is accepting a proton from water and virtually it is fully protonated.

Now, let us look at few more comments. The conjugate acid is a very weak proton donor. Now if this is a base, its conjugate acid is going to be 2OH minus this OH minus and OH minus is an extremely weak proton donor. It will not give proton its proton to water that is; what is the meaning of the sentence. The conjugate acid is a very weak proton donor and very weak proton donor means the acidity constant is going to be very very small and this conjugate acid OH minus is an extremely weak proton donor to H2O. So, these are some of the properties of the strong base and its conjugated acid.

Now, let us talk about a weak acid weak acid is a Bronsted acid that is incompletely ionized in solution there are several molecules which will not undergo complete ionization in an aqueous solution and this ionization, let us also keep in mind, whether something is fully ionized in a given solvent, it depends upon the type of the solvent, a certain molecule may not be ionized in a given solvent, but it may be fully ionized in a different solvent, but since here we are talking mostly about the aqueous solution. So, let us restrict our discussion to the aqueous solution

A weak acid; when we talk about an acid in an aqueous solution as seen in this slide, a weak acid is a Bronsted acid that is in completely ionized in solution.

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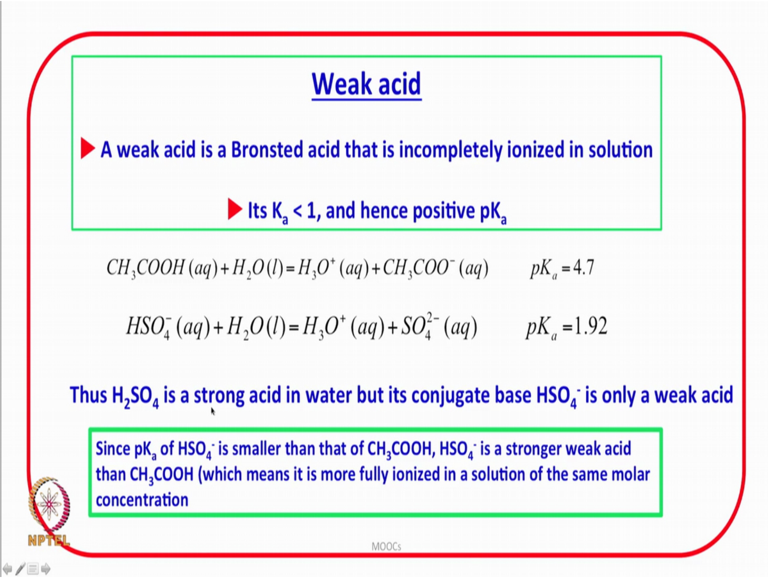

Weak acid

- A weak acid is a Bronsted acid that is incompletely ionized in solution
- Its $K_a < 1$, and hence positive pK_a

$$CH_3COOH\,(aq) + H_2O\,(l) = H_3O^+\,(aq) + CH_3COO^-\,(aq) \qquad pK_a = 4.7$$

$$HSO_4^-\,(aq) + H_2O\,(l) = H_3O^+\,(aq) + SO_4^{2-}\,(aq) \qquad pK_a = 1.92$$

Thus H_2SO_4 is a strong acid in water but its conjugate base HSO_4^- is only a weak acid

Since pK_a of HSO_4^- is smaller than that of CH_3COOH, HSO_4^- is a stronger weak acid than CH_3COOH (which means it is more fully ionized in a solution of the same molar concentration

That means, the K a is going to be less than 1 and since K a is less than 1, now let us go back to this discussion if K a is less than 1, I substitute over there then p K a will be greater than 0. Let us take certain examples, we take example of acetic acid; acetic acid in water will have this ionization reaction. The proton is donated to water and hydronium ion is produced plus CH3COO minus ion is formed and the p K a value is 4.7.

Now, let us take another example; HSO4 donates proton to water and forms H3O plus sulfate ion at the p K a value is 1.92. If you compare these 2 p K values, p K a value of acetic acid is higher than the p K a value of HSO4 that if p K a is high, K a value is low and if p K a value is low, K a value is high.

So, therefore, going back to this slide, the p K a value of the second reaction that is HSO4 minus plus water forming H3O plus plus sulfate p K a value is lower; that means, HSO4 is a stronger weak acid compared to the weak acid CH3COOH, why I am saying these weak acids because these are not completely ionized in solution and the ionization if it is not complete then K a is less than 1 and p K a values will be positive.

So, thus the comparison of these p K a values suggest that HSO4 is going to be a stronger weaker acid compared to acetic acid. In fact, HSO4 is a conjugate base of H2SO4; H2SO4 itself is a strong acid and its conjugate base is HSO4 minus and HSO4 minus is only a weak acid because this itself can further participate in protonation of water and act as a very weak acid.

Let us look at some of the comments, since p K a of HSO4 minus is smaller than that of acetic acid HSO4 minus is a stronger weak acid than acetic acid and that is what I was saying that the comparison of these p K a value suggest that HSO4 is a stronger weak acid than acetic acid this means that HSO4 is more fully ionized in a solution at the same molar concentration.

In other words, if you take equimolar solution of HSO4 minus and acetic acid then the ionization will be more in HSO4 compared to that in acetic acid. So, this kind of information is available. Once we have the values of p K a, we can comment upon their acidity or we can we can comment upon their proton donating abilities.

Now, let us talk about weak base, what is a weak base? A weak base is a Bronsted base that is only partly protonated, not fully protonated; it is partly protonated and again the usual example will be ammonia plus water forming ammonium ion plus hydroxyl ions and if NH3 is a base, its conjugate acid is NH4 plus, but this is an example ammonia is an example of Bronsted base that is only partly protonated.

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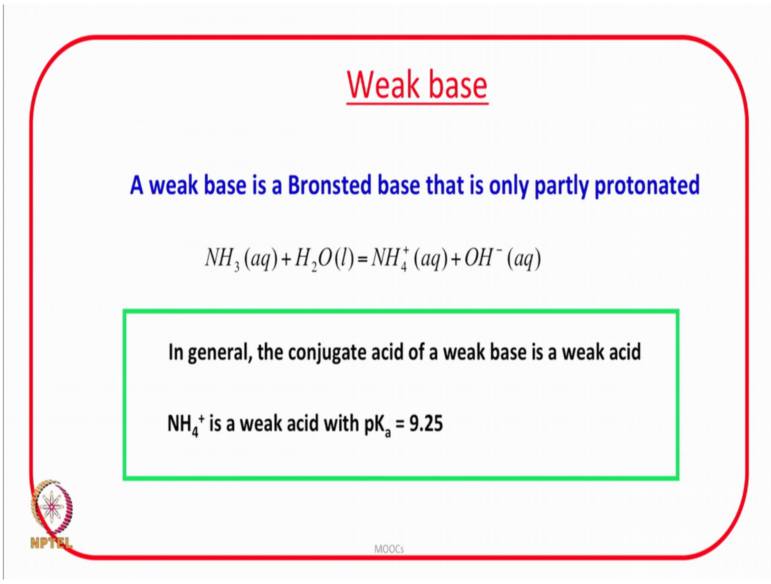

Weak base

A weak base is a Bronsted base that is only partly protonated

$$NH_3(aq) + H_2O(l) = NH_4^+(aq) + OH^-(aq)$$

In general, the conjugate acid of a weak base is a weak acid

NH_4^+ is a weak acid with $pK_a = 9.25$

MOOCs

In general, the conjugate acid of a weak base is a weak acid. For example, you see ammonia NH3 is a weak base and its conjugate acid which is NH4 plus is actually a weak acid.

Actually when you classify this acid and bases in Bronsted Lowry concept or classification whether we talk about an acid or we talk about a conjugate acid or whether we talk about a base or conjugate base and acid is an acid, a base is a base. Therefore, the classification applies to both the acid whether it is a strong acid or it is a weak acid or it is a conjugated acid, strong base weak base or conjugated base.

Now, let us look at the next comment NH4 plus ammonium, ion is a weak conjugate acid of ammonia and you see if the acid is very weak; that means, the p K a value is going to be high that is why p K a of ammonium ion is equal to 9.25. This is how the data on p K a value should be interpreted.

Whether a given molecule in aqueous solution turns out to be a strong acid or a weak acid, a strong base or a weak base, it will lead to change in pH of the solution and if the molecule ionizes completely in let us say aqueous solution.

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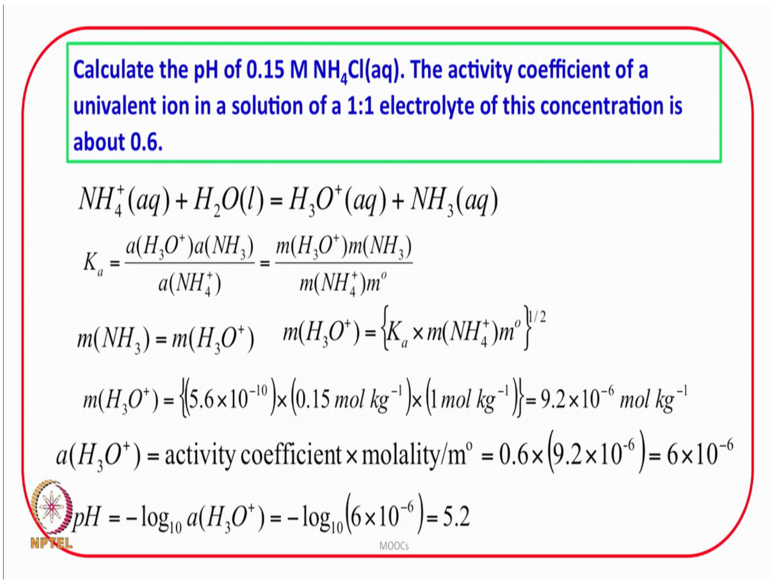

Calculate the pH of 0.15 M $NH_4Cl(aq)$. The activity coefficient of a univalent ion in a solution of a 1:1 electrolyte of this concentration is about 0.6.

$$NH_4^+(aq) + H_2O(l) = H_3O^+(aq) + NH_3(aq)$$

$$K_a = \frac{a(H_3O^+)a(NH_3)}{a(NH_4^+)} = \frac{m(H_3O^+)m(NH_3)}{m(NH_4^+)m^o}$$

$$m(NH_3) = m(H_3O^+) \qquad m(H_3O^+) = \left\{K_a \times m(NH_4^+)m^o\right\}^{1/2}$$

$$m(H_3O^+) = \left\{\left(5.6\times10^{-10}\right)\times\left(0.15\,mol\,kg^{-1}\right)\times\left(1\,mol\,kg^{-1}\right)\right\} = 9.2\times10^{-6}\,mol\,kg^{-1}$$

$$a(H_3O^+) = \text{activity coefficient} \times \text{molality/m}^{\circ} = 0.6\times\left(9.2\times10^{-6}\right) = 6\times10^{-6}$$

$$pH = -\log_{10} a(H_3O^+) = -\log_{10}\left(6\times10^{-6}\right) = 5.2$$

For example, if we talk about HCl and we said that HCl ionize is virtually completely in water then the p h calculations become a little easy.

However in the case of a weak acid or a weak base, since the ionization is not complete therefore, the calculation of pH values becomes a little difficult, a little tedious because you will have to account for the incomplete dissociation of acetic acid in solution or incomplete ionization of the weak acid or an incomplete protonation of the weak base in solution. Let us take an example, calculate the pH of 0.15 molar ammonium chloride the activity coefficient of a univalent ion in a solution of 1 is to 1 electrolyte of this concentration is about 0.6.

In fact, I am revisiting this question. This question, I have discussed earlier also and here again I am discussing in context of PH. So, let us quickly go through the solution, since we have ammonium chloride the corresponding equilibrium is ammonium ion plus water forming H3O plus plus ammonia and K a acidity constant for this, weak acid will be activity of hydronium ion into activity of ammonia divided by activity of ammonium ion and as we discussed earlier says, the solution is dilute, we can replace activity by molality and also further noticing that the 2 molalities of H3O plus on NH3 are going to be same by the reaction stoichiometry, we are assuming that the molalities are same and once again I will highlight here that we are approximating activities by molalities or by concentration.

And therefore, once you equate these 2; the molality of H3O plus can be calculated from this expression that is K a into m into ammonium ion m naught square root I am not going into that much detail because this question I have already discussed.

So, once we have the value of activity of hydronium ion or the molality of hydronium ion, we can easily calculate the PH. So, first the molality of hydronium ion is evaluated from the knowledge of K a and the concentration or molarity of ammonium ion and then m of S3O plus comes out to be 9.2 into 10 is to power minus 6 mol Kg.

And activity is equal to activity coefficient into molarity by m naught, m naught is 1 mole per kg activity, coefficient is 0.6 and molarity is given as or the calculated as 9.2 into 10 super minus the overall activity comes out to 6 into 10 is to power minus 6. Once you substitute this activity into the definition of PH, pH is minus logarithm of activity of hydronium ion concentration and activity of hydronium ion concentration, we just calculated and by solving this you get an answer of 5.2. So, pH turns out to be 5.2.

In this numerical problem, what we need to appreciate is that the activities can only be replaced by molality, if you assume the solution to be very very dilute and if the solution is not dilute, we must account for activity coefficients as it is done for ammonium chloride we are using the activity coefficient value of about 0.6.

So, what we have done is we have had a detailed discussion on what is an acid, how to classify a base, what is a strong acid, what is strong base, what is p K a and what information do we get from p K a, we also discussed about autoprotolysis constant of water and the temperature dependence of the autoprotolysis constant of water whether pH is temperature dependent or not, this also we discussed and we found out that yes, pH is dependent upon temperature we also discussed the method to calculate the pH of a solution and since we are talking about the weak acids and weak bases, there is one more question on equilibrium that I would like to discuss over here because these weak acids or there are many molecules which tend to dimerize in solution or make higher order oligomers.

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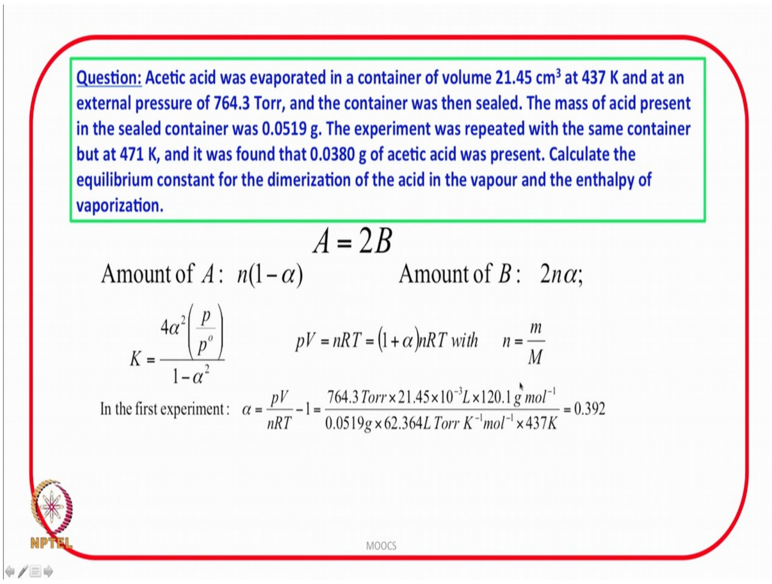

Question: Acetic acid was evaporated in a container of volume 21.45 cm^3 at 437 K and at an external pressure of 764.3 Torr, and the container was then sealed. The mass of acid present in the sealed container was 0.0519 g. The experiment was repeated with the same container but at 471 K, and it was found that 0.0380 g of acetic acid was present. Calculate the equilibrium constant for the dimerization of the acid in the vapour and the enthalpy of vaporization.

$$A = 2B$$

Amount of A: $n(1-\alpha)$ Amount of B: $2n\alpha$;

$$K = \frac{4\alpha^2\left(\frac{p}{p^o}\right)}{1-\alpha^2} \qquad pV = nRT = (1+\alpha)nRT \text{ with } \quad n = \frac{m}{M}$$

In the first experiment: $\alpha = \frac{pV}{nRT} - 1 = \frac{764.3\,Torr \times 21.45\times10^{-3}L \times 120.1\,g\,mol^{-1}}{0.0519g \times 62.364L\,Torr\,K^{-1}mol^{-1} \times 437K} = 0.392$

We will here talk about the acetic acid. This question is actually based upon the concept of equilibrium constant. Let us read the question, acetic acid was evaporated in a container of volume 21.45 centimeter cube at 437 Kelvin and at an external pressure of 764.3 Torr and the container was then sealed the mass of the acid present in the sealed container was 0.0519 gram, the experiment was repeated with the same container, but at 471 Kelvin and it was found that 0.0380 gram of acetic acid was present. Calculate the equilibrium constant for the dimerization of the acid in the vapor and the enthalpy of vaporization it is about acetic acid dimerization.

Let us consider a general process a in equilibrium with 2 B, right hand side is dissociation, left hand side is dimerization and if n is the number of moles at equilibrium and alpha is the degree of the dissociation.

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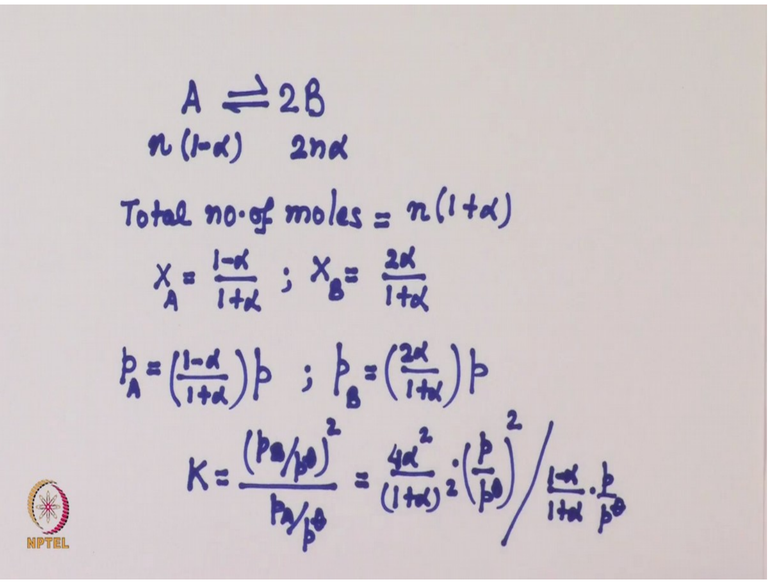

$$A \rightleftharpoons 2B$$

$$n(1-\alpha) \qquad 2n\alpha$$

Total no. of moles = $n(1+\alpha)$

$$X_A = \frac{1-\alpha}{1+\alpha} \; ; \; X_B = \frac{2\alpha}{1+\alpha}$$

$$p_A = \left(\frac{1-\alpha}{1+\alpha}\right)p \; ; \; p_B = \left(\frac{2\alpha}{1+\alpha}\right)p$$

$$K = \frac{(p_B/p^\ominus)^2}{p_A/p^\ominus} = \frac{4\alpha^2}{(1+\alpha)^2} \cdot \left(\frac{p}{p^\ominus}\right)^2 \Big/ \frac{1-\alpha}{1+\alpha} \cdot \frac{p}{p^\ominus}$$

You have 2 n alpha total n total number of moles is equal to you add both, it will come out to be n into 1 plus alpha n into 1 minus alpha plus 2 n alpha will come out to be n into 1 plus alpha.

So, mole fraction of A will be quall to this divided by this 1 minus alpha over 1 plus alpha mole fraction of B is equal to 2 alpha over 1 plus alpha. This divided by this therefore, partial pressure of A is going to be 1 minus alpha over 1 plus alpha into total pressure and partial pressure of B is equal to 2 alpha over 1 plus alpha into total pressure p and when we write the equilibrium constant for a going to 2 B. It is p B by p naught raise to the power 2 over p A by p naught and you need to substitute let us substitute for p B and p A p B p B is this, it will be 4 alpha square over 1 plus alpha square into p by p naught square that also will come divided by p A by p naught, it will be 1 minus alpha over 1 plus alpha into p by p naught.

Once you rearrange or once you saw; you know cancel out the common factors. We can go to the slide the for A going to 2 B as I just discussed that after this discussion K will come out to be 4 alpha square into p by p naught over 1 minus alpha square and once I know the value of alpha then I can easily get equilibrium constant.

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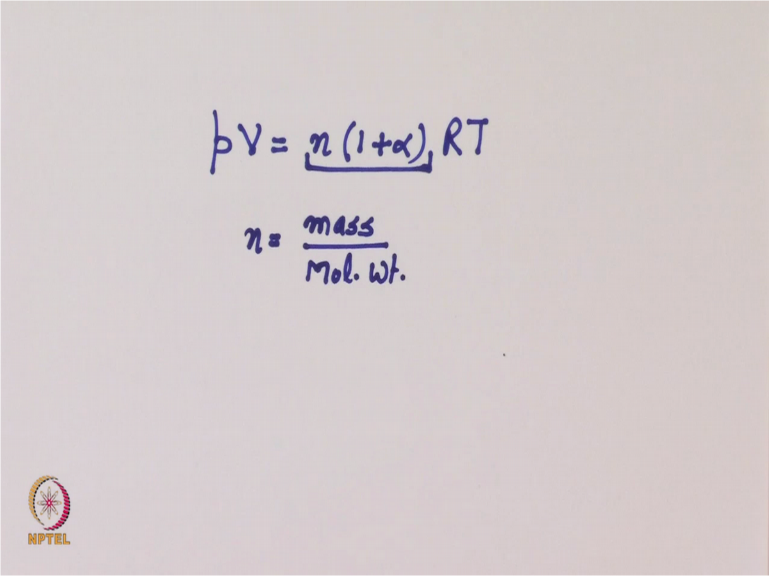

$$pV = \underbrace{n(1+\alpha)}\,RT$$

$$n = \frac{\text{mass}}{\text{Mol. wt.}}$$

If I treat the gas is to be ideal, then I can use this equation p V is equal to n R T, n is the total number of moles and the total number of moles we have found to be 1 plus alpha R T, this point is to be noted p V is equal n R T, but the total number of moles that we have just found out is n into 1 plus alpha.

So, therefore, one can get alpha from here, how do you get n here, n is equal to mass divided by molecular weight and in each case. Let us look at the slide in each experiment, the mass is given in one case it is 0.0519 gram. In other case it is 0.0380 gram.

So, therefore, p V is equal to n R T. In fact, this n should be read as n total.

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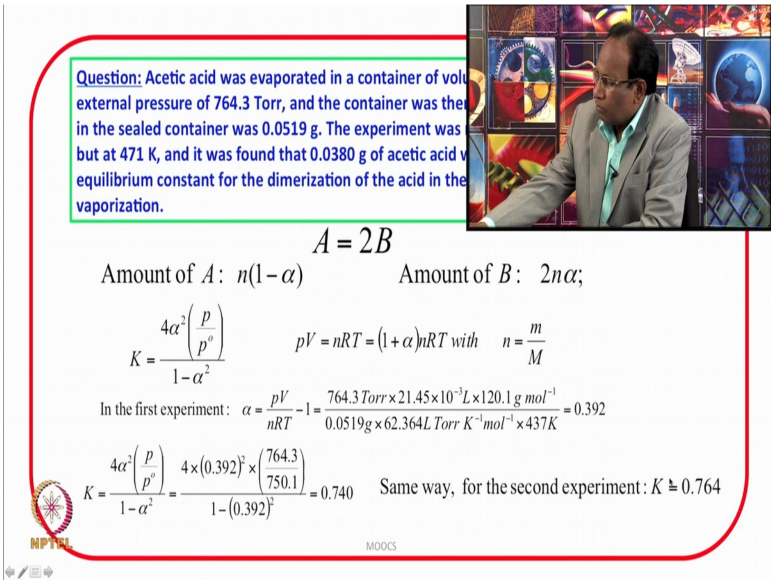

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external pressure of 764.3 Torr, and the container was the
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equilibrium constant for the dimerization of the acid in the
vaporization.

$$A = 2B$$

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$$K = \frac{4\alpha^2\left(\frac{p}{p^o}\right)}{1-\alpha^2} = \frac{4\times(0.392)^2\times\left(\frac{764.3}{750.1}\right)}{1-(0.392)^2} = 0.740$$

Same way, for the second experiment: $K \doteq 0.764$

Which is equal to 1 plus alpha into n R T with n is equal to mass divided by molecular weight we get alpha you rearrange this alpha will be equal to p V by n R T minus 1 and it comes out to be 0.392. So, once you know alpha, you can easily calculate K, what you are getting is K is equal to 0.34; 0.740. This is at 437 Kelvin. Similar calculations for the second experiment at 471 Kelvin K will be equal to 0.764.

Now, you have K at 2 different temperature and I can easily calculate the value of enthalpy this equation, we have discussed many times this comes from the integration of the Vant Hoff equation between 2 limits of T I and T f and after the substitution.

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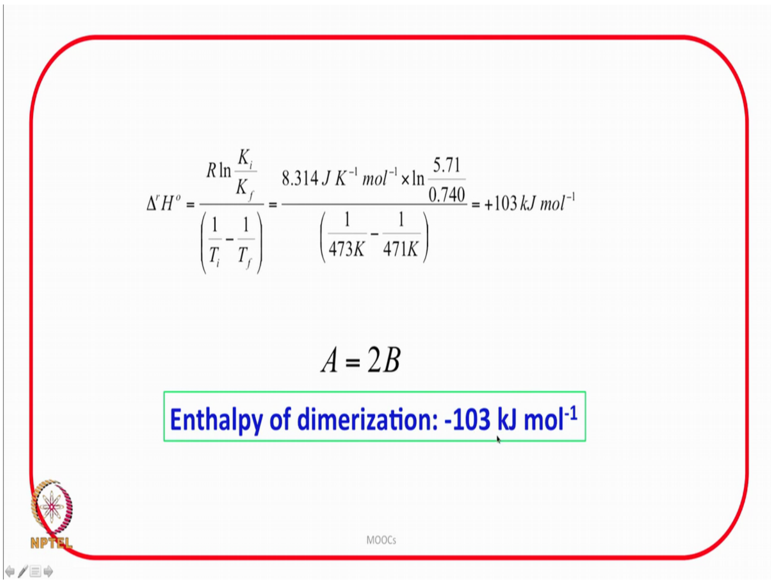

$$\Delta_r H^o = \frac{R\ln\frac{K_i}{K_f}}{\left(\frac{1}{T_i}-\frac{1}{T_f}\right)} = \frac{8.314\,J\,K^{-1}\,mol^{-1}\times\ln\frac{5.71}{0.740}}{\left(\frac{1}{473K}-\frac{1}{471K}\right)} = +103\,kJ\,mol^{-1}$$

$$A = 2B$$

Enthalpy of dimerization: -103 kJ mol^{-1}

We get the enthalpy to be plus 103 kilojoules per mole, but remember that this enthalpy is for the process a going to 2 B therefore, dimerization which is the reverse reaction the enthalpy of dimerization will be negative of this will be minus 103 kilojoules per mole.

So, we have discussed the various aspects of weak acids weak bases how to classify weak acids, how to classify weak bases p K a and its relation to its ability of the molecule to donate or accept protons and also how to deal with the values of p K a in terms of delta g naught as we described in the previous lecture that K a is eventually connected with the standard reaction Gibbs energy because K a is an equilibrium constant and whenever you have the values of equilibrium constant its temperature dependence can give you other thermodynamic properties.

So, I hope we appreciate that the thermodynamic properties and their temperature dependence gives a lot of information which can be used to discuss many processes both qualitatively and quantitatively and we have taken several examples to demonstrate this. There is still more to be discussed about acid and bases in relation to the buffers because when we talk about the biological systems, the choice of buffer becomes very important therefore, which salt to be chosen to prepare a buffer and what is a buffer these matters we will discuss in details in the next lecture.

Thank you very much.