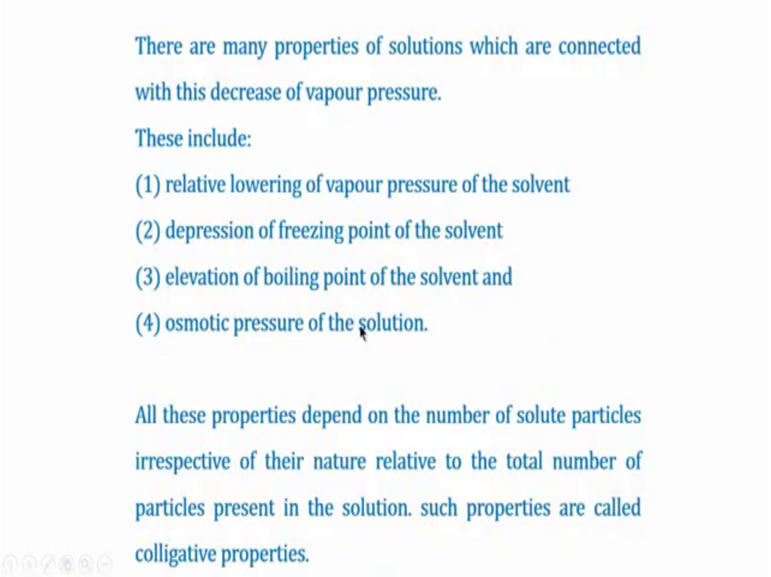
Electrochemical Technology in Pollution Control
Dr. J. R. Mudakavi
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture - 05
Typical Properties of the Solutions

We will continue our discussion on the Typical Properties of the Solutions; there are many properties of solutions which are connected with this decrease of vapour pressure in these systems.

(Refer Slide Time: 00:53)



There are many properties of solutions which are connected with this decrease of vapour pressure.

These include:

(1) relative lowering of vapour pressure of the solvent

(2) depression of freezing point of the solvent

(3) elevation of boiling point of the solvent and

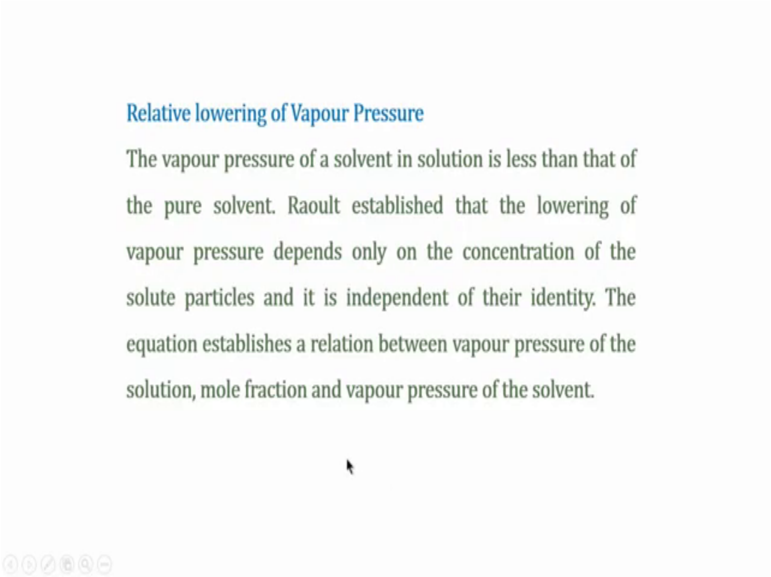
(4) osmotic pressure of the solution.

All these properties depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution. such properties are called colligative properties.

So, in they include relative lowering of vapour pressure of the solvent, depression of freezing point, elevation of boiling point and osmotic pressure of the solution; all these things will decrease. And all these properties depend upon the number of solute particles irrespective of their nature, relative to the total number of particles present in the solution.

So, such properties are called as colligative properties we are talking about vapour pressure of the solvent relative lowering of the vapour pressure. We are talking about depression of freezing point; we are talking about elevation of boiling point; all these things are called as colligative properties because they depend upon the total number of solute particles irrespective of their nature ok.

(Refer Slide Time: 01:37)

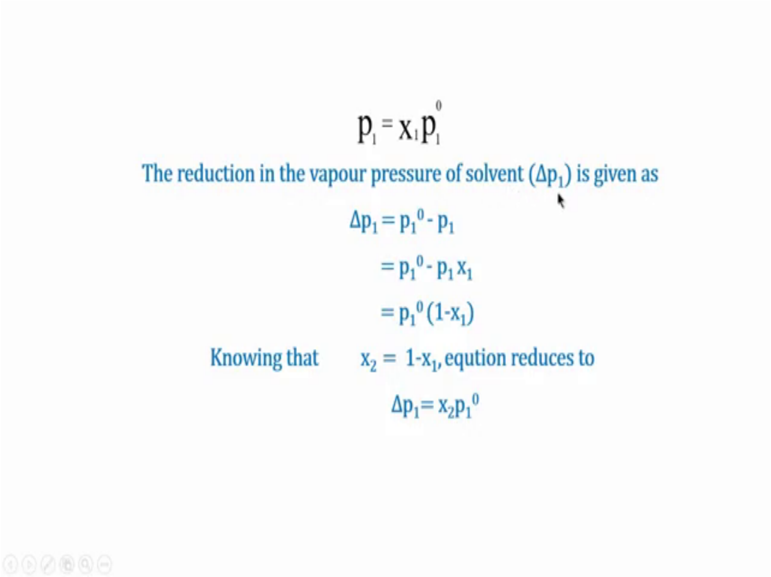


Relative lowering of Vapour Pressure

The vapour pressure of a solvent in solution is less than that of the pure solvent. Raoult established that the lowering of vapour pressure depends only on the concentration of the solute particles and it is independent of their identity. The equation establishes a relation between vapour pressure of the solution, mole fraction and vapour pressure of the solvent.

This is another property of the solution and here I give a brief introduction to relative lowering of the vapour pressure. So, the vapour pressure of a solvent in solution is less than that of the pure solvent; definitely this point you should appreciate now. So, Raoult established that the lowering of the vapour pressure depends only on the concentration of the solute particles; that is independent of their identity; that means, it is mainly dependent upon the solvent irrespective of whatever you take a solvent, whatever you add a little bit its all; vapour pressure will come down. So, this equation establishes a relationship between vapour pressure and mole fraction of the solvent.

(Refer Slide Time: 02:36)



$$p_1 = x_1 p_1^0$$

The reduction in the vapour pressure of solvent (Δp_1) is given as

$$\Delta p_1 = p_1^0 - p_1$$

$$= p_1^0 - p_1 x_1$$

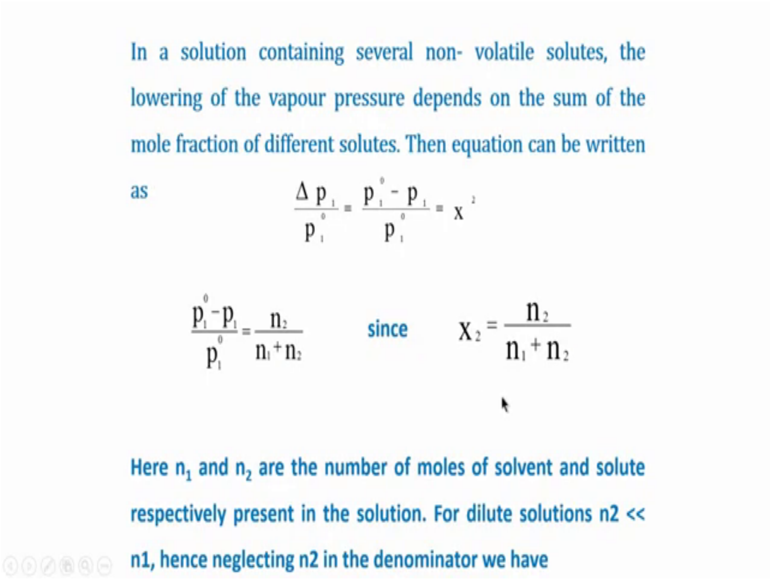
$$= p_1^0 (1 - x_1)$$

Knowing that $x_2 = 1 - x_1$, eqution reduces to

$$\Delta p_1 = x_2 p_1^0$$

So, here I write p 1 is equal to x 1 into p 1 naught; a very simple expression which you have seen earlier. So, the reduction in the vapour pressure is given as delta p 1 should be p 1 naught minus p 1 because p 1 will be lower than that it; because it contains solute. So, I can write this will be I can write it as a p 1, x 1; here I have I am just substituting and p 1 0; I can take out and what I have is 1 minus x 1 knowing that x 2 should be x 1 minus x 1 because it is mole ratio x 2 is nothing, but 1 minus 1; we can write delta p 1 should be equal to x 2 into p 1 0 ok.

(Refer Slide Time: 03:27)



In a solution containing several non- volatile solutes, the lowering of the vapour pressure depends on the sum of the mole fraction of different solutes. Then equation can be written as

$$\frac{\Delta p_1}{p_1^0} = \frac{p_1^0 - p_1}{p_1^0} = x^2$$

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2} \quad \text{since} \quad X_2 = \frac{n_2}{n_1 + n_2}$$

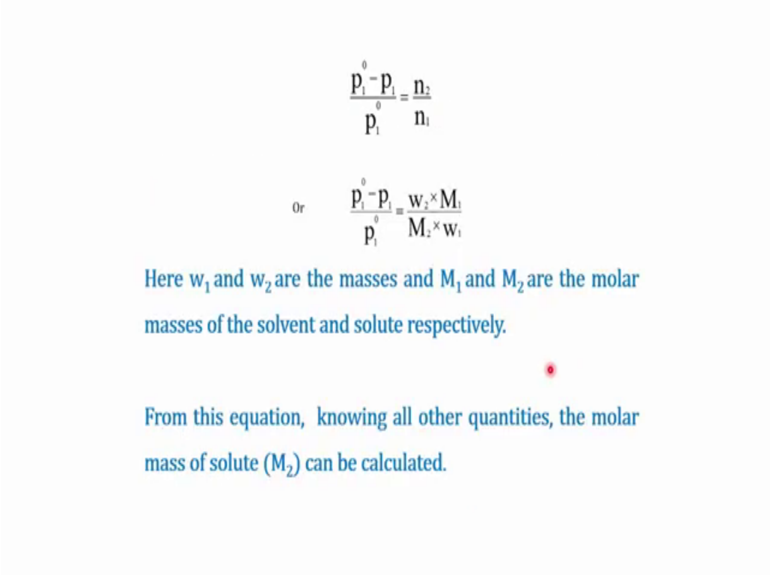
Here n_1 and n_2 are the number of moles of solvent and solute respectively present in the solution. For dilute solutions n2 << n1, hence neglecting n2 in the denominator we have

So, in a solution containing several non volatile solutes, the lowering of the vapour pressure depends on the sum of the mole fraction of different solutes. So, we can write the equation something like this; in a solution containing several non volatile solute, the lowering of the vapour pressure depends upon the sum of the mole fractions of different solutions total. Suppose there is one component p 1 and it will lower the vapour were boiling where vapour pressure a little bit less, another component is there p 2 that also will lower to some extent.

So, like that there it will be different solutes that will lower the boiling; vapour pressure of the substance and that depends on the sum of the mole fractions of the different solutes. You suppose there are two, then it is sum of two mole fractions then the equation we can write the equation something like delta p 1 by p 1 naught is equal to p 1 naught minus p 1 divided by p 1 naught that should be equal to x square; you can p 1 naught minus p 1 so it should be equal to n 2 by n 1 plus n 2 number of molecules it is same essentially instead of in concentration; we are writing mole number of molecules.

Since x 2 is nothing, but n 2 bar n 1 plus n 2; so n 1 and n 2 are the number of moles of the solvent and solute respectively present in the solution, for dilute solutions n 2 should be much much lower than the and then n 1; hence neglecting n 2 in the denominator, we can neglect this n 2.

(Refer Slide Time: 05:27)



$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1}$$

Or $$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

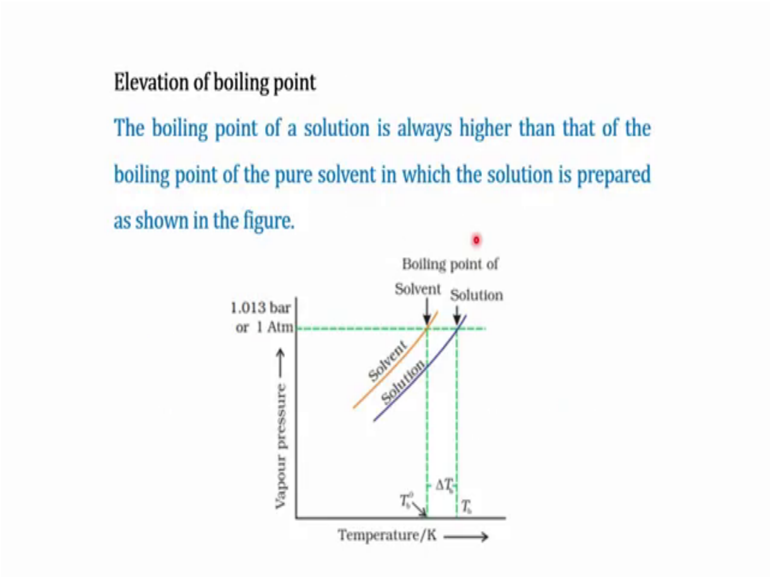
Here w_1 and w_2 are the masses and M_1 and M_2 are the molar masses of the solvent and solute respectively.

From this equation, knowing all other quantities, the molar mass of solute (M_2) can be calculated.

And then we can write p 1 minus p naught minus p 1 divided by p 1 naught should be n 2 by n 1; this is because we are neglecting n 2 in the denominator here, it should have been n 2 because it is much lesser than n 1. So, we can write this is n 2 is nothing, but w 1 and w 2; mass we convert it into mass w 1 into a molecular weight one and masses of the solvent and w 2 are the; w 2 is the solute and its molecular weight.

From this equation knowing all other quantities, the molar mass of solute M 2 can be calculated that is given any two substances; given any two substances binary system, you can determine the molar mass of a given solution; just by measuring the vapour pressure of the solvent ok.

(Refer Slide Time: 06:18)



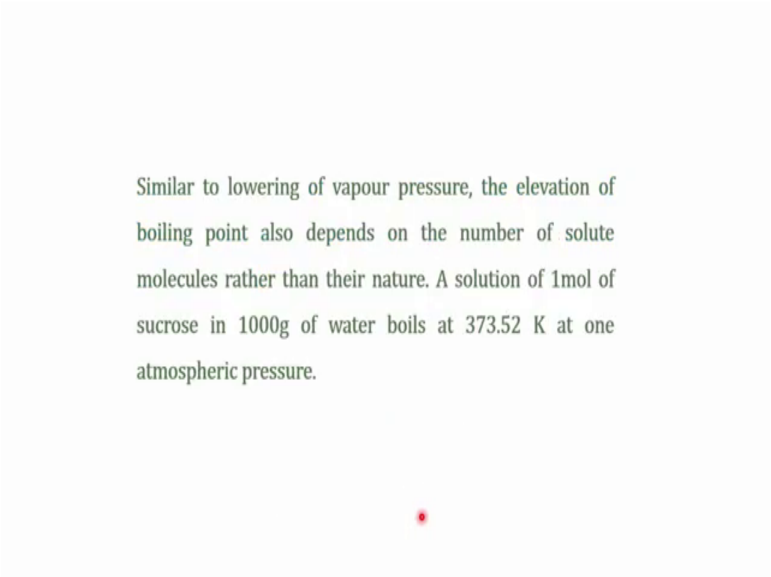
Elevation of boiling point

The boiling point of a solution is always higher than that of the boiling point of the pure solvent in which the solution is prepared as shown in the figure.

Now, we go to another feature that is essentially a colligative property that is elevation of boiling point. Here also, it is a similar system the boiling point of a solution is always higher than that of the boiling point of the pure solvent; in which the solution is prepared as shown in the figure. Here I have a boiling point of the solvent top one and this is the atmospheric pressure vapour pressure; this is the temperature. So, I have a solution that is boiling point is given at this temperature ok.

So, this is the boiling point of the solvent, but if I dissolve a substance; boiling point curve will go like this. So, where is the new boiling point now? It is it is T b here it is T r here. So, there is a small increase in the boiling point of the mixture ok. So, this figure you should try to remember.

(Refer Slide Time: 07:51)



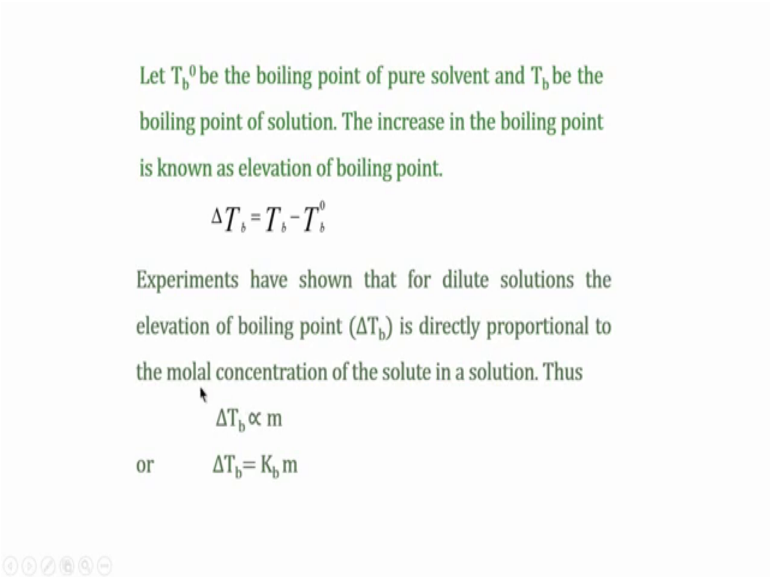
Similar to lowering of vapour pressure, the elevation of boiling point also depends on the number of solute molecules rather than their nature. A solution of 1mol of sucrose in 1000g of water boils at 373.52 K at one atmospheric pressure.

So, similar to lowering of the vapour pressure; the elevation of boiling point also depends on the number of solute molecules rather than their nature; that is irrespective of the nature of the chemical whatever you put in a liquid; its boiling point will increase. So, it is you can find out whether a substance is a pure liquid or not pure liquid; just by looking at the boiling point, isn’t it? So, boiling point will increase if anything is dissolved; anything is dissolved means it is polluted ok, it is a different than the pure solvent.

So, you can find out how much depending upon the increase in the boiling point; you can say how much has been dissolved. It may not tell you exactly what is dissolved, but the solvent is pure only to some extent 98 percent then 2 percent is the elevation in boiling point; something like that we can estimate.

So, a solution of 1 mole of sucrose in 1000 grams of water boils at 373.52 at one atmospheric pressure. This is a simple explanation because water should boil at what temperature? 100 degree centigrade know; so 273, it should boil. Now, a solution of 1 mole of sucrose; if I dissolve it in one water; what temperature it will boil? Instead of 373.00; it boils at 373.52 Kelvin at one atmospheric pressure. So, this is how we express K is Kelvin degree Kelvin ok.

(Refer Slide Time: 09:45)



Let T_b^0 be the boiling point of pure solvent and T_b be the boiling point of solution. The increase in the boiling point is known as elevation of boiling point.

$$\Delta T_b = T_b - T_b^0$$

Experiments have shown that for dilute solutions the elevation of boiling point (ΔT_b) is directly proportional to the molal concentration of the solute in a solution. Thus

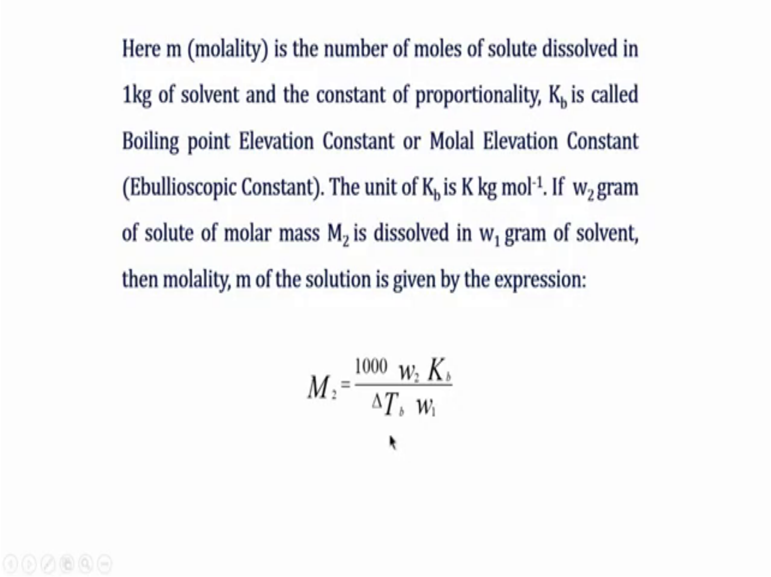
$$\Delta T_b \propto m$$

or $$\Delta T_b = K_b m$$

So, look at the previous diagram now; this diagram I here I have written T b and T b etcetera T r T; T r. So, delta T b that is increase in the boiling point of the solute; solvent of a solution is T b minus T b naught ok, this is the solute solution and this is pure solvent. So, experiments are shown that for dilute solutions; the elevation of boiling point is directly proportional to the molal concentration of the solute in a solution that is so many grams of; of the solute in so many kg; you know you remember our discussion.

So, we can write delta T b is proportional to the m that is molal concentration; I can also write delta T b should be equal to K b into m.

(Refer Slide Time: 10:56)



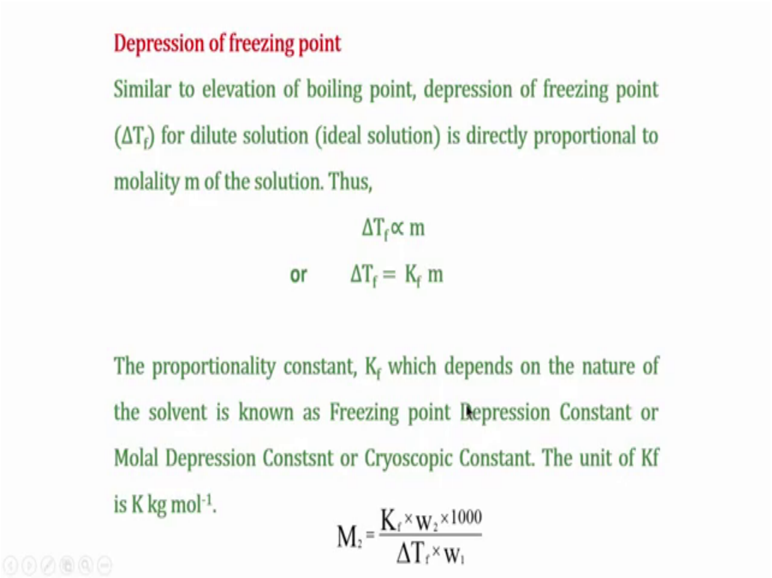
Here m (molality) is the number of moles of solute dissolved in 1kg of solvent and the constant of proportionality, K_b is called Boiling point Elevation Constant or Molal Elevation Constant (Ebullioscopic Constant). The unit of K_b is K kg mol^{-1}. If w_2 gram of solute of molar mass M_2 is dissolved in w_1 gram of solvent, then molality, m of the solution is given by the expression:

$$M_2 = \frac{1000\ w_2\ K_b}{\Delta T_b\ w_1}$$

So, here m is the number of moles of solute dissolved in 1 kg of the solvent and constant of proportionality K b is called boiling point elevation constant or molal elevation constant; it is also known as ebullioscopy constant.

The unit of K b is so many kg per mole unit of K b degrees per K degrees kg per mole. If w 2 gram of the solute; so of solar mass M 2 is dissolved in w 1 gram, this is I am trying to write an equation; then I can write M 2 should be equal to 1000 into w 2 into K b into delta T b divided by delta divided multiplied by w 1 in the denominator.

(Refer Slide Time: 11:48)



Depression of freezing point

Similar to elevation of boiling point, depression of freezing point (ΔT_f) for dilute solution (ideal solution) is directly proportional to molality m of the solution. Thus,

$$\Delta T_f \propto m$$

$$\text{or} \quad \Delta T_f = K_f\, m$$

The proportionality constant, K_f which depends on the nature of the solvent is known as Freezing point Depression Constant or Molal Depression Constsnt or Cryoscopic Constant. The unit of Kf is K kg mol^{-1}.

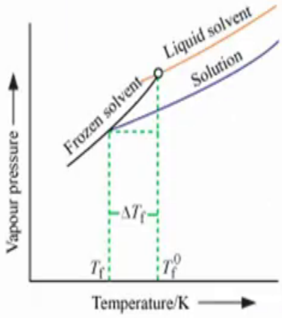
$$M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1}$$

So, we have a similar experience of depression of freezing point. So, here what we have? Similar to elevation of boiling point, depression of freezing point also happens; it is a common phenomenon lot of people who want do not want ice to become solid; they had a little bit of salt into ice. So, especially in areas where there is lot of ice snowfall; people do not want ice to fall on the roads. So, what they do is they keep on sprinkling salt because the; the ice will melt will melt and the freezing point will go down.

So, when the freezing point goes down, the ice will melt a little bit and it will be more comfortable; it is a very common phenomena. So, depression of freezing point is a similar situation that is irrespective of the nature of the substance; the; the freezing point decreases; boiling point increases and freezing point decreases. So, we can write an expression something like this delta T f is proportional to m; smilaric exercise what we did for boiling point.

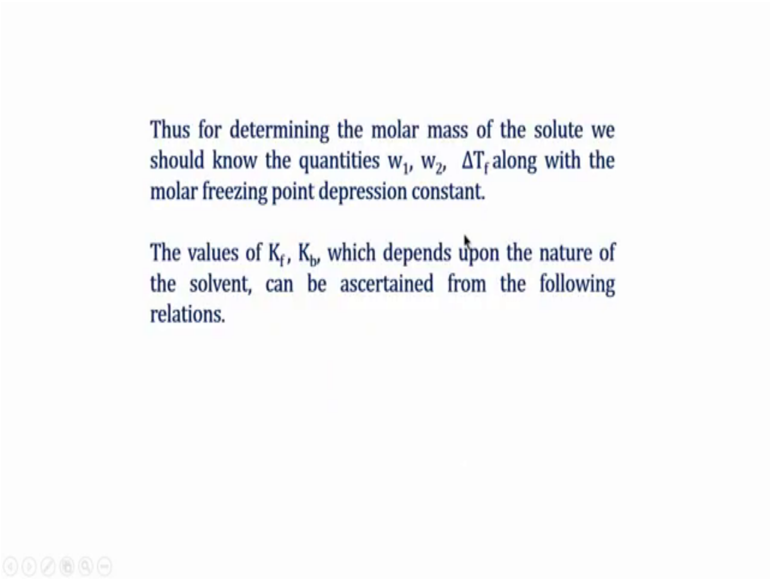
Then we have delta T f is equal to K f; that is f constant and I can write M 2 should be equal to K f into w 2 into 1000 divided by delta T f into w 1. This is essentially similar equation like what we have seen for elevation of boiling point. So, it is also known as depression constant or molal depression constant or cryoscopy constant; several names are available and the unit of K f should be kilogram in a degrees Kelvin per mole ok.

(Refer Slide Time: 14:00)



So, here is an anti elevated figure that shows you the depression of freezing point; it keeps on increasing as you keep on adding and a solute and for a solution it is so much lower delta T f is the depression of freezing point ok.

(Refer Slide Time: 14:28)

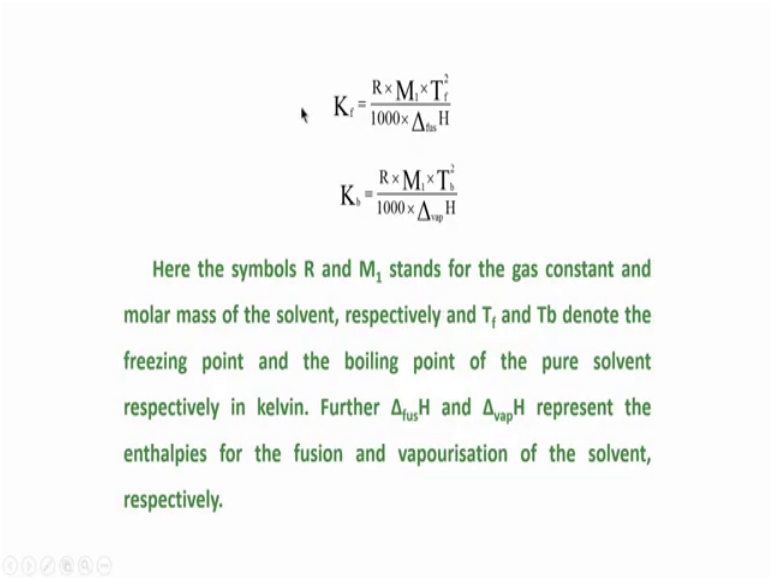


Thus for determining the molar mass of the solute we should know the quantities w_1, w_2, ΔT_f along with the molar freezing point depression constant.

The values of K_f, K_b, which depends upon the nature of the solvent, can be ascertained from the following relations.

So, for determining the molar mass of the solutes; we should know the quantities w 1, w 2 and delta T f along with the molar freezing point. If we know all other things, the values of K f and K b depend on the nature of the solvent and they can be ascertained from the following relations.

(Refer Slide Time: 14:48)



$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{fus} H}$$

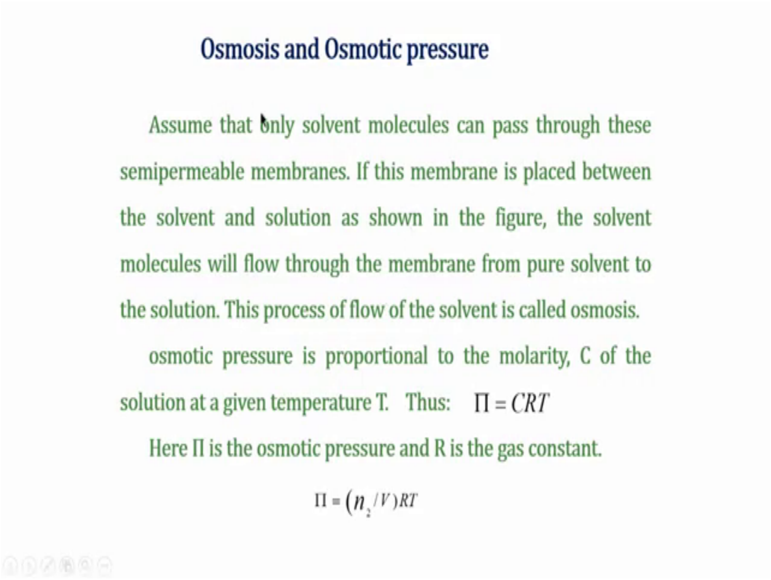
$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{vap} H}$$

Here the symbols R and M_1 stands for the gas constant and molar mass of the solvent, respectively and T_f and Tb denote the freezing point and the boiling point of the pure solvent respectively in kelvin. Further $\Delta_{fus}H$ and $\Delta_{vap}H$ represent the enthalpies for the fusion and vapourisation of the solvent, respectively.

What are the relations? So, these are the relations; here the symbol R and M 1 stand for the gas constant and molar mass of the solvent and T f and T b denote the; we have T f here, we have T b here; they denote the freezing point and the boiling point of the pure solvents in degree Kelvin. And further delta fusion and here it is the change in the heat of fusion and here it is change in the and now here we are talking about the boiling point. So, it is change in vaporization; delta vaporization enthalpy of the vaporization, here it is enthalpy of fusion.

So, enthalpies of the fusion and vaporization of the temperature; these two equations will tell us exactly what is the problem.

(Refer Slide Time: 15:42)



Osmosis and Osmotic pressure

Assume that only solvent molecules can pass through these semipermeable membranes. If this membrane is placed between the solvent and solution as shown in the figure, the solvent molecules will flow through the membrane from pure solvent to the solution. This process of flow of the solvent is called osmosis.

osmotic pressure is proportional to the molarity, C of the solution at a given temperature T. Thus: $\Pi = CRT$

Here Π is the osmotic pressure and R is the gas constant.

$$\Pi = (n_2/V)RT$$

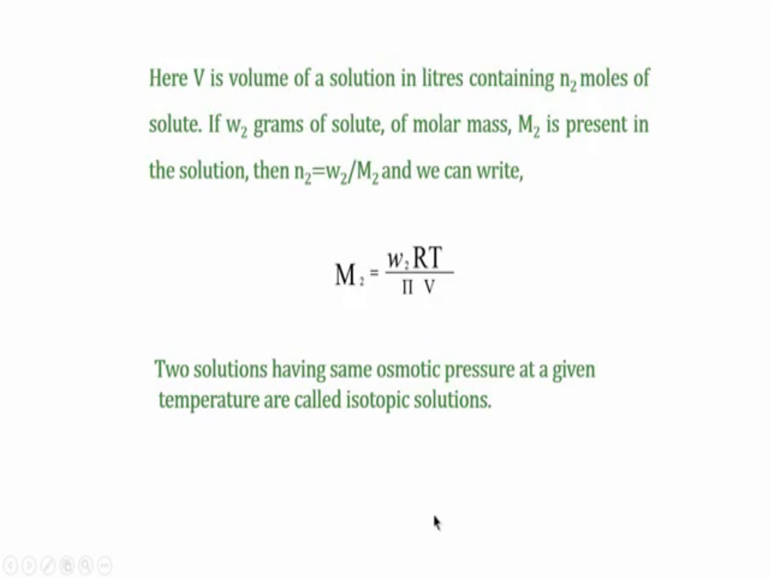
Now, we discuss another property that is known as osmosis and osmotic; osmotic pressure. So, I had explain a little bit too about this to you; we are not going too much into details, but I will just give you a small intro ok.

So, assume that we have only solvent molecules passing through semipermeable membrane. I think most of you have heard of RO; Reverse Osmosis correct? So, most of us, our houses have RO units available; what do they contain? They contain a semipermeable membrane in which water will pass through and whatever is dissolved in water will not pass through; that is a semi permeable membrane. Impermeable membrane means no water, no salt; permeable membrane means everything will pass through. Semipermeable membrane will preferentially allow the solvent to go through holding the solute back.

So, the theoretical basis is fairly simple what happens is assume that solvent molecules like water; it will pass through a membrane. So, if this membrane is placed between a solvent and the solution; we the solvent molecules will fall through and solute molecules are held back in the solution. So, this process of flow is called as osmosis very simple ok; so a flow of the solvent only. So, there is certain amount of pressure that is exerted during osmosis that is known as osmotic pressure. So, osmotic pressure is proportional to the morality of the solution at any given temperature and that is understood now ok.

So, I can write pi is equal to CRT here; in the slide I am writing pi is equal to CRT concentration into RT; that is R is gas constant and pi is the osmotic pressure ok, T is temperature. So, I can write concentration as number of molecules divided by volume right. So, pi should be equal to n 2 by V into RT.

(Refer Slide Time: 18:23)



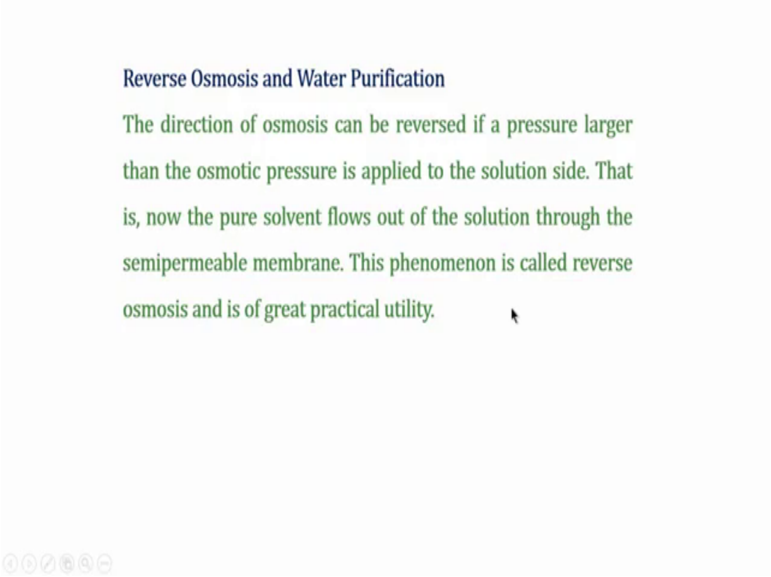
Here V is volume of a solution in litres containing n_2 moles of solute. If w_2 grams of solute, of molar mass, M_2 is present in the solution, then $n_2=w_2/M_2$ and we can write,

$$M_2 = \frac{w_2 RT}{\Pi V}$$

Two solutions having same osmotic pressure at a given temperature are called isotopic solutions.

So, V is the volume of the solution in liters containing n 2 molecules of the solute and w grams of the solvent molar solute M 2 is present in the solution; then n 2 would be w 2 by M 2; so I can write M 2 should be equal to w 2 into RT by pi into V. So, the two solutions having the same atmospheric pressure at a given temperature are called as isotopic solutions; if there are two solutions having same osmotic pressure, then they are called as isotopic solutions.

(Refer Slide Time: 19:01)

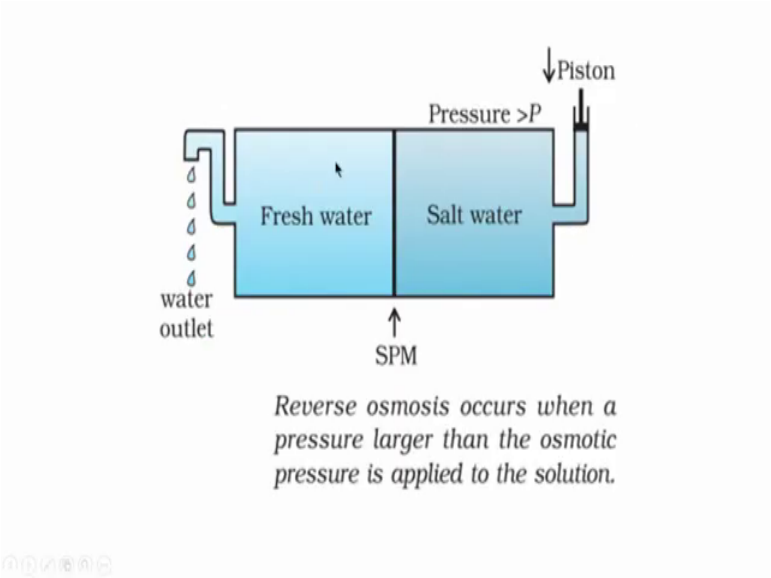


Reverse Osmosis and Water Purification

The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. That is, now the pure solvent flows out of the solution through the semipermeable membrane. This phenomenon is called reverse osmosis and is of great practical utility.

So, what is reverse osmosis? So, the direction of the osmosis can be reversed; if I put a pressure larger than the osmotic pressure that is applied to the solution side.

(Refer Slide Time: 19:20)



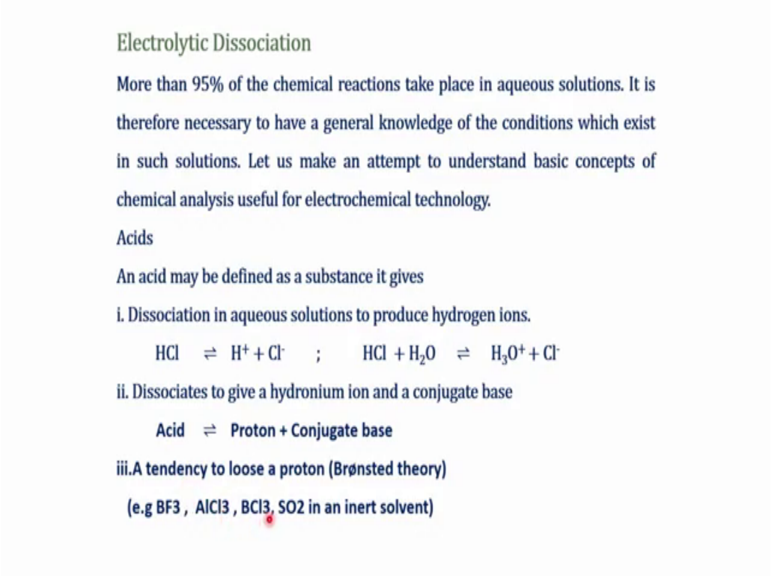
Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.

Now, imagine here I am drawing a picture of reverse osmosis and this is a SPM; semipermeable membrane and I have put salt water and osmotic pressure is there and I have a; I put pressure on this solution and fresh water is; it is allow fresh water on the other side ok.

Now, normal osmosis; salt water will remain this side and in fresh water will remain that side only that much will go through that is exerted by the osmotic pressure. Now, if I put additional pressure then reverse osmosis occurs when a pressure larger than the osmotic pressure is applied; this will force the solution to go into this, but not the solvent solutes.

So, fresh water I am collecting this side, what remains here is more of the salt water that is remaining here. This is the principle of all ROs what we have it in our houses and this is how it will work. So, now the direction of the osmosis can be reversed if a pressure larger than the osmotic pressure is applied. So, the pure solvent flows out of the solution.

(Refer Slide Time: 20:49)



Electrolytic Dissociation

More than 95% of the chemical reactions take place in aqueous solutions. It is therefore necessary to have a general knowledge of the conditions which exist in such solutions. Let us make an attempt to understand basic concepts of chemical analysis useful for electrochemical technology.

Acids

An acid may be defined as a substance it gives

i. Dissociation in aqueous solutions to produce hydrogen ions.

$HCl \rightleftharpoons H^+ + Cl^-$; $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

ii. Dissociates to give a hydronium ion and a conjugate base

Acid $\rightleftharpoons$ Proton + Conjugate base

iii.A tendency to loose a proton (Brønsted theory)

(e.g BF3 , AlCl3 , BCl3, SO2 in an inert solvent)

Now, we want to talk about other properties of the electrolytic dissociation; nearly 95 percent of the chemical reactions take place in aqueous solutions. You all agree with me now? Isn’t it? I am going to talk I mentioned several times now that 90 percent of the this course discussion will be on aqueous solutions. And it is therefore, necessary to have a general knowledge of the conditions which exist in such solutions.

Let us make this make an attempt to understand basic concepts of chemical analysis using electrochemical useful for electrochemical technology. What we are going to; I am going to define again several terms chemical terms associated with chemical reactions. So, I want to define an acid; what is an acid? Dissociation, acid is defined as a substance; it gives a hydrogen molecule hydrogen atom ion sorry in aqueous solution.

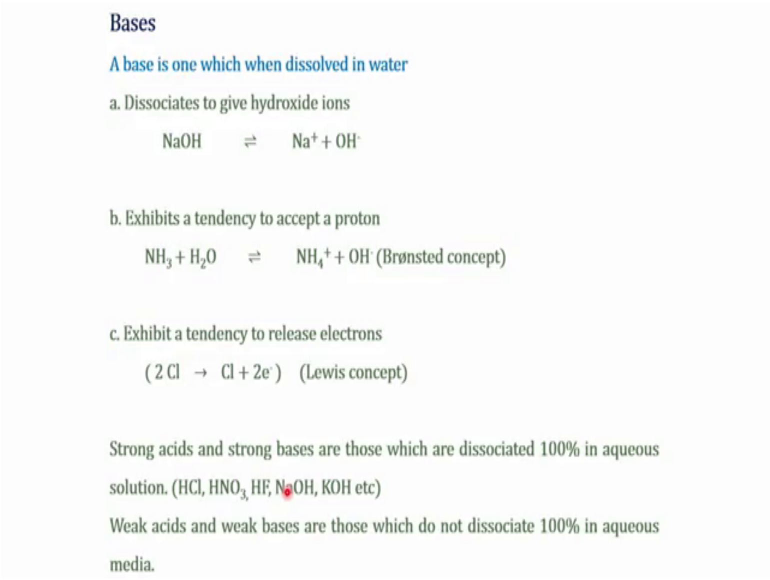
So, an acid may be defined as hydrochloric acid or something like that, but its dissociation in aqueous solutions; it will dissociate as H plus and Cl minus, but it may also live because there are a lot of what our molecules in HCl solutions ok.

We write it as this H plus will react with one more molecule of water to give you H 3 O plus that has got independent existence as an ion; the H plus does not have an independent existence, but it will not remain like H plus. So, this is a very standard way of writing in all modern textbooks that HCl dissociates to give you H plus and Cl minus, but we do not write HCl will dissociate and react with water to give you H 3 O plus that is hydronium ion and chloride ion.

So, and it dissociates to give we can also write this is a proton H plus. I can write acid is in equilibrium with proton and its conjugated base; what is the base? What remains if you take out the proton is base ok. Normally, our concept of base is that sodium carbonate is a base, sodium hydroxide is a base, potassium hydroxide is a base, calcium hydroxide is a base like that, but we are extending the same definition that acid is one in which a proton is there; in along with its conjugate base in equilibrium with the undissociated acid; some part of acid dissociates.

So, it is also a tendency to lose a proton; this is the definition of acid from the Bronsted theory. Again all this is PUC stuff; in a college chemistry, nothing much in this and examples are BF 3 AlCl 3 BCl 3, SO 2; in an inert solvent. Here you can see that; in HCl there is H plus in acid there is proton and proton is nothing, but H plus, but in BF 3; there is no hydrogen here still it is an acidic solution. Similarly, aluminum chloride BCl 3; S0 2; there are no protons here correct?

(Refer Slide Time: 24:59)



Bases

A base is one which when dissolved in water

a. Dissociates to give hydroxide ions

$NaOH \rightleftharpoons Na^+ + OH^-$

b. Exhibits a tendency to accept a proton

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ (Brønsted concept)

c. Exhibit a tendency to release electrons

$(2\,Cl \rightarrow Cl + 2e^-)$ (Lewis concept)

Strong acids and strong bases are those which are dissociated 100% in aqueous solution. (HCl, HNO_3, HF, NaOH, KOH etc)

Weak acids and weak bases are those which do not dissociate 100% in aqueous media.

So, and I say this is the definition of an acid; it may that is known as Lewis acid; this BF 3, aluminum chloride BCl 3 these are all called as Lewis acid. Here we define acid as one which is which has got a tendency to lose; to accept electrons that is the acid that is Lewis acid third one ok.

So, we can similarly define what is base; a base is one which is which when dissolved in water should dissociate to give you a hydroxide ion; the other part that is cation and anion. So, H minus is anion, Na plus is cation. So, it may be suppose it is KOH; then it will give K plus and OH minus.

So, OH minus is very common in all bases that is for normal draw a day to day in this thing. It exhibits a tendency to accept a proton; it need not dissociate ok; this is Bronsted concept. A base is one which can react with water to accept one hydrogen from here; NH 3 will become

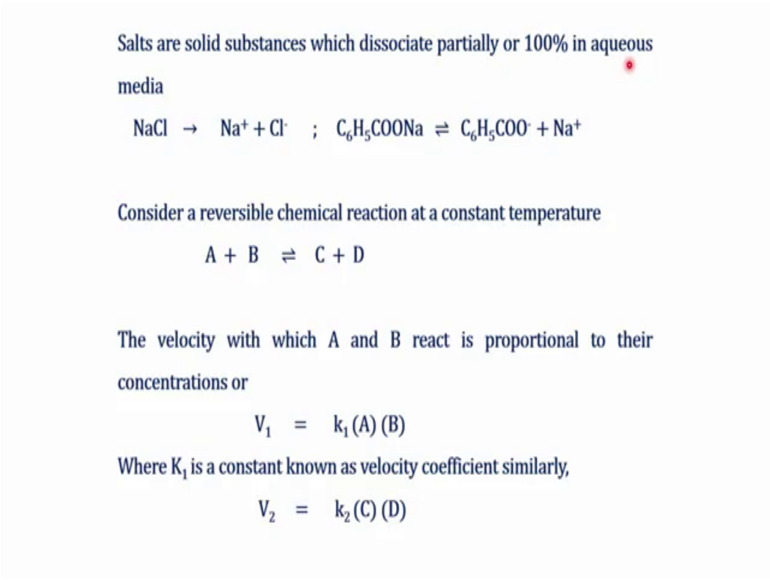
NH 4 because it is a proton, it will be NH 4 plus. And then once this loses H minus H plus what remains is two electrons are remaining here extra; so H minus is produced; this is a Bronsted concept, all these definitions represent the acid base concept.

So, we also have another definition that is Lewis concept; it must exhibit a tendency to release electron; that means, it must be electron rich. For example, two chlorine atoms can give you chlorine chloride ions and it is a 2 e minus ok. Strong acids and strong bases are those which are dissociated 100 percent in aqueous solutions. We now; you are going to define what is a strong acid and what is a strong base; some acids are strong, some acids are weak acids for example, hydrochloric acid, nitric acid they are all very strong acids.

If they fall on your hands; your hand will burn if this HF is a very strong acid and NaOH is a strong base, potassium hydroxide is a strong base. Even if; if you put NaOH in your hand, your hand will skin will burn. Even if you put KOH in your hand a skin will burn. So, all the things that are dissociated 100 percent are called as strong acids and strong bases. We also come across in our day to day life weak acids and weak bases. So, you must be very well aware of the weak acids in our day to day life; isn’t it? There is citric acid.

So, citric acid is a very weak acid; you know all the oranges there is citric acid, mosambi; there is citric acid. You put it in your mouth you will enjoy that; lemon also has got citric acid acetic acid vinegar we eat it in the food we use it for cooking salads and Chinese foods etcetera. So, there are lots of weak acids and weak bases around us and they also; they are those which do not dissociate 100 percent in aqueous media. So, that is how the definition goes and salts we define salts as substances which dissociate partially or 100 percent in aqueous media aqueous media means water ok.

(Refer Slide Time: 29:30)



Salts are solid substances which dissociate partially or 100% in aqueous media

$NaCl \rightarrow Na^+ + Cl^-$; $C_6H_5COONa \rightleftharpoons C_6H_5COO^- + Na^+$

Consider a reversible chemical reaction at a constant temperature

$$A + B \rightleftharpoons C + D$$

The velocity with which A and B react is proportional to their concentrations or

$$V_1 = k_1 (A) (B)$$

Where K_1 is a constant known as velocity coefficient similarly,

$$V_2 = k_2 (C) (D)$$

So, if I have take sodium chloride salt table salt; I put it in water what it will give? Na plus and Cl minus ok. So, if I put this will be totally dissolved; so totally dissolved means all of it all the salt that we put in water is contained in as a sodium ions and chloride ions ok. Then I have what is known as benzo sodium benzoate sodium; benzoate this compound C 6 H 5 COO Na; if it is H here it is C benzoic acid now it is benzoate sodium benzoate. So, sodium benzoate can also dissociate into benzoic acid the anion and sodium plus cation.

So, all these things you must remember that I have put here there is an equilibrium sign; here it is one single arrow correct. So, this single arrow shows that there is no equilibrium whatever you put is totally ionized. Here in this case it is partially ionized there is whenever you put benzoic acid in solution part of it will dissolve to give you C 6 H 5 COO Na plus cation plus some of the undissociated by sodium benzoate ok; now sodium benzoate is used lot of pickles you know in as a preservative.

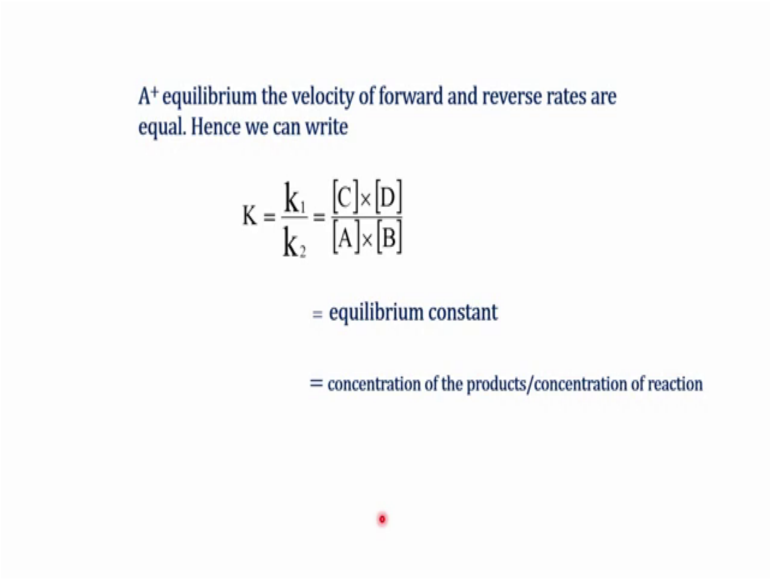
So, it is a very useful chemical that is why I put it here in the slide; this sodium benzoate does not dissolve totally it is all partially. So, a solution of sodium benzoate will contain c sodium, benzoate benzoic acid and Na plus ion benzoic acid anion and sodium plus. So, three entities here it is only two entities.

So, coming back to this discussion consider we are going to write a chemical reaction at a constant temperature. We write A plus B going to C plus D correct; reactant A will react with reactant B to give you a product C and another product D. So, the velocity with which the forward reaction goes is proportional to their concentrations very fundamental equations and college chemistry still.

So, V 1 I can write velocity V 1 is equal to k 1 into a plus b that is a I put it here in the bracket that represents concentration; lot of people write it as the square bracket also A and B. So, V 1 is equal to k 1 into A B; concentration of A multiplied by concentration of B; the proportionate is proportional to forward reaction. So, the proportionality constant is k 1.

So, similarly I can write V 2 is equal to k 2 into C D; that is the reverse reaction. So, C plus D is also going to A plus B now.

(Refer Slide Time: 33:34)



A^+ equilibrium the velocity of forward and reverse rates are equal. Hence we can write

$$K = \frac{k_1}{k_2} = \frac{[C]\times[D]}{[A]\times[B]}$$

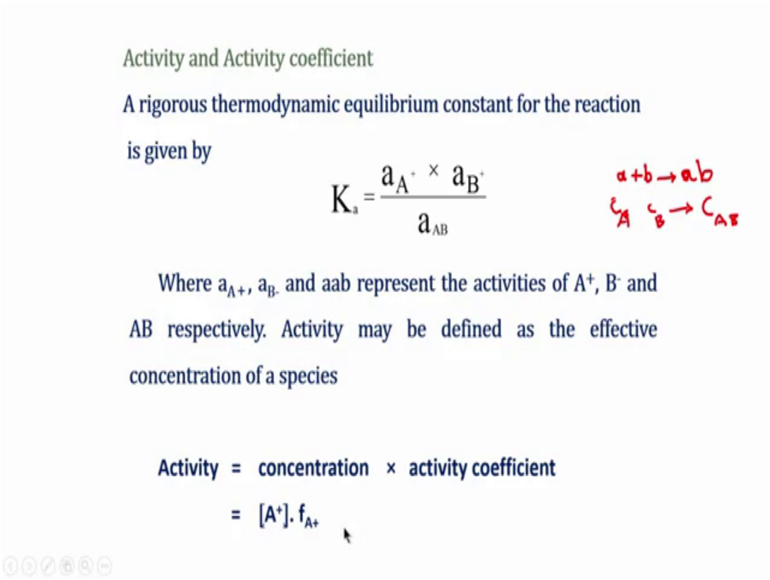
= equilibrium constant

= concentration of the products/concentration of reaction

So, for this reaction I can write another equation like this; then at equilibrium what I have the forward reaction should be equal to the forward reaction should be equal to backward reaction. So, k 1 into A B should be equal to k 2 into C D ok. So, I am going to write k 1 by k 2; if they are going on simultaneously and if they are equal k 1 by k 2 should be equal to C D by A B.

You measure the concentration of the products, divided by the concentration of the reactants and you will get another constant that is known as K that is equilibrium constant. So, actually what it means? It is the concentration of the products divided by the concentration of the reactants ok. Again I must say that it is reactants here; it is not reaction and there is an error in this please correct it if you are noting down ok.

(Refer Slide Time: 34:41)



Activity and Activity coefficient

A rigorous thermodynamic equilibrium constant for the reaction is given by

$$K_a = \frac{a_{A^+} \times a_{B^+}}{a_{AB}}$$

$a + b \rightarrow ab$

$C_A \; C_B \rightarrow C_{AB}$

Where a_{A+}, a_{B-} and aab represent the activities of A^+, B^- and AB respectively. Activity may be defined as the effective concentration of a species

Activity = concentration × activity coefficient

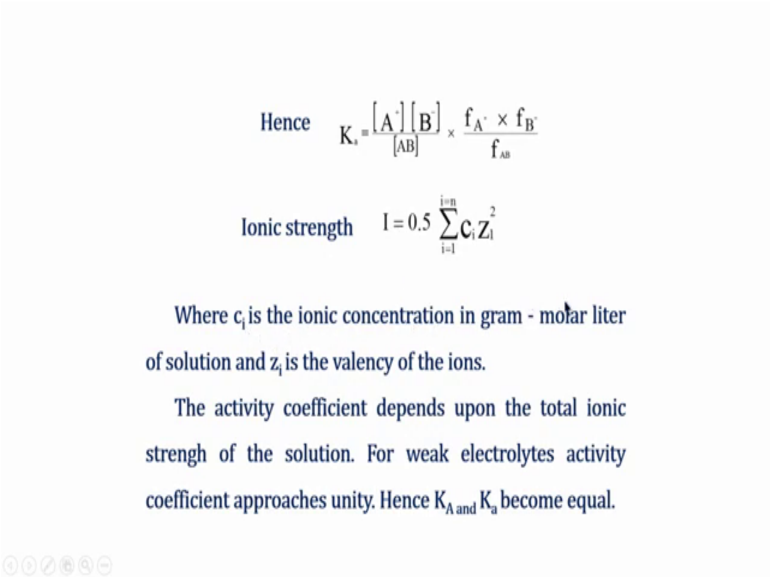
$= [A^+] . f_{A+}$

So, I define now another concept that is activity and activity coefficient. So, here in the previous equation we had written concentrations in their square brackets isn't it? That is equilibrium constant, but its not actually the concentration calculated from the existing system, but a rigorous thermodynamic equilibrium constant of the reaction tells us that the concentrations are not exactly the same what it should have been. For example, I can write an equation something like this K a is equal to a into A plus into multiplied by b a into B plus divided by a AB.

So, here I write it is not the concentration, but it is product; it is the another product related to the concentration that is known as activity. So, activity is replacing concentration here ok. So, here we are going to write an equation like A plus B going to C. So, instead of concentration of C A and C B; I have got C AB ok; here it is A B. So, instead of writing CA: I am going to write a A plus that is concentration of a I am going to write activity of A into activity of B divided by activity of AB.

So, here these things represent the activities of A plus and B minus and A B respectively here in this equation. So, what do we do? We write activity as a effective concentration of a species; it will not be very different from concentration, but slightly different, but thermodynamically we should not write CA concentration terms. So, we define activity as activity is equal to concentration into activity coefficient; that is A plus into this is the activity and activity coefficient is f A plus. So, that is a notation normally accepted.

(Refer Slide Time: 37:56)



Hence $K_a = \frac{[A^+][B^-]}{[AB]} \times \frac{f_{A^+} \times f_{B^-}}{f_{AB}}$

Ionic strength $I = 0.5 \sum_{i=1}^{i=n} c_i Z_i^2$

Where c_i is the ionic concentration in gram - molar liter of solution and z_i is the valency of the ions.

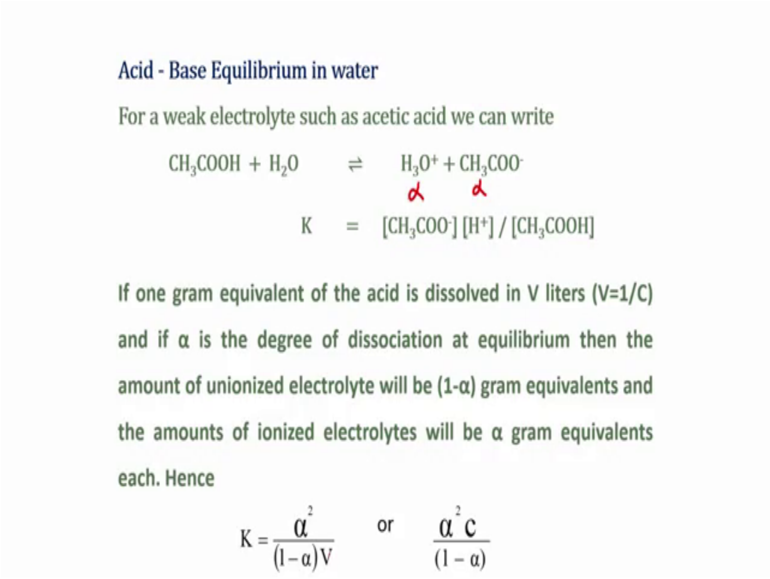
The activity coefficient depends upon the total ionic strengh of the solution. For weak electrolytes activity coefficient approaches unity. Hence K_A and K_a become equal.

So, I can write Ka is nothing, but concentration of A multiplied by concentration of B divided by AB ok; that is for the forward reaction. But they should be multiplied by activity coefficients if I want to do the correct technical representation of the reaction. So, this concentration of A and if A plus that will represent activity of A, this and this will represent activity of B and this will represent A B; that is the product.

So, we also define another term that is I; that is ionic strength this is very important it is approximately 0.5 times; all the concentrations of all the ions present in the solution and their charge z 1 is a discharge valency of the ions and this is a very important term which we keep on using in our course regularly; so 1 to n all ok. So, here c i is the ionic concentration in gram moles molar this thing per gram moles per liter and z i is the valency. So, the activity coefficient depends upon the total ionic strength of the solution; for weak electrolytes activity coefficient approaches unity, for very dilute solutions activity coefficient becomes unity.

So, concentration we; we are not wrong in writing concentrations as a equilibrium in; in the equilibrium reactions. Technically speaking thermodynamically to be correct we write activity, but very dilute solutions activity is one almost. So, we can write concentrations. So, 99 percent of the time we use both these systems and we write this and activity coefficient depends upon the total ionic strength of the solution. For weak electrolytes activity coefficient approaches unity hence ka and ka become equal; here it I had written capital A using concentrations and here it is small a using activity ok.

(Refer Slide Time: 40:48)



Acid - Base Equilibrium in water

For a weak electrolyte such as acetic acid we can write

$$CH_3COOH + H_2O \rightleftharpoons \underset{\alpha}{H_3O^+} + \underset{\alpha}{CH_3COO^-}$$

$$K = [CH_3COO^-][H^+] / [CH_3COOH]$$

If one gram equivalent of the acid is dissolved in V liters (V=1/C) and if α is the degree of dissociation at equilibrium then the amount of unionized electrolyte will be $(1-\alpha)$ gram equivalents and the amounts of ionized electrolytes will be α gram equivalents each. Hence

$$K = \frac{\alpha^2}{(1-\alpha)V} \quad \text{or} \quad \frac{\alpha^2 c}{(1-\alpha)}$$

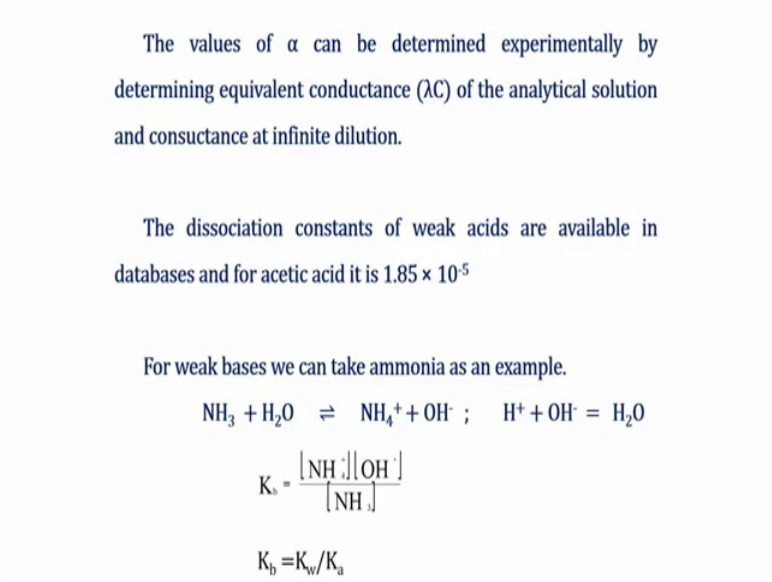
So, we continue our discussion regarding the acids and bases a little bit more. So, acid base equilibrium; we discuss for the as the next part of our understanding of the basic technology basic techniques in chemistry or electrochemical technology.

So, I can write for a weak electrolyte such as acetic acid CH 3, COOH that is the formula for acetic acid plus H 2 O going to H 3 O plus and CH 3 COO minus. I can write K is equal to CH 3 COO minus into H plus m CH 3 COO minus. Actually, you should notice that I should write H 3 O plus here and this; this is concentration I should write a activity, but as you we assume that these are all weak acids; so we can replace weak acids with the with the concentration terms.

So, if 1 gram equivalent of the acid is dissolved in V liters and if alpha is the degree of dissociation; alpha percent degree of dissociation at equilibrium, then amount of unionized acetic acid if 1 is this and alpha is the degree of dissociation unassociated undissociated acid will be 1 minus alpha; alpha is dissociated. So, maximum concentration is 1; so 1 minus alpha gram equivalent would be the undissociated. So, the amounts of ionized electrolytes will be alpha gram.

So, I can write this is alpha I can write this is alpha this is alpha ok; so product I can write two of the products concentration alpha into alpha is alpha square divided by 1 minus alpha that is the product multiple into divided by V. So, or I can say alpha square c divided by 1 minus alpha.

(Refer Slide Time: 43:12)



The values of α can be determined experimentally by determining equivalent conductance (λC) of the analytical solution and consuctance at infinite dilution.

The dissociation constants of weak acids are available in databases and for acetic acid it is 1.85×10^{-5}

For weak bases we can take ammonia as an example.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \; ; \quad H^+ + OH^- = H_2O$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$K_b = K_w/K_a$$

So, this is the mathematical expression for weak acids. The value of alpha can be determined experimentally by determining the equivalent conductance of the analytical solution and conductance at infinite dilution. So, the dissociation constants of weak acids are available in data bases and for acetic acid it is about 1.85 to 10 raised to minus 5.

We will stop here for this session and we will continue our discussion on weak bases also say similar exercise in the next class.

Thank you.