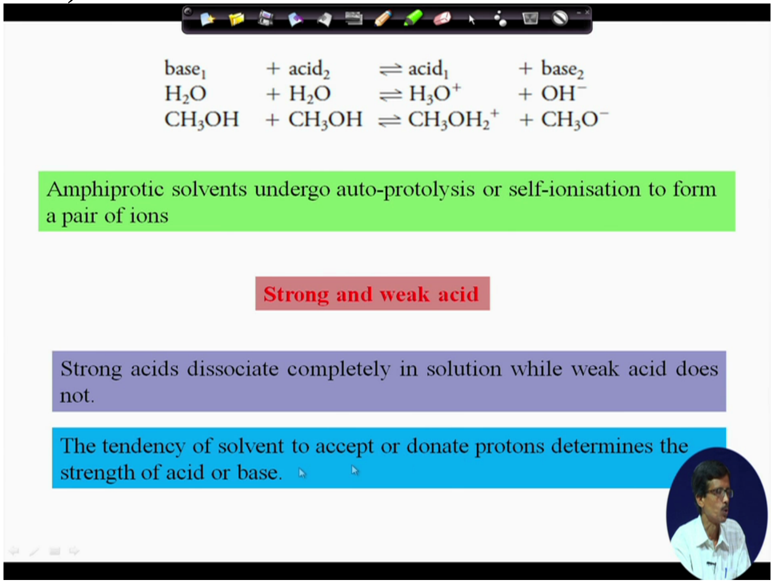
Course on Analytical Chemistry
Professor Debashis Ray
Department of Chemistry
Indian Institute of Technology Kharagpur
Module No 03
Lecture 13: Chemical Equilibria (Contd.)

Good evening, welcome to this class of analytical chemistry where we are discussing about the chemical equilibrium and why we are talking about this chemical equilibrium?

(Refer Slide Time: 0:31)



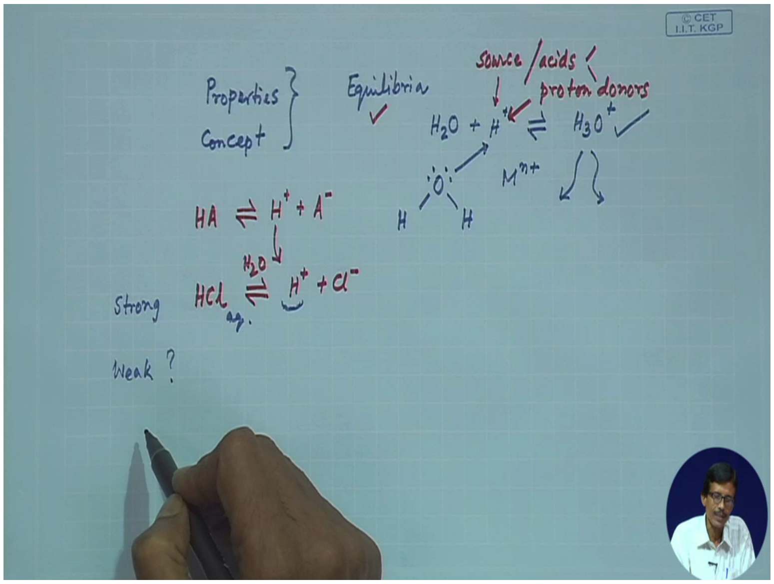
$$\text{base}_1 + \text{acid}_2 \rightleftharpoons \text{acid}_1 + \text{base}_2$$
$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$
$$CH_3OH + CH_3OH \rightleftharpoons CH_3OH_2^+ + CH_3O^-$$

Amphiprotic solvents undergo auto-protolysis or self-ionisation to form a pair of ions

Strong and weak acid

Strong acids dissociate completely in solution while weak acid does not.

The tendency of solvent to accept or donate protons determines the strength of acid or base.



Because 2 things of this that particular equilibrium, that means uhh its properties and concept, we will be utilising in future for the particular type of analysis. So we have the equilibria and that particular equilibrium what we are talking about in terms of very simple reaction what we all know that the corresponding reaction of water with that of H plus. That means the proton forming H3O plus. So any of the type of solvent where you can have the lone pair of electrons on oxygen atom of this H2O molecule, that means water molecule, so this is a particular thing, that means H plus, that means one single electron is also not there.

So if it can form some interaction, that means the coordinate bond that we all know, that a lone pair of electron when utilised, that means it can be donated to some other species which is positively charged, which is devoid of electron such that we call in terms of the corresponding coordination compounds when the water is bound to Mn plus. Similarly this H plus can also bound to this water molecule giving rise to H3O plus.

So there are several consequences of all these things, that means when you from this H3O, how this particular species is forming and this we all know that this particular proton where the source is, that means the acids and we are talking about the different acids. And we exposed yourself that in one particular case we have the corresponding strong acid case and in either case, the weak acid case the how these 2 things, that means they are basically wired this we are talking, this is because this H plus, this acid that means strong acid or weak acid can provide these protons as they are good proton donors.

So what we have seen so far that when these 2 are reacting, so one particular example what we are talking about is not only the interaction of the corresponding only proton to water molecule but if we consider theta as that H2O and instead of talking in terms of H plus, we can consider this another water molecule. So one of them, that means one of the water molecule can function as a base and another can function as an acid.

So there will be an acid-base equilibrium, so this equilibrium is a typical acid-base equilibrium. So the water molecule what we are considering as acid can donate the electron, so sorry the proton. So the donation of that particular proton is coming from this water molecule and is going from this to this base. So this base will be now H3O plus and it will the base remaining from the acid 2 is that HO minus. So what we discussed in the previous class that this is the corresponding conjugate base.

So H2O will be giving you the corresponding conjugate base which is hydroxide ions. Similarly this base what we are considering is accepting the proton giving you the corresponding conjugate acid as H3O plus. Similarly, 2 molecules of methanol can also behave in a similar fashion and one of the methanol molecule can be a proton donor and other can be the proton except. So the by definition, one of them can be considered as a acid and another can be considered as an base.

So these things we have discussed so far that amphiprotic protons or the auto protolysis or self ionisation can take place on water as well as the water like methanol molecule. So these 2 things, that means the we can have other proton donor, so how good the proton donor is and how weak or strong the proton donor is. So the strong acids, if we consider the strong acids, what we will consider or focus our attention that the corresponding before creation reaction.

So if we have a corresponding acid as HA and when we for talking or realising the corresponding chemical equilibrium in terms of the corresponding HA dissolved in aqueous medium. Whether you will have type of dissociation like H plus A minus, that we will try to see. And how far this equilibrium is going from left to right or from right to left, that means what percentage of HA is getting dissociated between H plus and A minus, that will also tell us that how much of this H plus is being provided to the solution after dissociation.

So if we consider some other acid we all know that typical hydrochloric acid, that means the aqueous solution of hydrochloric acid if it dissociates like H plus and Cl minus and if the dissociation is going from left to right almost completely, so 90 or 90 plus or 99 plus percentage of dissociation can take place in water medium.

So this is the medium is the water. So this can happen so happen that you can have large amount of this supply of H plus and this particular one can give rise to the amount of H which is originally bound as or in the corresponding form to in the gaseous hydrochloric acid we all know the aqueous solution is your corresponding acid where the dissociation can take place.

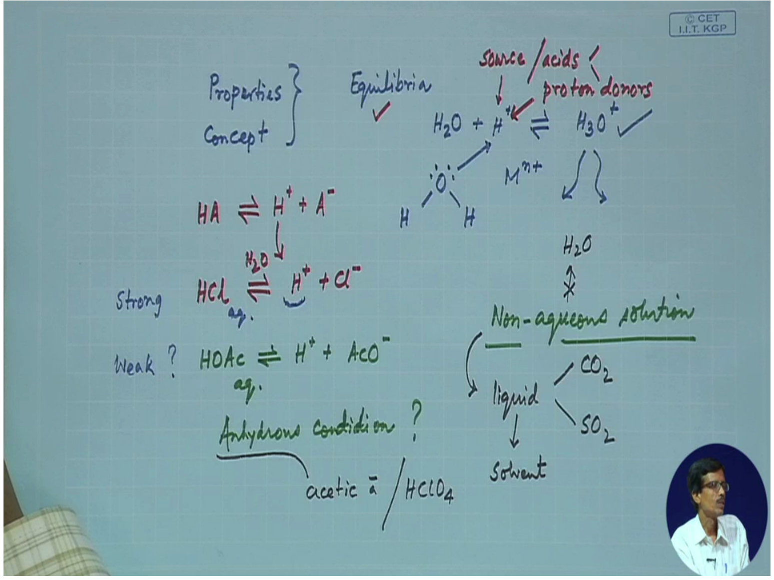
And if all of them almost give you the H plus, whatever number of H you can is available from the HCl molecule itself so if the dissociation is very large and there will be a complete almost complete dissociation they can label this as a strong acid. But what about the weak one? The weak one will not go like this. So weak one will not dissociated in that particular fashion. So by definition, we can consider it as that strong acid dissociates completely whether the weak acid does not.

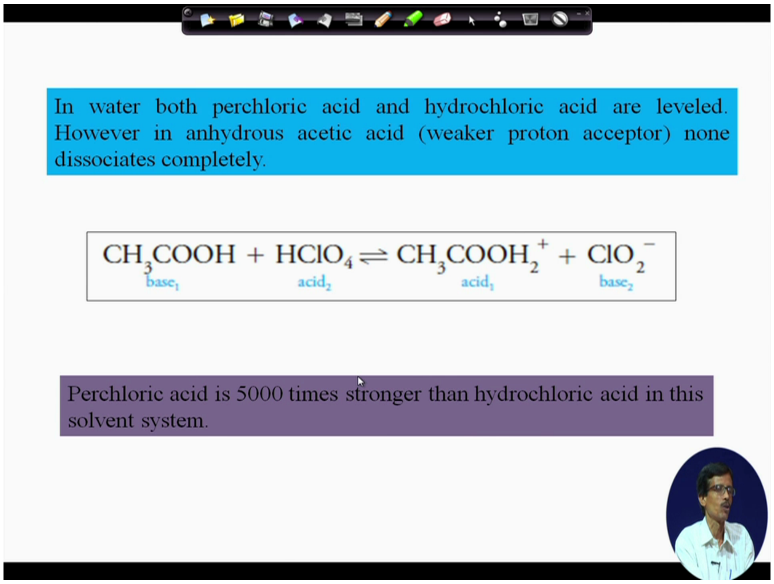
So the tendency of the solvent, so we are bringing now the involvement of the corresponding solvent. That is why I just not told you that your HCl it is a gas and when it is dissolved in water solvent, water is your solvent, it can function as a very good acid. So this particular solvent where we are discussing this from this very 1st part of this particular slide that you have these 2 water molecules and all we know that water molecules are very good solvent molecules.

Similarly, this methanol, the CH3OH molecules are good solvent molecules. So how solvent can play some important role over here during this donation and acceptance of these protons? So the tendency of the solvent to accept or donate protons determine the strength of the acid and the base. So what you see? That you have a medium and that medium playing some important role that such that your water medium if it accepts the proton, so if we bring this water molecule over here and if it accepts water, so that will give rise to H3O plus.

So water can play some dominant role for accepting that particular H plus. So if you have another water molecule as I know this H plus is coming from the another water molecule. So this formation of this H3O plus and the amount of H3O plus forming over there will tell you how strong your acid is but in case of the weak acid, this kind of dissociation or this much amount of H plus will not form. So the equilibrium again plays some important role for the strength of the acid and the strength of the weak acid as well.

(Refer Slide Time: 9:35)





In water both perchloric acid and hydrochloric acid are leveled. However in anhydrous acetic acid (weaker proton acceptor) none dissociates completely.

$$\underset{\text{base}_1}{CH_3COOH} + \underset{\text{acid}_2}{HClO_4} \rightleftharpoons \underset{\text{acid}_1}{CH_3COOH_2^+} + \underset{\text{base}_2}{ClO_2^-}$$

Perchloric acid is 5000 times stronger than hydrochloric acid in this solvent system.

So what we get in water again the medium is water. These two acids we are now comparing. Just now we have seen, it is hydrochloric acid and another acid we are considering now is your perchloric acid acid HClO4. Again both of them are monoprotic acid because the formula of hydrochloric acid we all know that HCl another one is HClO4. So in water medium, they both of them are levelled.

So that means you have complete dissociation, that is water molecules are functioning in a nicer way to accept protons from both the hydrochloric acid the aqueous hydrochloric acid or aqueous

HCl aqueous perchloric acid. But if we think that there is anhydrous acetic acid, so acetic acid itself it can also function because wherever you have the oxygen and hydrogen. So in acetic acid medium, this is we all know this weaker corresponding weaker proton donor.

That we will consider that what is your weak acid. So weak acid is nothing but your acetic acid and this particular equilibrium is not moving very far towards the right-hand side. So we will get a very few or very less amount of H plus from this particular medium. But remember, in all these cases we are talking about aqueous acetic acid. Now for this particular type of levelling effect, what we consider that anhydrous condition we are trying to think of.

So what about in case of the corresponding anhydrous condition? That means no water molecule is present and these water molecules whatever they are showing, their typical affinity or the function towards this particular proton will not be shown by this kind of acetic acid. So in anhydrous acetic acid which is a weaker proton acceptor, none of them, that means the perchloric acid as well as hydrochloric acid will not dissociate completely.

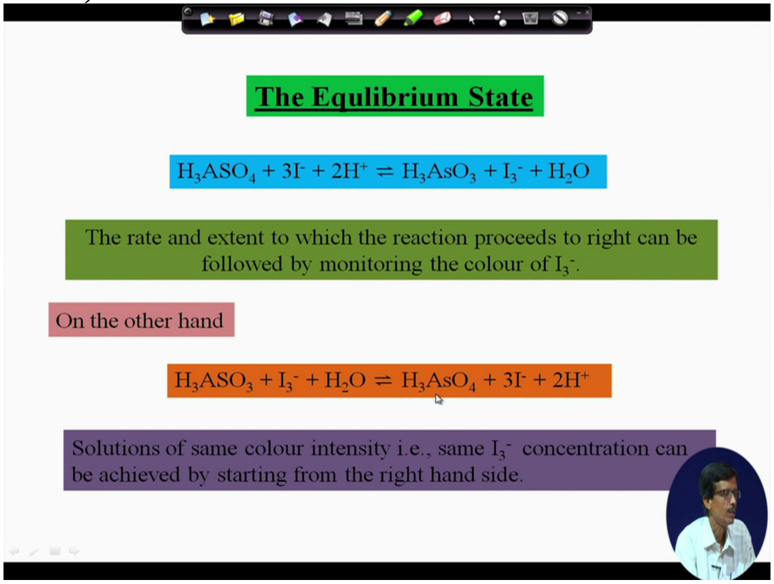
That means we are tampering, we are just interfering the corresponding acidity or the strength of the corresponding acids, that means the perchloric acid and hydrochloric acid. So if they do not dissociate nicely or whatever amount of dissociation we find for water as the solvent, we cannot consider these 2 acid as the strong acid in anhydrous acetic acid medium. So this is a very important area of thinking and important area of knowledge, so where we consider something that means all these reaction conditions, the equilibrium and all other things can change also when we go for anything which can be tied as non-aqueous solution okay, so this non-aqueous solution.

So how you can think of this non-aqueous solution is very simple that we will not have water over there. So anything which can be liquid, that means if we have liquid carbon dioxide, liquid sulphur dioxide and other things which can function we all know that which can function as a solvent, similarly this anhydrous acetic acid, anhydrous acetic acid can be considered as another non-aqueous solution where we try to get or try to involve the corresponding equilibrium that means the chemical equilibrium what is happening and what how it can function for these 2 acids, one is HCl and another is HClO4 okay?

So these are the things. That means how solvent can play some important role as the basis for this dissociation reaction. Okay? So whatever reaction we are thinking of and we are talking about all these things, so is HClO4 so if the proton is moving, so is not ClO2 minus, is ClO4 minus. Sorry, this is not ClO2 minus. So this is the perchlorate anion is moving. So only this proton is moving from COOH to COOH plus.

So this thing we are not getting. So that is why in this particular medium, your perchloric acid only, so perchloric acid will be stronger in this particular solvent medium. So if the perchloric acid can show dissociation in any other medium apart from our water medium, we can consider them as a good acid if only you have the corresponding dissociation.

(Refer Slide Time: 14:54)



The Equlibrium State

$H_3ASO_4 + 3I^- + 2H^+ \rightleftharpoons H_3AsO_3 + I_3^- + H_2O$

The rate and extent to which the reaction proceeds to right can be followed by monitoring the colour of I_3^-.

On the other hand

$H_3ASO_3 + I_3^- + H_2O \rightleftharpoons H_3AsO_4 + 3I^- + 2H^+$

Solutions of same colour intensity i.e., same I_3^- concentration can be achieved by starting from the right hand side.

So a particular type of equilibrium state we are considering and how this equilibrium state will be discussed? Will be discussed in terms of any other typical example. So any chemical equilibrium or a chemical reaction if we talk about, this particular chemical reaction can be your simple oxidation reduction reaction. So we will just simply see one of the example where we can have the corresponding oxidation reduction reaction where the oxidation states of the species we change from one particular oxidation state to the other particular oxidation state.

So we will come back once again for the equilibrium which is happening between the corresponding acids and bases and so many things we can calculate out, so many things we can understand from the typical acid-base reaction. But if we think of considering another equilibrium where a redox reaction is taking place and where we can have the electron transfer reaction, so we can have the electron transfer reaction. So here we have taken one particular example.

That means H3ASO4, sorry this is AS is smaller S is smaller. So is arsenate ion. So ASO43 minus, that means A3SO4 which is reacting with iodide ion. So this iodide ion reaction with iodide ion in acidic medium can take place through the formation of a corresponding Uhh this is in the plus 5 oxidation state and this is in the plus 3 oxidation state, that means arsenic centre, so the arsenic centre is getting reduced.

So this particular one will be therefore we are getting that this particular sentence reducing. So this is functioning as an arsenate Uhh as arsenic acid this H3ASO4. So arsenic acid is functioning as an oxidising agent. So 1 is to 3 reaction, one mole of this is reacting with 3 moles of Iodide ion producing a tri iodide species. So what is happening over there? So iodide, 2 of the iodide ions are oxidized to I2 and that I2 when reacts or attached to the 3rd I minus forming I3 minus.

So this can be considered as a very good example of chemical equilibrium where we visually understand or visually we can see how far the reaction is going from left to right or if we start from right or right to left, where the equilibrium stands. So if we have these species because we are not considering this proton, so protons are always there.

So if we consider the one species like A plus B producing C plus D, so we will be able to write down a corresponding equilibrium constant for this particular equilibrium state and the rate of the reaction basically 2 things we will be considering, the extent of the reaction, how far it is moving from left to right, that can again be just from the corresponding K value, the equilibrium constant value and other thing is also how fast that particular equilibrium is reached.

So the rate and extent to which the reaction proceeds to right can be followed by monitoring the colour of this tri-iodide ion because tri-iodide ion is nothing but the corresponding attachment of the iodine molecule to the iodide ion. So tri-iodide ion is red brown in colour and visually we can see it nicely. So the formation of this, so through this reaction from left to right if you are able to produce large amount of I3 minus which is coloured, visually you can detect by your eyes, otherwise you can spectrophotometrically determine the exact concentration of this I3 minus due to the reaction from left to right.

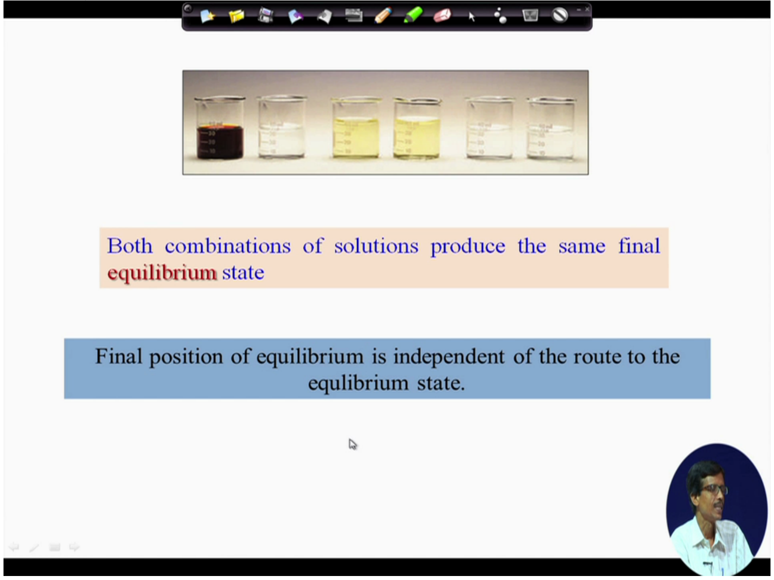
So if we consider the same reaction from the other side, that means from the right to left, so from the right to left reaction is the reverse one. So this will be reacting. So the reverse one is reacting M producing this one. So we can start from if some reaction is not going from left to right, say 90 percent if we are going say about 50 percent or 40 percent from left to right, what we see that for this particular reaction also we get something where these are present but not that much of I3 minus which is strongly coloured is present.

So this particular, so the colour of this I3 minus because in the previous case this colour is developing from a particular reaction condition. We are not considering that the left hand side the solution mixture, the reaction mixture is colourless. It can have some faint yellow colour also but on the right-hand side, you have a dark red thing which is being produced at the iodine elimination. So that we will also consider when we will be talking about the corresponding redox reaction in terms of the corresponding iodometric titrations. Okay?

So is a well-known and well established analytical procedure where we consider Uhh the corresponding iodometric reaction where iodides are oxidised to produce iodine, simple copper 2 plus in the solution in acidic medium can produce iodine and that iodine which is found in the reaction medium can be titrated by a solution or a standard solution of sodium disulphate. So that we will find in some of our future class that how we can utilise this particular chemical equilibrium for iodometric titration.

So this particular thing, so if we have two species on the left, that means A and B and on the right, you have C and D, so what all the corresponding effect? That means the colour change what is happening over there? So that is why all the analytical chemistry thing, that means whatever we get, so that particular thing is dependent on the corresponding colour formation or the disappearance of the colour. So solution of same colour intensity, that is same I3 minus concentration can be achieved by starting from right-hand side as well. So if we go from left to right or from right to left, at equilibrium we will be having the same solution, the same coloured solution when the equilibrium has been reached. Okay?

(Refer Slide Time: 22:24)



Both combinations of solutions produce the same final equilibrium state

Final position of equilibrium is independent of the route to the equlibrium state.

So let us see how this thing can happen. So this is the thing, that means the typical example from those colour reactions from the beaker. So what we find, that is a very interesting thing that how you get this. So these are the things. These 3 beakers for the 1st type of reaction and the other reaction is for the other 3. So if you either you go from left to right or from right to left, so this is the corresponding material what we are getting.

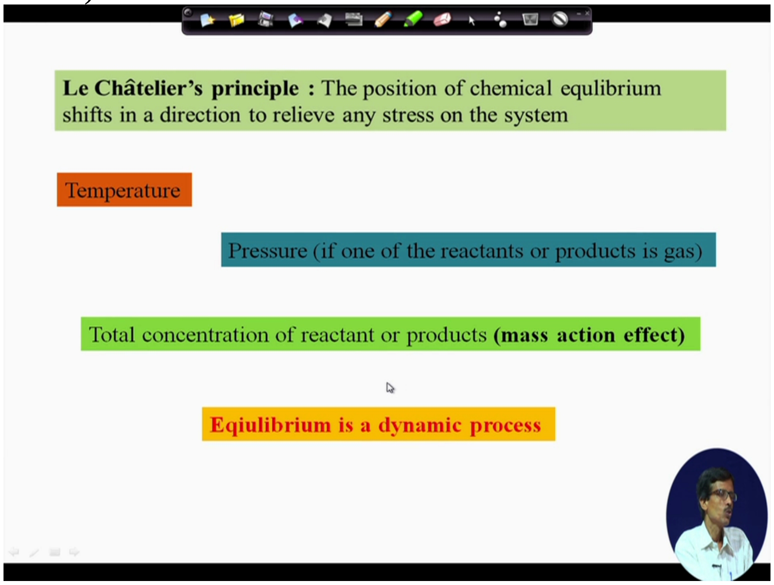
That means the tri-iodide formation over there and that is the thing that this tri-iodide is reacting with that of our corresponding arsenic acid, one of the arsenous acid and forming this final product like this. And in another case, see the iodide things are not there but some of the coloured thing is that that when we reach the corresponding equilibrium state, we basically get all the species what is present that we have seen that in your solution, you have this particular species, that means H3ASO3 I3 minus ASO43 and 3I minus.

So at the beginning when we have, we are not having the tri-iodide species, both these 2 things are colourless. So when you start from right-hand side, both these things are colourless but when you get these from the triiodide, if only this tri-iodide ion, so triiodide ion is strongly coloured. Saw them things what is happening, so at the equilibrium when we reached from any of the sides, from left to right or right to left, both combination of solution thus produce the same final solution, that means the final equilibrium state.

So this particular equilibrium state what we are reaching from this side or the other equilibrium state from the right-hand side, we are getting the same solution. So when the equilibrium is reached which should be very much careful in knowing that particular thing that how this particular final condition we are achieving. So final position of the equilibrium where we are, suppose we are going from left to right, so a 30 percent of the reaction or a 40 percent reaction or a 50 percent of the reaction A plus B, 50 percent of A and 50 percent of B is reacting to give 50 percent of C and 50 percent of D.

So is independent of the root of the equilibrium state. That means which direction and which way it is going, is independent of that particular rule but we are reaching these 2 final solutions somehow. So we are going from one particular way, so the equilibrium for this particular reaction is achieved and we get all these things in a possible way such that we can apply the principle of Le Chatelier.

(Refer Slide Time: 25:08)



Le Châtelier's principle : The position of chemical equlibrium shifts in a direction to relieve any stress on the system

Temperature

Pressure (if one of the reactants or products is gas)

Total concentration of reactant or products **(mass action effect)**

Eqiulibrium is a dynamic process

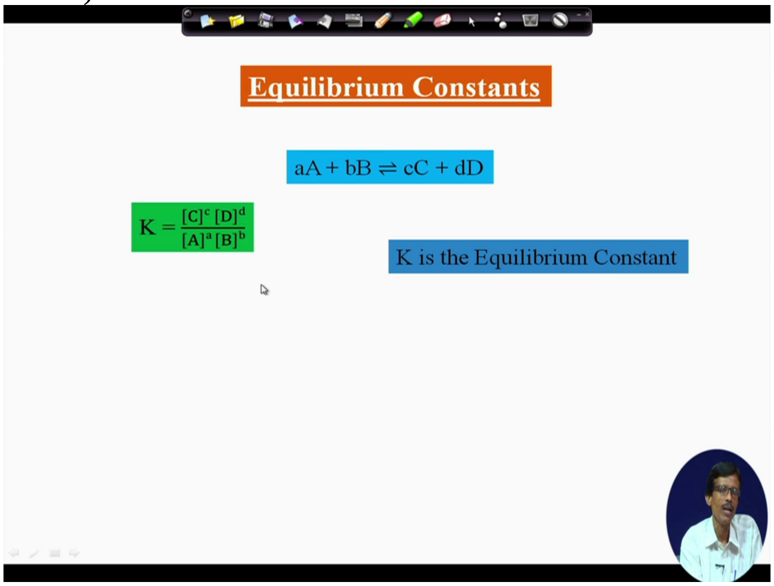
The Le Chatelier principal is telling us that talking in terms of the corresponding position of the equilibrium and the position of the equilibrium can sit in a particular direction to relieve any stress on the system. As we all know that if we change uhh the particular parameter, that means the temperature what we see that a particular temperature or pressure if one of the products of the reaction are gas, that means the pressure is relieved from their and the temperature is dependent on your exothermic reaction or endothermic reaction.

The equilibrium can be achieved from one side to the other side. Suppose the metal ion is reacting with some anion or the ligand, one colour reaction can take place. So is that particular reaction is endothermic is the cool down the solution, so more and more of this thing will be forming. So this principle all we know that the total concentration of the reactant and the products will be dependent on the mass action effect.

So this particular mass action effect therefore is controlling that particular equilibrium which is a dynamic process. So if we change the temperature and pressure, only thing that we can just change the position of that particular equilibrium that how much product is forming. So temperature and pressure is basically we control for a particular type of reaction. Suppose your ammonia we are forming from reaction of nitrogen and hydrogen.

We all know that that particular reaction is taking place at a very high temperature and pressure. But if we can consider at a very high temperature only and pressure is the atmospheric pressure, but still some amount of ammonia definitely will be formed but which is not very high, the concentration of the ammonia formation is not very high. So that is why the haver process which should be in the industrial process and which is also economically viable is used for the production of the ammonia where these 2 parameters that means the temperature and pressure is applied such that your most of this hydrogen and nitrogen can be converted to your ammonia solution.

(Refer Slide Time: 27:25)

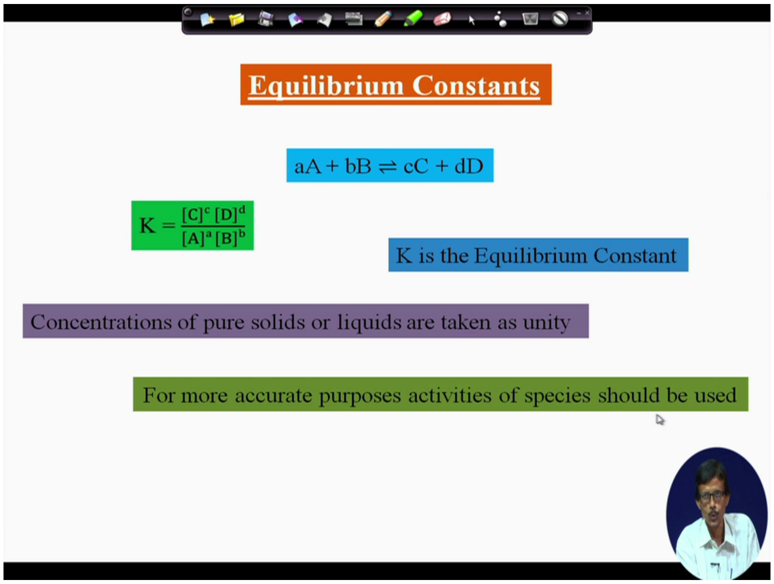


Equilibrium Constants

$aA + bB \rightleftharpoons cC + dD$

$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$

K is the Equilibrium Constant



Equilibrium Constants

$aA + bB \rightleftharpoons cC + dD$

$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

K is the Equilibrium Constant

Concentrations of pure solids or liquids are taken as unity

For more accurate purposes activities of species should be used

So now we can think or we can talk about the corresponding equilibrium constants. So if we can have a particular reaction, how we can consider about how we can talk about the corresponding KA value. This we will be considering is the equilibrium constant and which is there Uhh can have for any simple reaction that we can have more than one equilibria, suppose we can have H plus and A minus forming HA and similarly H plus is reacting with a simple base forming HB plus.

So these 2, that means this H plus and this H plus are common but we can have 2 different equilibria where one is the corresponding conjugate anion, that means it can be your conjugate base, it can be your acetate ion from acetic acid or it can be simple base like ammonia, it trimethylamine or triethylamine so you have a base and you have conjugate acid of a particular acid which can function as a base. So these 2 common species can have and we can have a simultaneous equilibrium or a competitive equilibria competitive equilibria.

So that we will consider in terms of the corresponding KA value. So for a very basic or a very standard reaction of this AA plus BB producing CC and DD where K is the equilibrium constant and sometimes, K is written as KA, A stands for the corresponding acid and if we consider this concentration of C times the number of moles, concentration of D times the number of moles D and in the Uhh Uhh A for the case of this A also, Uhh so and for D also, is powered by the corresponding moles, we get the K.

So at equilibrium, just now what we have seen, the corresponding reactions of tri-iodide, iodide, arsenic acid and the corresponding arsenous acid so we get this all 4 species are present together but how far this particular reaction will be intense depending upon the concentration of I minus I3 minus, that will be dictated by the K value which will tell you that how far the equilibrium can go.

So concentrations of pure solids and liquids are taken as unity because pure solids and pure liquids will not interfere over there. And for more accurate purposes, activities of the species should be used. So that will give rise to the corresponding K value and that we will see in our next class that how we can propose and how we can establish a particular equilibrium value for the simple acid base reaction. Okay? Thank you very much.