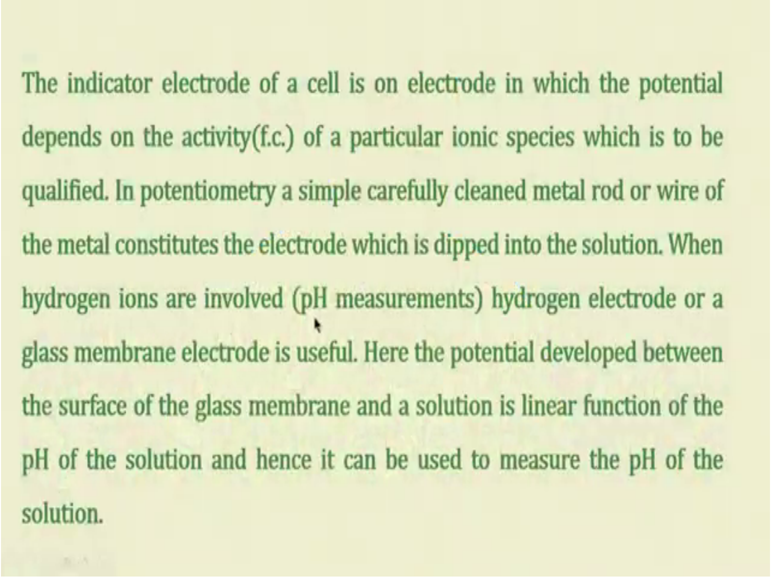
Electrochemical Technology in Pollution Control

Dr. J. R. Mudakavi
Department of Chemical Engineering
Indian Institute of Science, Bangalore

Lecture – 21
Ion Selective Electrodes 2

Greetings to you, we have been discussing about the Ion Selective Electrodes. Actually, ion selective electrodes is nothing but an extension of glass electrode and pH meters. So, the indicator electrode of a cell is on an electrode in which the potential depends upon the activity of the particular ionic species, which is to be quantified.

(Refer Slide Time: 00:52)



The indicator electrode of a cell is on electrode in which the potential depends on the activity(f.c.) of a particular ionic species which is to be qualified. In potentiometry a simple carefully cleaned metal rod or wire of the metal constitutes the electrode which is dipped into the solution. When hydrogen ions are involved (pH measurements) hydrogen electrode or a glass membrane electrode is useful. Here the potential developed between the surface of the glass membrane and a solution is linear function of the pH of the solution and hence it can be used to measure the pH of the solution.

In potentiometry, normally a simple a carefully cleaned metal rod or wire of the metal etcetera constitutes the electrode, which is dipped into solution, all those we have covered. Electrodes of the first kind, electrodes of the second kind etcetera and, then we have discussed about the pH meters; pH measurements and activity and all those things we have covered earlier.

So, here a glass electrode is a contains a gas membrane, which is a permeable to hydrogen ions. So, an ion selective electrode would be having a membrane, which is permeable to the particular ion in which we are interested in the determination.

So, in most of the glass electrode membranes I have already told you that pH there will be a pH error of about 1 unit, when you are measuring the pH of around 12 or alkaline range, soda lime glass, and any other glass containing lithium, lead and cadmium etcetera. Most of them would be if you prepare the thin membrane, they would be responsive to those ions like, sodium, potassium, lithium, lead, cadmium etcetera, if you make any electrode out of a semipermeable membrane made of the glass containing those elements.

So, we have described one such a system earlier containing Ag AgCl and that is dipped in HCl and glass membrane, test solution followed by a potassium chloride and salt bridge, and Hg2Cl2 say mercury as the calomel electrode. So, such EMF such cells the EMF is maintained by a very simple relationship, which is equivalent to Nernst equation, that is E is equal to E naught plus RT by N F ln log ln oxidant divided by reductant.

When we say oxidant divided by reductant, we mean concentrations; actually concentrations are we do not mean we write the activity; activity of the oxidant and activity of the reductant. In this case we do not write E naught also instead of that we replace it with a another constant K, that is known as asymmetry constant. So, the asymmetry constant will be different for different ions. It may be different for sodium, potassium, calcium, lead all those things are possible.

So, the glass electrode can be used for alkali metals very regularly it has been used, even before the advent of other redox reagents, other ion selective electrodes. So, I had given you a definition called SPM just like, pH we can refer to pM, negative log off metal ion concentration. And, then I had described to you couple of electrodes. One of them was iodide that is silver silver iodide in contact with a HI, followed by a membrane and then KCl HgCl 2 and mercury as the reference electrode.

So, that would be responsible for responsive to silver or iodide any one of them. And, then we had described lanthanum fluoride electrode and lanthanum fluoride is basically a an insoluble material, which is sealed to the bottom of a plastic container, containing potassium chloride etcetera. And, I had also described to you the electrode, how the electrode is to be made because, the fluoride ions need to move from the solution into the to the electrode surface membrane and then into the inner solution.

So, the mechanism of fluoride ion transport is nothing but the movement of the fluoride ions from one lattice defect to another lattice defect. So, the movement through the membrane would be through vacant spots from through the lattice defects.

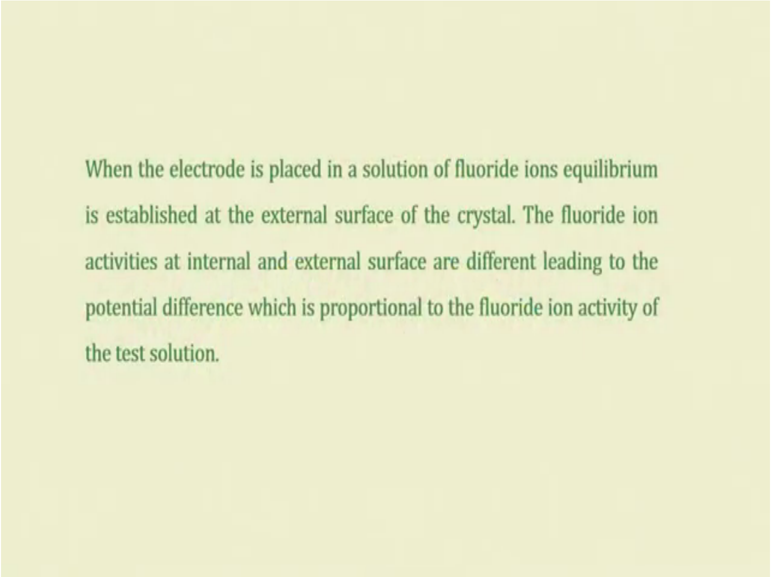
So, this lead to a beautiful fluoride meter, which is available in the market today. It costs about 1 to 1.5 lakhs or something like that, but it can be carried anywhere we want and I had explained to you the significance of fluoride in the environment, what I had conveyed is that fluoride is a very dangerous element a lot of people in Karnataka, Andra, Maharashtra and Rajasthan, Madhya Pradesh all the states people are suffering from high fluoride content.

And, you can see that their teeth become yellow and then legs become hands become like this, they cannot walk, they cannot lift things pick up etcetera. These kind of problems are there most of the time whenever for people, who are exposed to high levels of fluoride.

And, what is a high level of fluoride? The high level of fluoride is more than 1.5 ppm. If, it is more than that you continuously keep on drinking that water, you will have teeth problem, you will have hands problem, you will have folded hands and bent legs, all kinds of problems, keep on happening that is why fluoride determination has become a must in all underground water source resources. Whenever, we dig borewell we need to check fluoride and fluoride meter is a very convenient way of checking fluoride content and it can be given to any school, any village, any community wherever there is total dependency on the borewell.

So, I had also told you that fluoride ion should be less than 1.5 ppm. In India I have come across up to 3 ppm. That is very high almost 100 percent know double. So, this slide lanthanum fluoride, I wanted you to see, what basically, what we are see, what you are seeing in the slide is this that LaF 3 lanthanum fluoride is sealed into the bottom of a container and that you can carry as an electrode dipped in a solution.

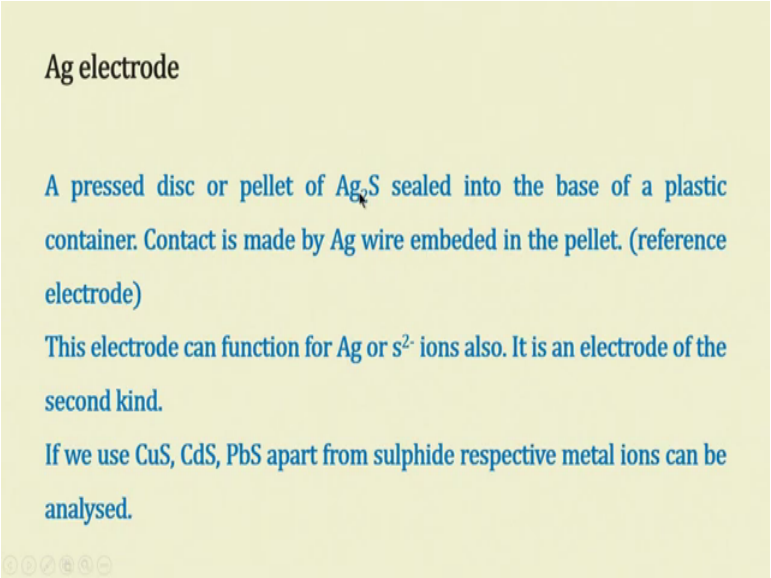
(Refer Slide Time: 08:53)



When the electrode is placed in a solution of fluoride ions equilibrium is established at the external surface of the crystal. The fluoride ion activities at internal and external surface are different leading to the potential difference which is proportional to the fluoride ion activity of the test solution.

So, when the electrode is placed in a solution of fluoride ions equilibrium gets established and where the external surface of the crystal, and the fluoride ion activities at internal and external surface are different leading to their potential difference, which is proportional to the fluoride ion activity of the test solution, that is sample whatever you want to test it with.

(Refer Slide Time: 09:18)



Ag electrode

A pressed disc or pellet of Ag_2S sealed into the base of a plastic container. Contact is made by Ag wire embeded in the pellet. (reference electrode)

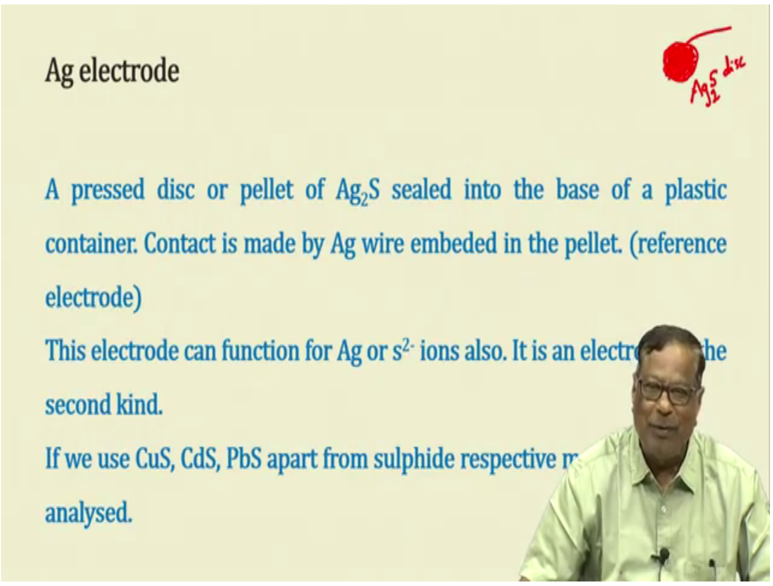
This electrode can function for Ag or s^{2-} ions also. It is an electrode of the second kind.

If we use CuS, CdS, PbS apart from sulphide respective metal ions can be analysed.

Now, I want to I actually I do not want to go into details of such ion selective electrodes, because it is very difficult to go into construction of such electrode membranes etcetera. But, I will give you an overview of what kind of electrodes are available in the market for our for different ions.

So, if you can even have a big library of metal ion electrodes in a carry bag, in a briefcase and you have the capability of determining several metal ions, if you have different, metal ion electrodes that is ion selective electrodes. So, now, I am describing a silver electrode. What is the silver electrode? It is nothing but a small pressed disc of about 1 about 5 mm dia.

(Refer Slide Time: 10:39)



Ag electrode

A pressed disc or pellet of Ag_2S sealed into the base of a plastic container. Contact is made by Ag wire embeded in the pellet. (reference electrode)

This electrode can function for Ag or s^{2-} ions also. It is an electr he second kind.

If we use CuS, CdS, PbS apart from sulphide respective m analysed.

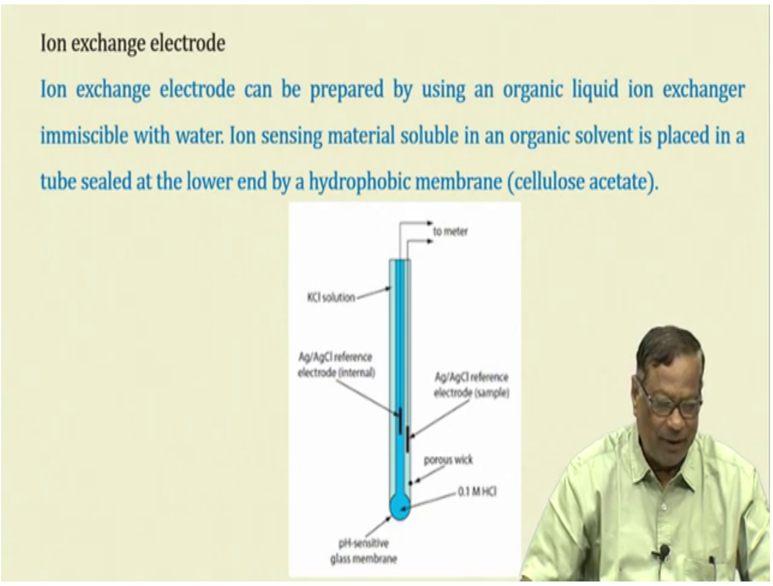
So, the silver electrode is nothing but it is a small 0.5 mm dia of this size, this is a disc made of lanthanum fluoride. This disc you can seal it into an electrode and on this electrode on this disc you can put a silver silver chloride wire, silver wire and then take the connection, this is just like a glass electrode.

So, a pressed disc or a pellet of Ag 2 S silver sulphide. You can seal it into the base of a plastic container and then contact is made by fitting an electric wire, silver wire embedded in the pellet. So, there is lot of chemistry involved in the preparation of Ag 2 S itself. And, you also need some sort of a binder to make the Ag 2 a silver sulphide as its paste and that solution should evaporate and make a compact disc, which can be hand, which can be mechanically stable and then you insert it dry it and lot of chemistry work is involved, but it is mostly easily done or guessed.

There are lot of literature, how to prepare a silver sulphide disc and many other discs also. For example, for cadmium, we can do cadmium sulphide disc like that, many other ions. Now, this electrode silver silver sulphide can be used for silver or sulphide both, it is an electrode of the second kind that is a metal in contact with a solution, metal wire or metal oxide in contact with a solution is electrode of the second kind. So, if we use copper sulphate.

Here I had written copper sulphate know. I can use Copper Sulphate, I can use Cadmium Sulphate, I can use Lead Sulphate sulphide all these are sulphides. Apart from sulphide respective metal ions also can be analysed, that is a very simple common sense, because when the ions are in equilibrium the concentrations of the anion and cation also would be in equilibrium. So, the ionic concentration would be stoichiometrically equivalent to either cation or anion.

(Refer Slide Time: 13:26)



Ion exchange electrode

Ion exchange electrode can be prepared by using an organic liquid ion exchanger immiscible with water. Ion sensing material soluble in an organic solvent is placed in a tube sealed at the lower end by a hydrophobic membrane (cellulose acetate).

So, then now I am describing to you ion exchange electrode. What is an ion exchange electrode? Say, sounds confusing a little bit, but it can be prepared by using an organic liquid, ion exchanger immiscible with water.

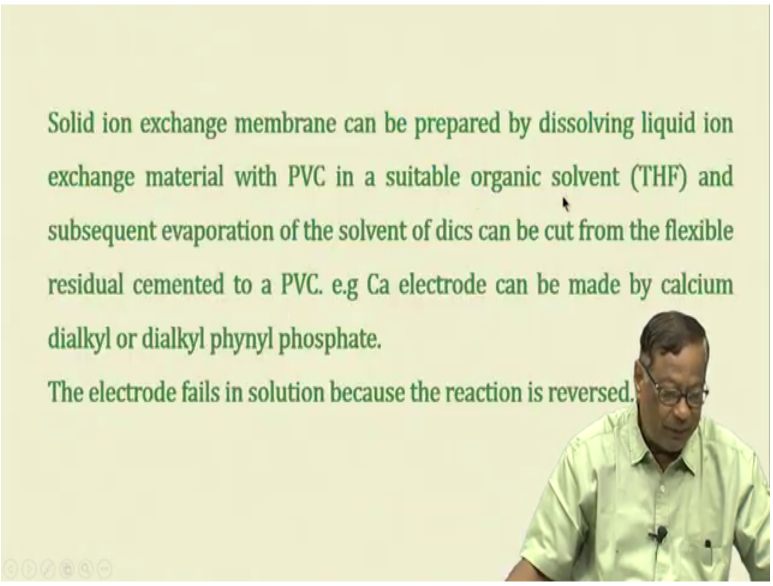
So, it is a basically some sort of a membrane. Ion sensing material soluble in an organic solvent is placed in a tube sealed at the lower end of a hydrophobic membrane that is we can use cellulose acetate. Very simple cellulose acetate is available in the market, you can buy it mix it with water and spread it as a thin sheet, dry it there you have the cellulose acetate membrane.

And, that you put the ion exchange in the material, ion exchange resin, organic liquid ion exchange your material you can sprinkle on that or you can dip it into that. So, the organic ion exchange ion exchanger will be coated on the membrane. So, the membrane should be hydrophobic. Is not it, that is very important, because hydrophobic membranes do not get affected by aqueous solutions, water.

So, they remain intact and reacted with water. So, they can be used again and again. So, what is the construction? The construction is very simple, I have a membrane here pH sensitive and then I have a reference electrode, and one internal, and one external, and there is a solution here, and a there is a porous wick to put the sample solutions etcetera, just like construction of glass electrode. And, then we can keep on working put the take this electrode, dip it in a solution which we want to determine. Then, the other parts that is external parts would be voltmeter, galvanometer and then ammeter and all those things plus better power supply.

So, this contains 0.1 molar HCl also, we have a silver silver chloride reference electrode. So, totally almost solid, ion exchange, electrode with the help of ion exchange or material, that is some sort of a resin which is dissolved in the solvent. I coated on to the silver cellulose acetate membrane.

(Refer Slide Time: 16:35)



Solid ion exchange membrane can be prepared by dissolving liquid ion exchange material with PVC in a suitable organic solvent (THF) and subsequent evaporation of the solvent of dics can be cut from the flexible residual cemented to a PVC. e.g Ca electrode can be made by calcium dialkyl or dialkyl phynyl phosphate.

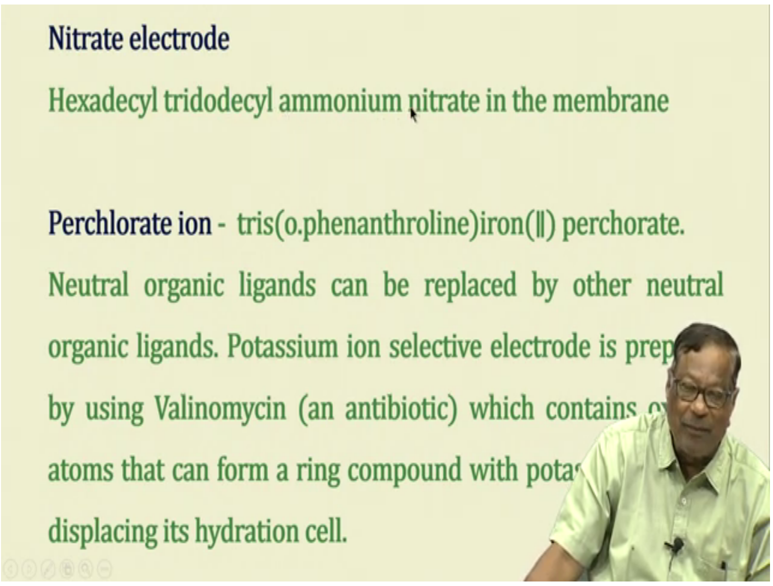
The electrode fails in solution because the reaction is reversed.

So, solid ion exchanged membrane can be prepared by dissolving liquid ion exchange material with PVC, we can use PVC in a suitable organic solvent, that is tetrahydrofuran and subsequent evaporation of the solvent we should do, and then the disc the membrane can be cut into small small discs and we have so, many electrode membranes available and we can use them for the ion exchange resin.

So, I can have a calcium mix electrode, it can be made by calcium dialkyl phynyl phosphate, or simply dialkyl phosphate also we can use, or dialkyl phynyl phosphate. So, this is the liquid ion exchange or material. So, but the electrode fails in solution, because the reaction is reversed. Sometimes, such electrodes we do not want somehow if the concentration is very less, then from the ion exchanger electrons can move the calcium ions can move out into the solution. So, that danger is always there.

So, one has to be a little careful whenever we use liquid ion exchange electrodes.

(Refer Slide Time: 18:02)



Nitrate electrode

Hexadecyl tridodecyl ammonium nitrate in the membrane

Perchlorate ion - tris(o.phenanthroline)iron(II) perchorate.

Neutral organic ligands can be replaced by other neutral organic ligands. Potassium ion selective electrode is prep
by using Valinomycin (an antibiotic) which contains o
atoms that can form a ring compound with pota
displacing its hydration cell.

Then, I am describing you a nitride electrode. In the nitride electrode what we have is a hexadecyl tri dodecyl ammonium nitrate in the membrane. So, this nitrate what is hexadecyl? I think you should fresh up your organic chemistry; it is nothing but a hydrocarbon chain containing 10 carbon atoms CH 3 CH 2 CH 2 etcetera.

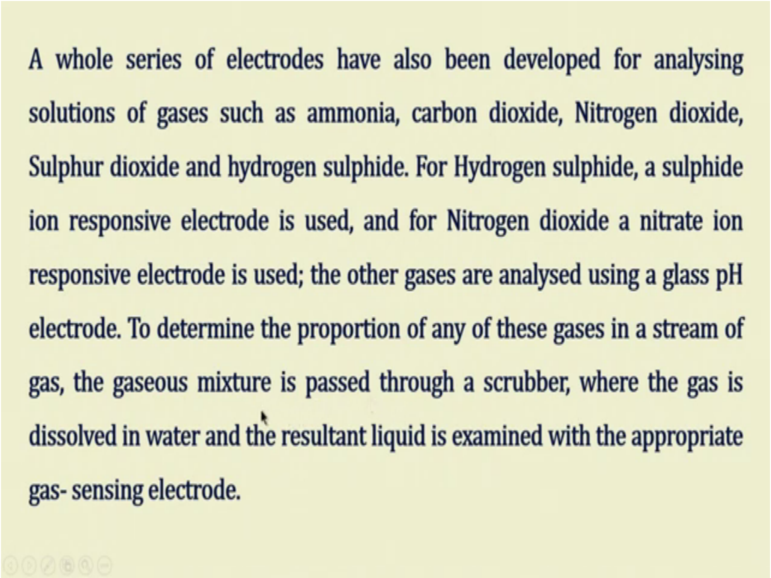
So, hexadecyl tri dodecyl, 3 dodecyl groups and then 1 hexadecyl group connected to a carbon atom and the 3 dodecyl groups are ending with ammonium nitrate, in the as a it is a cationic surfactant ok. So, it is a cationic ion exchange material and nitrate is the one which is getting exchanged here, that is the ion that is determined using this material.

Hexadecyl tri dodecyl ammonium nitrate is available in the market, in the laboratory; you can buy that and then dissolve it. So, perchlorate ion if you want to prepare, that is still simpler, because we can use tris ortho phenanthroline iron II perchorate. So, what do we do here? Is take some ferrous ion react it with ortho phenanthroline, that is available in the laboratory, any organic laboratory, inorganic laboratory will have this ortho phenanthroline, it will give a dark red precipitate with iron and then you add a little bit of perchloric acid, and then the iron perchlorate tris ortho phenanthroline iron perchlorate is the is precipitated.

So, we can also prepare neutral organic ligands and they can be replaced by other neutral organic ligands also, which we need not necessarily use tris ortho phenanthroline salt alone. We can use any other neutral organic ligands or those ligands also can be replaced by other neural neutral organic ligands.

So, for example, this potassium ion selective electrode, next one here I am showing you with the mouse, potassium ion selective electrode is prepared by using Valinomycin. It is something equivalent to ortho phenanthroline, but it is an antibiotic. So, that contains oxygen atoms that can form a ring compound with potassium ions, by displacing it is hydration cell. So, such materials also can be used for preparing an ion selective electrode.

(Refer Slide Time: 21:23)



A whole series of electrodes have also been developed for analysing solutions of gases such as ammonia, carbon dioxide, Nitrogen dioxide, Sulphur dioxide and hydrogen sulphide. For Hydrogen sulphide, a sulphide ion responsive electrode is used, and for Nitrogen dioxide a nitrate ion responsive electrode is used; the other gases are analysed using a glass pH electrode. To determine the proportion of any of these gases in a stream of gas, the gaseous mixture is passed through a scrubber, where the gas is dissolved in water and the resultant liquid is examined with the appropriate gas- sensing electrode.

A whole series of electrodes have been developed for analyzing solutions of gases. Now, we are moving from the ions in solution to the determination of gases in solution, gases not necessarily in solution, but in the atmosphere also. So, what are the things that we can estimate using ion selective electrodes? We can use ammonia, ammonia can dissolve in water, and giving you an ammonia (Refer Time: 22:04) solution, and then carbon dioxide also can dissolve in water, or most of the soda what we drink contains carbon dioxide and then nitrogen dioxide yes.

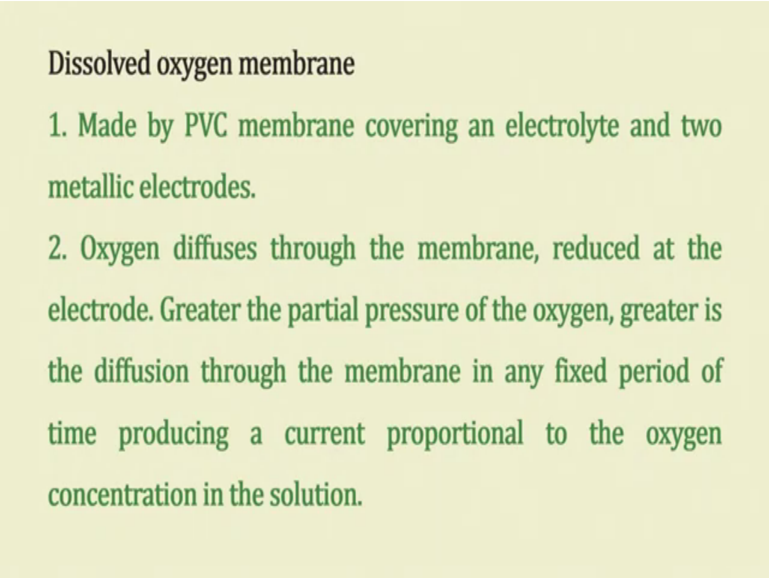
We can determine that is a pollutant, in the urban atmosphere, nitrogen dioxide gas is there. And, then sulphur dioxide, hydrogen sulphide all these are gases. For hydrogen sulphide determination I can use a hydrogen ion responsive electrode and for nitrogen dioxide, I can use a nitrate ion responsive electrode. Why do we use sulphide ion responsive electrode, for hydrogen sulphide? Because stoichiometrically we can convert any sulphide ion in the air or in a solution to the hydrogen sulphide, that is what we mean.

So, for nitrogen dioxide I need to use a nitrate ion, because nitrogen dioxide, if it is in solution, it will be in equilibrium with nitrate ion; the other gases are analysed using a simple glass electrode. To determine the proportion of any of these gases in a stream of gas, the gaseous mixture is passed through a scrubber, there is there has to be some sort of wetness aqueous interface. That is why we have to pass them through a scrubber, where the gas is dissolved in water and the resultant liquid must be in equilibrium with the solution with how is the solution of where the solution is coming? When the gas is scrubbed with water there will be enough water vapour and there will be some amount of solution in the gaseous mixture that is coming out.

So, a scrubber is a must if you want to determine gases in a using gases using a an ion selective electrode.

So, the gas is dissolved in water when you pass it through the scrubber and the resultant liquid is examined with appropriate gas sensing electrode.

(Refer Slide Time: 24:29)



Dissolved oxygen membrane

1. Made by PVC membrane covering an electrolyte and two metallic electrodes.
2. Oxygen diffuses through the membrane, reduced at the electrode. Greater the partial pressure of the oxygen, greater is the diffusion through the membrane in any fixed period of time producing a current proportional to the oxygen concentration in the solution.

So, dissolved oxygen again, here I want to tell you something more about dissolved oxygen. Dissolved oxygen is a great boon for all of us. We all are capable of eating fish, because fish survive on the dissolved oxygen. And, we need dissolved oxygen for several other biotic species including microbes, planktons, and then a small animals big animals for everyone is dependent upon, the dissolved oxygen in water.

In fact, the solubility of water solubility of oxygen in water is approximately 6 to 7 milligrams per litre not much, but that is enough for many of the for thousands of aquatic flora and fauna to survive.

So, dissolved oxygen is a very important concept and we do not want our rivers and ponds devoid of oxygen, dissolved oxygen. Usually, oxygen is dissolved from the air, water interface, into the water and if we pollute our rivers and ponds etcetera, there would not be there will be chemicals in the water, that needs they will consume the oxygen dissolved in water for their oxidation. So, once the oxygen is consumed by the dissolved chemicals water becomes poorer, in the dissolved oxygen content and the flora planktons this that and so many other viruses, aerobic viruses they all die.

So, the water body will move towards anaerobic system. So, once the anaerobic system sets in algae will die and other things will die and there will be loading, for the additional loading, that is how ponds and lakes will die, that is now the process is known as eutrophication. And, we also need good oxygen for drinking, we are taking bath etcetera, we cannot use anaerobic system water for our routine regular uses.

So, dissolved oxygen is a very important aspect and it is very conveniently determined by the by dissolved oxygen membranes. Nowadays, even in India we have a lot of people who will supply you DO meter, dissolved oxygen meter, that can be carried away in your pocket using a pen or there are meters, which are like pH meter, which can be used for in the laboratory.

So, all you have to do is replace the electrode, glass electrode with a DO meter. So, dissolved oxygen electrode and that electrode contains a membrane which is responsive to oxygen in solution as well as outside. So, these dissolved oxygen membranes are made by PVC covering an electrolyte and two metallic electrodes. So, oxygen diffuses through the membrane gets reduced at the electrode and how much does it get reduced?

It depends on the partial pressure. So, greater the partial pressure of oxygen; that means, if there is more oxygen in the sample greater is the diffusion through the membrane at any fixed time. And, produce it produce then it will produce a current proportional to the oxygen concentration in the solution, operation is very simple, there is nothing very complicated all it all you need is two electrodes in and a membrane in between.

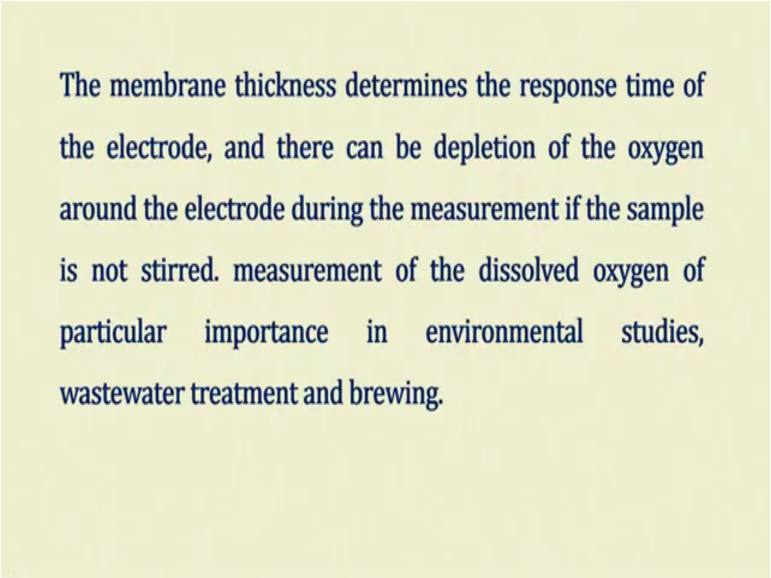
Two electrodes; one on the top, one on the bottom, and a membrane, which is responsive to dissolved oxygen, the whole thing is dipped. Higher the oxygen content more is the current produced very simple arrangement.

The membrane thickness determines the response time of the electrode that is also important. And, there can be depletion of oxygen around the electrode during the measurement if the sample is not stirred. So, it is very important while determination of the dissolved oxygen that the solution should be stirred nicely.

Otherwise, there will be wrong readings. See, it is a question of few milligrams per litre, if you do not stir 1 or 2 milligrams will be less. So, 1 milligram less out of 6 ppm is almost like 18 percent error, that is not acceptable in milligram per litre concentration know. So, the small little things in the laboratory can be can lead to great errors.

For example, if somebody puts the stirrer off during measurement there will be 18 percent error minimum plus or minus 1 milligram. So, measurement of the dissolved oxygen is especially important, in environmental studies wastewater treatment, brewing, you know making beer, wine etcetera, all those places we need dissolved oxygen determination continuously all the time.

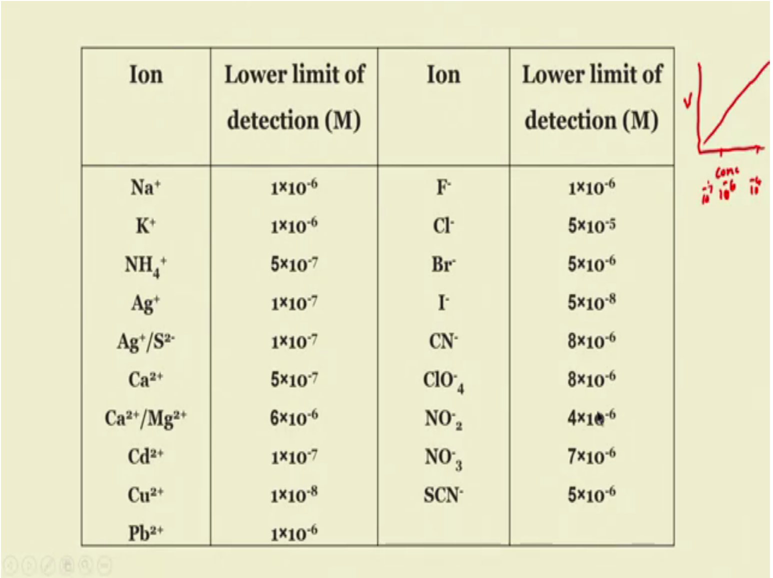
(Refer Slide Time: 30:57)



The membrane thickness determines the response time of the electrode, and there can be depletion of the oxygen around the electrode during the measurement if the sample is not stirred. measurement of the dissolved oxygen of particular importance in environmental studies, wastewater treatment and brewing.

So, the membrane thickness should be very proper and we must have different kinds of stocks of membranes, because if for some reason the membrane is not working properly, then we can change the membrane quickly and then determine the dissolved oxygen using another smaller membrane. So, the remaining part of the electrode will remain same.

(Refer Slide Time: 31:28)



Ion	Lower limit of detection (M)	Ion	Lower limit of detection (M)
Na^+	1×10^{-6}	F^-	1×10^{-6}
K^+	1×10^{-6}	Cl^-	5×10^{-5}
NH_4^+	5×10^{-7}	Br^-	5×10^{-6}
Ag^+	1×10^{-7}	I^-	5×10^{-8}
Ag^+/S^{2-}	1×10^{-7}	CN^-	8×10^{-6}
Ca^{2+}	5×10^{-7}	ClO^-_4	8×10^{-6}
Ca^{2+}/Mg^{2+}	6×10^{-6}	NO^-_2	4×10^{-6}
Cd^{2+}	1×10^{-7}	NO^-_3	7×10^{-6}
Cu^{2+}	1×10^{-8}	SCN^-	5×10^{-6}
Pb^{2+}	1×10^{-6}		

So, here is a list of materials, which interfere which are the detections sorry not interfere, it is the detection limit of metal ions in solution using ion selective electrodes. So, I have here sodium Na plus how much I can determine, 1 in to 10 raise to minus 6 molar concentration.

These are all in molar concentration not in ppm. So, there is a difference. Is not it? This, I have explained to you the concept of molar solutions ppm solutions etcetera. Molar is not equivalent to ppm. So, the concentration of normally ppm level concentrations are of the order of about 10 raised to minus 4 or minus 5 ppm, so, molar. Sodium can be determined in 1 into 10 raised to minus 6 molar concentrations, potassium is also almost same, ammonia is still lower 10 raise to minus 7, silver is again 1 into 10 raise to minus 7, silver sulphide electrode can be almost same and calcium 5 into 10 raise to minus 7 molar.

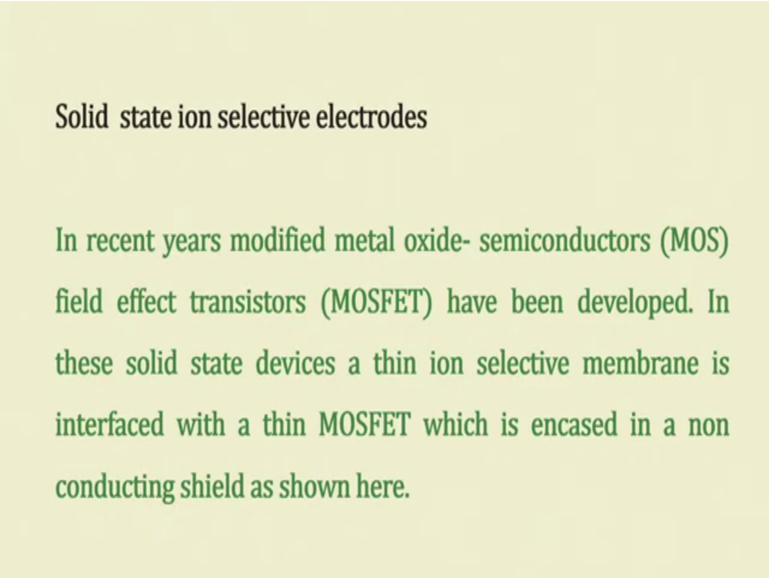
You can convert this into ppm by a simple calculations, then calcium magnesium almost all of them cadmium, copper, cadmium; copper and these two are 10 raise to minus 7 and 10 raised to minus 8 molar concentrations, that is fantastic actually. And, he that is why we always say, the ion selective electrodes are very important. If, you want to determine very low concentrations of the solution in molar quantities, and the response would be linear over several orders of magnitude that is you will get a linear curve, if you plot concentration versus concentration versus EMF.

So, this is concentration this would be EMF. So, if I get a linear this thing, here it will be 1 into 10 raise to minus 7 and minus 6, and here it would be 10 raise to minus 4, like that you will get orders of concentration can be 10 times more than the 10 times more than the spectrophotometric or atomic absorption systems, because all of them will appear give you the linear curve only in the same ppm range. Maybe 1 to 5 ppm, maybe 1 to 10 ppm, but here it is 1 ppm, 100 10 ppm, 100 ppm, 1000 ppm, like that the order will be higher and the range of determination would be larger.

So, the freedom of concentration dependence on concentration is avoided in ion selective electrodes, or even potentiometric glass electrode etcetera, because the linearity is of the order of in the multiples of 10. So, molarity that is what we are talking about.

So, coming back to the slide, I am going to talk about fluoride ions now. Fluoride would be 10 raise to minus 6 molar detection limit, chloride will be 10 raise to minus 5 molar, bromide would be 10 raise to minus 6 molar, iodine 10 raise to minus 8, then cyanide, chlorate NO 2, NO 3, SCN, thiocyanate all these things are about the order of about 10 raise to minus 6 molar.

(Refer Slide Time: 36:18)



Solid state ion selective electrodes

In recent years modified metal oxide- semiconductors (MOS) field effect transistors (MOSFET) have been developed. In these solid state devices a thin ion selective membrane is interfaced with a thin MOSFET which is encased in a non conducting shield as shown here.

See the beauty is we do not know, we do not know what are the problems with the determination of ppm level or we do not know the solutions for chemical analysis of anions at very low concentrations. If, it is chloride I can in milligram quantities etcetera, I can do a gravimetry and then I can say a precipitate silver chloride, calculate chloride concentration. If, it is sulphate I will say determinate as barium sulphate and you can determine the concentration of sulphate in milligram quantities, but if it is in microgram we have a problem.

So, microgram that will not be in molar, but in ppm, but if it is in 10 raise to minus 6 molar, we do not have any other method that can be used for the determination of such anions at such low concentrations, that is the beauty. See, determination of anions and cations at very low concentrations is a very important task.

Quite often whenever we need analar grade reagents or super pure compounds ultra-pure compounds, we need to determine all the elements cations, anions and other materials, in 10 raise to minus 5 10 raise to minus 6 molar solutions only. Especially, if you want to determine this silicon we need purity of 10 raise to minus 6 or minus 9; that means, 1 atom or 1 part in 10 raise to 9 parts allowed, higher than that the whole material becomes useless it cannot be used for solar panels.

So, that is why the production of high purity, ultra-purity materials, requires the analysis of parts per million or 10 raise to minus 6, minus 7, minus 8, molar concentrations of these ions. And, we do not know any other method except ion selective electrodes which permit us to determine the ionic concentrations in such low concentrations.

We do not have any other method, technical method for the determination that is why ion selective electrodes are very important in day to day life also. And, we will continue our discussion on the solid state ion electron ion selective electrodes in the next class.

Thank you very much.