Electrochemical Technology in Pollution Control
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Lecture - 20
Karl Fisher titration 1, Ion selective electrodes 1

Greetings to you, we are looking at the Karl Fisher reaction. In my last class, I had explained to you that Karl Fisher titration is carried out using iodine sulphur dioxide and pyridinium pyridine, where the an inner complex is formed in presence of water and that can be titrated to determine. The concentration of water because water reacts stoichiometrically in the whole reaction of the pyridinium salt formation.

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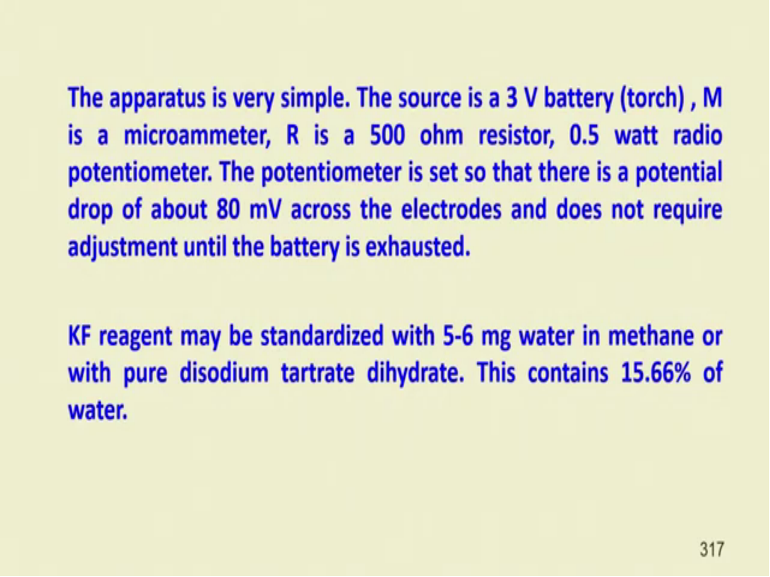

The apparatus is very simple. The source is a 3 V battery (torch) , M is a microammeter, R is a 500 ohm resistor, 0.5 watt radio potentiometer. The potentiometer is set so that there is a potential drop of about 80 mV across the electrodes and does not require adjustment until the battery is exhausted.

KF reagent may be standardized with 5-6 mg water in methane or with pure disodium tartrate dihydrate. This contains 15.66% of water.

So, we look at the apparatus also the apparatus was very simple using a very simple battery microammeter ohm resistor and radio potentiometer. So, 50 80 milli volts across the electrodes should not be a problem and it can be used until the battery is exhausted, then you have to replace the battery and again start off.

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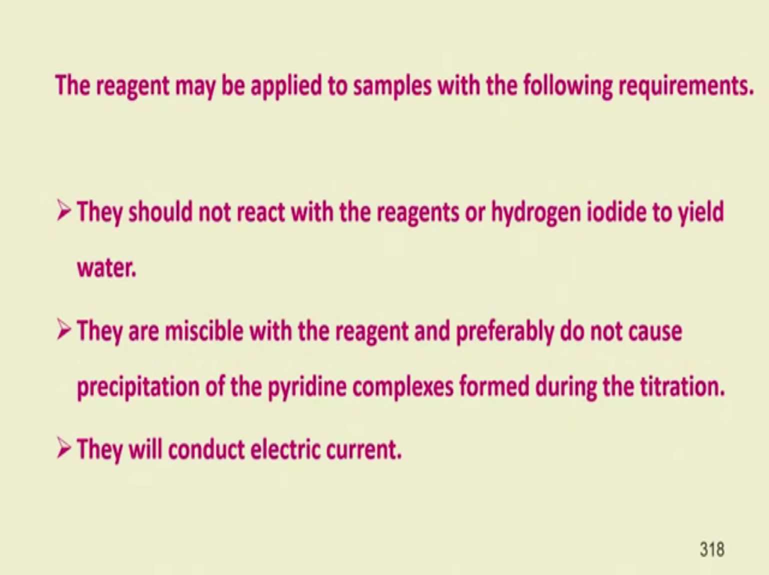

The reagent may be applied to samples with the following requirements.

- They should not react with the reagents or hydrogen iodide to yield water.
- They are miscible with the reagent and preferably do not cause precipitation of the pyridine complexes formed during the titration.
- They will conduct electric current.

So, we I had suggested that the reagent may be applied to the samples with the following requirements, they should not be reacting with the reagents or hydrogen iodide to yield water. This is one of the conditions know. So, the sample what you want to analyze should not be reacting with any of the reagents or Hydrogen Iodide HI to yield water, that is that will defeat the purpose of water analysis using Karl Fisher reagent.

And the sample should be miscible with the reagent and preferably does not cause precipitation of the pyridine complex formed during the titration. This is also fairly simple to understand they should be miscible with the reagent do not cause precipitation. So, otherwise sample will be lost pyridine will be lost. And they should also be able to conduct electric current; this is also one of the preconditions in case you are not able to do the titration.

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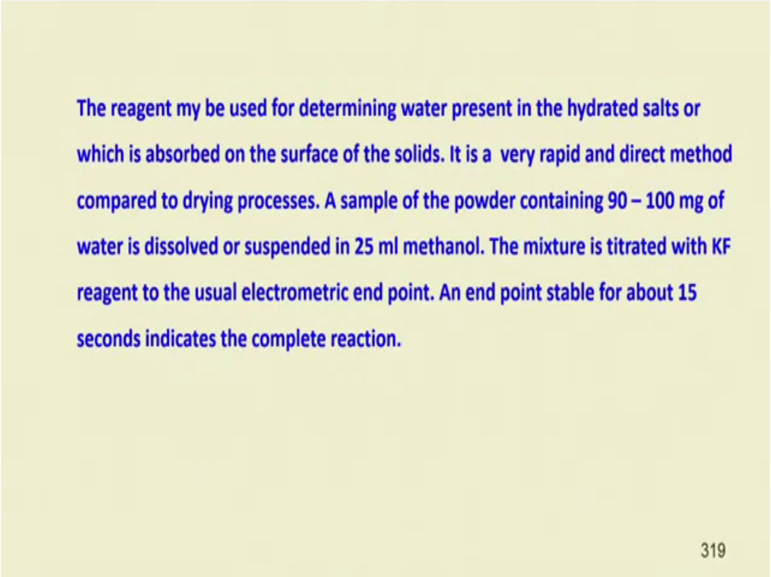

The reagent my be used for determining water present in the hydrated salts or which is absorbed on the surface of the solids. It is a very rapid and direct method compared to drying processes. A sample of the powder containing 90 – 100 mg of water is dissolved or suspended in 25 ml methanol. The mixture is titrated with KF reagent to the usual electrometric end point. An end point stable for about 15 seconds indicates the complete reaction.

So, they must conduct the electric current. So, the reagent may be used for determining the water present in hydrated salts, potassium titrate is one of them which we had used as a standard I had mentioned earlier know, disodium titrate dihydrate.

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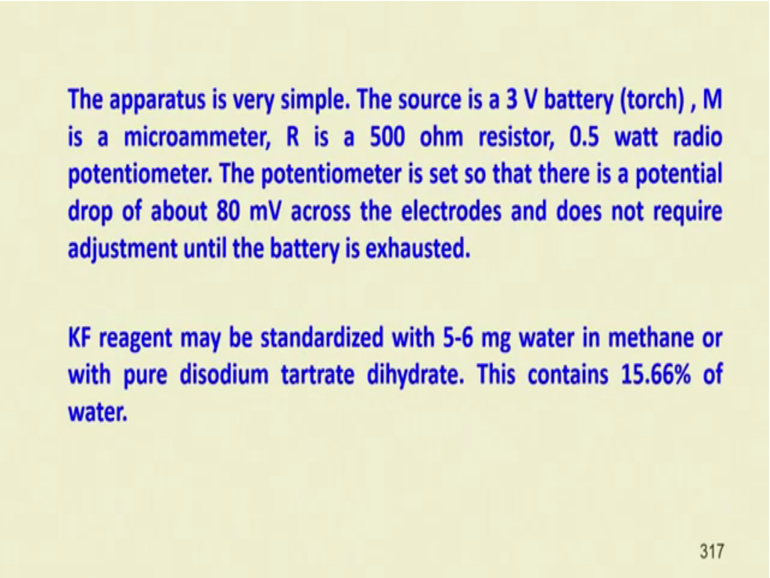

The apparatus is very simple. The source is a 3 V battery (torch) , M is a microammeter, R is a 500 ohm resistor, 0.5 watt radio potentiometer. The potentiometer is set so that there is a potential drop of about 80 mV across the electrodes and does not require adjustment until the battery is exhausted.

KF reagent may be standardized with 5-6 mg water in methane or with pure disodium tartrate dihydrate. This contains 15.66% of water.

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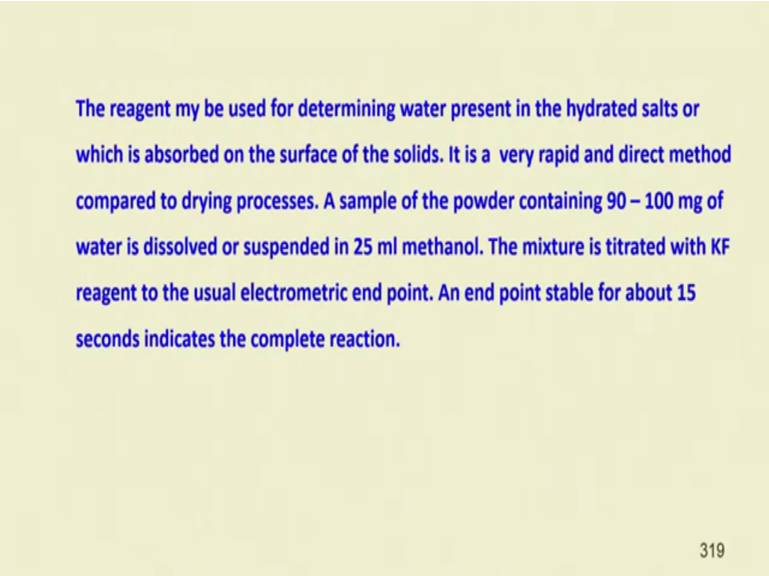

The reagent my be used for determining water present in the hydrated salts or which is absorbed on the surface of the solids. It is a very rapid and direct method compared to drying processes. A sample of the powder containing 90 – 100 mg of water is dissolved or suspended in 25 ml methanol. The mixture is titrated with KF reagent to the usual electrometric end point. An end point stable for about 15 seconds indicates the complete reaction.

And which is absorbed on the surface of the solids, we can determine that also. Some substances are there, which will absorb water from the atmosphere. So, you quite often that is not desirable. So, quite often we would like to determine how much of water is its absorbed and desorb it and then use it in our day to day life Karl Fisher titration is one of the best methods; because it can determine ppm level of water not in percentage or in grams or milligrams, its in ppm.

So, a sample of the powder containing 90 to 100 milligram of water can be dissolved and or suspended in methanol and the mixture can be titrated very easily with Karl Fisher reagent to the usual electrometric endpoint. So, an end point is stable for about 15 seconds should be more than enough to indicate that the reaction is complete.

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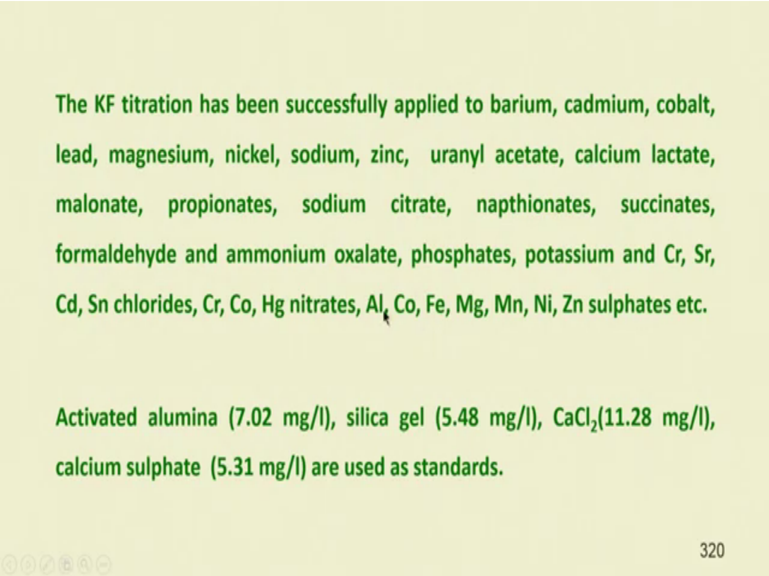

The KF titration has been successfully applied to barium, cadmium, cobalt, lead, magnesium, nickel, sodium, zinc, uranyl acetate, calcium lactate, malonate, propionates, sodium citrate, napthionates, succinates, formaldehyde and ammonium oxalate, phosphates, potassium and Cr, Sr, Cd, Sn chlorides, Cr, Co, Hg nitrates, Al, Co, Fe, Mg, Mn, Ni, Zn sulphates etc.

Activated alumina (7.02 mg/l), silica gel (5.48 mg/l), $CaCl_2$(11.28 mg/l), calcium sulphate (5.31 mg/l) are used as standards.

So, the there is a certain fewer waiting time of 15 minutes before you close the titration. And regarding the application of Karl Fisher titration, I can say that it has been successfully applied to the salts of barium, cadmium, cobalt, lead, magnesium, nickel, sodium, zinc, uranyl acetate, calcium lactate, calcium malonate, propionates, sodium citrate, napthionates, succinates, formaldehyde, ammonium list is endless phosphates, potassium, chromium, stransium, cadmium and tin chlorides.

And then nitrates of chromium cobalt and mercury, we can add their add to the list. Aluminum, cobalt, iron, magnesium, manganese, nickel, zinc as a most of the sulphates. In short what I want to tell you is, suppose a laboratory supplying company is there, they have to give a certificate for the like contents as say water content, purity, impurities etcetera depending upon the whether the reagent is technical grade nlr grade or laboratory grade or something like that.

So, a chemical supplies laboratory will be supplying many of these salts what I had mentioned earlier for the consumers. So, they have it normally any tech chemical analysis must accompany a chemical that is the rule, otherwise we will not know what chemical we are handling. If it does not have a label and the label should also contain what are the impurities and what are the actual contents.

So, if it contains water of hydration it has to be mentioned. So, regularly lot of people use Karl Fisher titration in their factory. So, activated alumina contain is one of the standard that is used because it contains exactly 7.02 milligram per liter, milligram per liter is ppm. Then I can use silica gel , I can use that contains 5.48 milligram per liter calcium chloride that is about 11.28 milligram per liter and calcium sulphate also can be used as standards.

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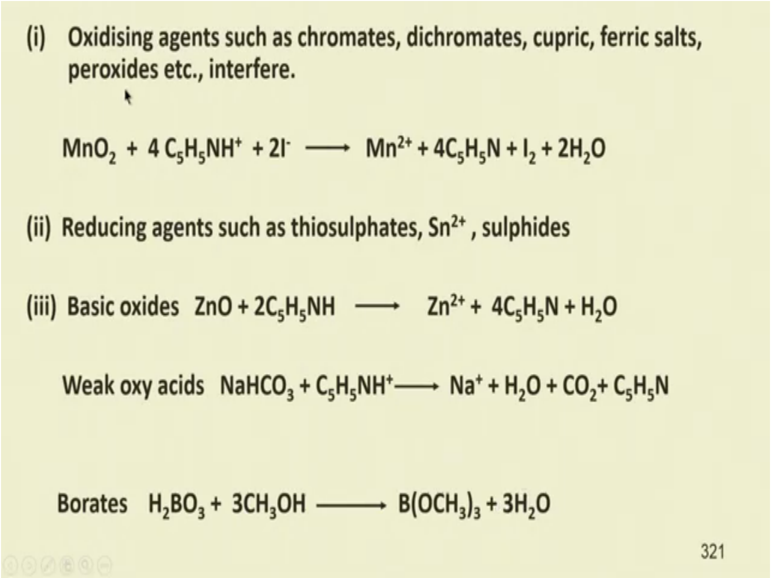

(i) Oxidising agents such as chromates, dichromates, cupric, ferric salts, peroxides etc., interfere.

$MnO_2 + 4\,C_5H_5NH^+ + 2I^- \longrightarrow Mn^{2+} + 4C_5H_5N + I_2 + 2H_2O$

(ii) Reducing agents such as thiosulphates, Sn^{2+}, sulphides

(iii) Basic oxides $ZnO + 2C_5H_5NH \longrightarrow Zn^{2+} + 4C_5H_5N + H_2O$

Weak oxy acids $NaHCO_3 + C_5H_5NH^+ \longrightarrow Na^+ + H_2O + CO_2 + C_5H_5N$

Borates $H_2BO_3 + 3CH_3OH \longrightarrow B(OCH_3)_3 + 3H_2O$

So, what are the interferences? The interferences are like this, that oxidizing agents such as chromates dichromates cupric and ferric salts peroxides etcetera interfere, why do they interfere? Because many of these are oxidizing agents they oxidize iodide to iodine in presence of metals. Here first reaction I have written that M n O 2 plus 4 molecules of pyridine, plus 2 I minus goes to M n 2 plus, plus 4 molecules of pyridine plus iodine plus 2 water.

Here the problem is not the preparation of the sample, but also the it should not be reacting with pyridine and iodine iodide. So, similarly reducing agents such as thiosulphates tin etcetera sulphides etcetera should not be there. Basic oxides also react with pyridinium C 5 H 5 N H ions and then they give you zinc metal and water plus pyridine. This is not the Karl Fisher titration because here the zinc reacts not with iodide iodine or pyridinium ion.

So, the its typically not there is no water molecule it is being produced here, but not getting reacted. Similarly, weak oxy acids N a H CO 3 C 5 H 5 NH plus all these things are N a H CO 3 you know it is stable around p H 4. So, many of the salts what do we analyze them here, usually contain the they should not be reacting with pyridine they should react with iodide iodine.

So, N a HCO 3 cannot be analyzed weak oxy acids because they react to produce water. So, the more and more you analyze more and more water will be produced, more of this pyridine will be consumed. And there will be problem in finding out when the reaction will end. So, we also cannot handle salts like this H 3 BO 3 borates H 2 BO 3, H 3 BO 3.

Because they react with methanol, which is one of the component of the Karl Fisher reagent. So, that reaction is given like this H 3 BO 3 H. So, this is an ester, methyl ester containing borate plus 3 molecules of water as a reaction product that is also not very convenient.

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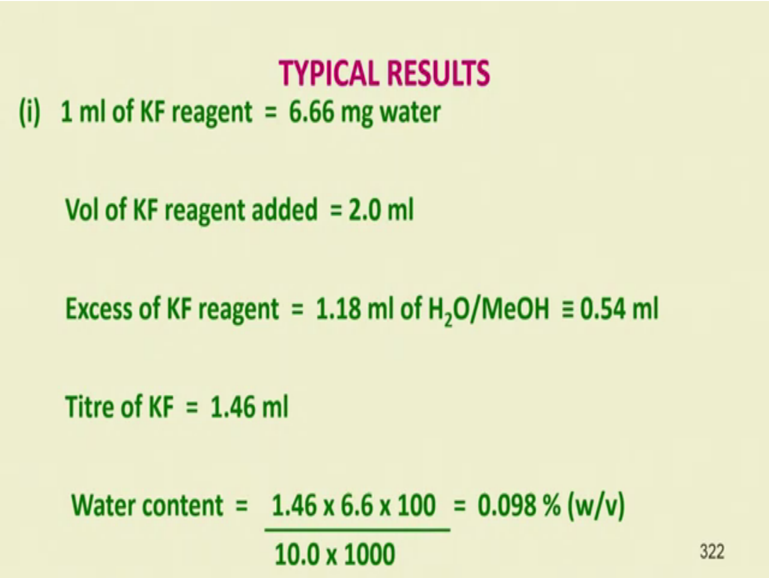

TYPICAL RESULTS

(i) 1 ml of KF reagent = 6.66 mg water

Vol of KF reagent added = 2.0 ml

Excess of KF reagent = 1.18 ml of H_2O/MeOH ≡ 0.54 ml

Titre of KF = 1.46 ml

$$\text{Water content} = \frac{1.46 \times 6.6 \times 100}{10.0 \times 1000} = 0.098\ \%\ (\text{w/v})$$

So, if I have to do a titration of Karl Fisher reagent what do I do? I just take a small sample now I will give you an example then you will be able to appreciate what are the problems. So, the example is like this, in the look at the slide 1 ml of Karl Fisher reagent is equivalent to 6.66 milligram of water. So, if I had to titrate I have added Karl Fisher reagent of 2 ml. So, access is determined by the titration and when I did this for a given sample, I got 1.18 milliliter of water methanol as a titrent finish that is the excess and how much is consumed? That is 0.54 ml.

So, titre value I got is 1.46 one per that is 2 ml minus 0.54; that will be 1.46. So, water content I can calculate 1.46 multiply it by 6.6 and this 100 comes from percentage to calculate the percentage, this 10 ml is the volume of the sample and 1000 is the per liter. So, that is to convert milligram into grams. So, if you do everything, according to this calculation you will end up with 0.098 percent of water weight by volume percentage weight by volume ok. So, that is where we complete our discussion on ion. This Karl Fisher reagent and then we move on to the next model that is ion selective electrodes.

So, there is not much to tell about the ion selective electrodes, because it is something like extension of a glass electrode, but we can do wonders with many of the ions selective electrodes; because that permits us to determine unknown concentrations of the metal ions and nonmetals also sometimes gases etcetera using ion selective electrodes.

Because, as the name suggest ion selective electrode is that electrode which gives a response selectively two particular ions. So, if I want to determine sodium I just need a sodium electrode that is a glass electrode. So, potassium electrode, potassium cadmium, cadmium electrode like that, in the market if you want to buy there are many ions selective electrodes which you can plug into a p H meter, but not exactly a p H meter its something similar to p H meter.

Because for p H meter we the range is somewhat fixed, for the reduction of ions is a electro selective electrodes the reduction potential will be different. So, the meter would be different for compare to glass electrode.

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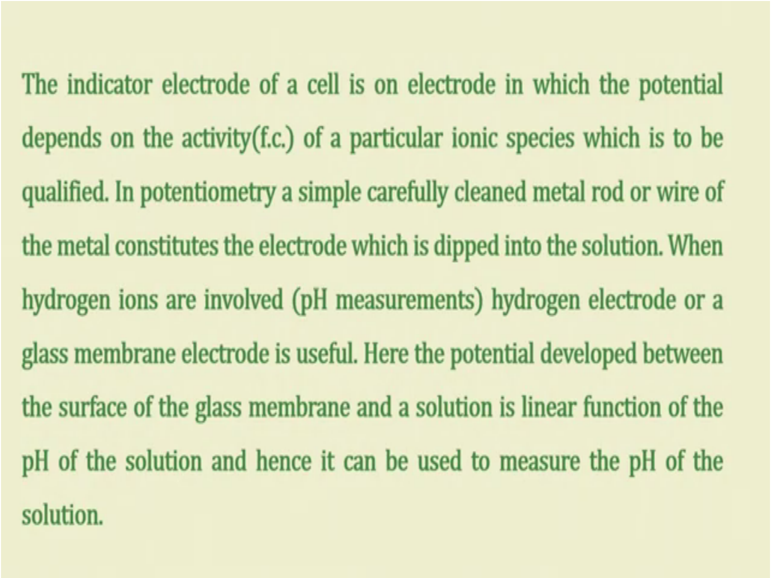

The indicator electrode of a cell is on electrode in which the potential depends on the activity(f.c.) of a particular ionic species which is to be qualified. In potentiometry a simple carefully cleaned metal rod or wire of the metal constitutes the electrode which is dipped into the solution. When hydrogen 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.

So, the indicator electrode of a cell is an electrode in which the potential depends upon the activity of a particular ionic species. This I all we already know is not it? The indicator electrode of any cell is of a is depends upon the activity coefficient or activity. What is activity? Activity coefficient f multiplied by the concentration that is f into c. So, particular ionics species that is the formula and which is to be qualified.

So, in potentiometry, a simple carefully cleaned metal rod or wire of the metal constitutes the electrode which is dipped into the solution or it is just like glass electrode. What do I have here? In potentiometry, I take a metal rod and then dip it in a solution and then make the complete electrical arrangement with 2 electrodes and then batteries at the outside external circuit voltmeter and current meter and all those things that is potentiometry.

So, when hydrogen ions are involved, we have a hydrogen electrode that is specific for hydrogen or a glass membrane is useful also. Here the potential developed between the surface of the glass membrane and a solution is a linear function of the p H of the solution and hence it can be used to measure the p H of the sample.

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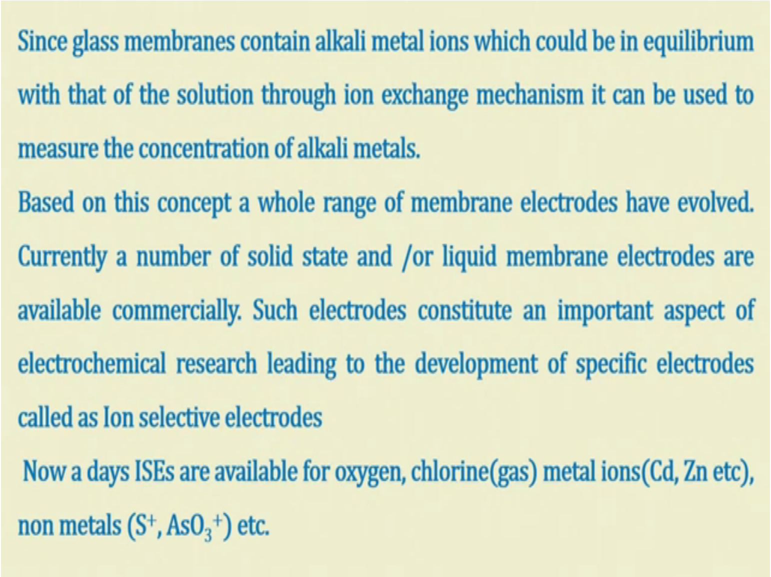

Since glass membranes contain alkali metal ions which could be in equilibrium with that of the solution through ion exchange mechanism it can be used to measure the concentration of alkali metals.

Based on this concept a whole range of membrane electrodes have evolved. Currently a number of solid state and /or liquid membrane electrodes are available commercially. Such electrodes constitute an important aspect of electrochemical research leading to the development of specific electrodes called as Ion selective electrodes

Now a days ISEs are available for oxygen, chlorine(gas) metal ions(Cd, Zn etc), non metals (S^+, AsO_3^+) etc.

Since, glass membranes contain alkali metals that also can be use for alkalied metal determination just like we use it for hydrogen ion so, why? Because the alkali metals also would be in equilibrium with the solution in the if it is alkaline; that is why we always say do not use a glass electrode in the alkaline range, there may be errors if you want to determine the p H.

I had mentioned earlier that the if you want to measure the p H of an alkaline solution the error could be plus or minus one unit around p H 12. So obviously, at that range, the electrode will be behaving as if it is in equilibrium in the responding or it is in equilibrium with the alkaline ions. It may be sodium ions or potassium ions or ammonium ion, but glass electrode is be is be particular is usually in equilibrium with sodium ions.

So, it can be used to measure alkali ions also provided you make the certain changes of the measurement parameters. There is nothing much in chemistry involved in that maybe a little bit of instrumentation. So, based on this concept, if a membrane electrode is a responsive towards a alkali ion, why not have an electrode which can be responsive towards other metals also should be, there is nothing wrong with that.

So, I can prepare a whole range of membrane electrodes made of a membrane, which is responsive towards a ion of which the membrane is response is responsive to the ion in solution as well as ions in the inner jacket of the glass electrode. So, only the membrane is different again just like same principle.

So currently, a number of solid state or liquid membrane electrodes are available commercially. You can name it, we have it sodium, potassium, ammonium, cyanide, chloride, bromide, iodide and then sulphide electrode is available fluoride electrode is available, chloride meters are available. And you name it we have it. And there are a couple of national and international manufacturers who will give you ion selective electrode provided you have the redox measurement system.

So, it is known as ORP Oxidation Reduction Potential. So, the as I told you, it will not be exactly same as any p H meter so, that you cannot use a p H meter as ion selective electrode unless you make the range different. So, that is why almost of the ion selective electrode membrane manufacturers, sell the ion selective electrode as a separate unit along with the meter.

So, you buy the meter, buy the electrode and the when you buy the electro when you want to buy an electrode they will say sir do you have a meter? If you say no, then they will say sir you buy that meter as well as electrode from us. So, it becomes a marketing technique. So, such electrodes constitute an important part of the electro chemical research, leading to the development of specific electrodes they are called as ion selective electrodes.

Nowadays, ion selective electrode in short we call it ISE; ISE Ion Selective Electrodes they are available for oxygen, chlorine, metal ions, nonmetals and so, many of the things nearly. There are about 50 to 60 kinds of ion selective electrodes available from national and international manufacturers. Here in this list you can see that ISEs are available for gases, that is oxygen and chlorine metal ions in solution nonmetal ions also in solution etcetera.

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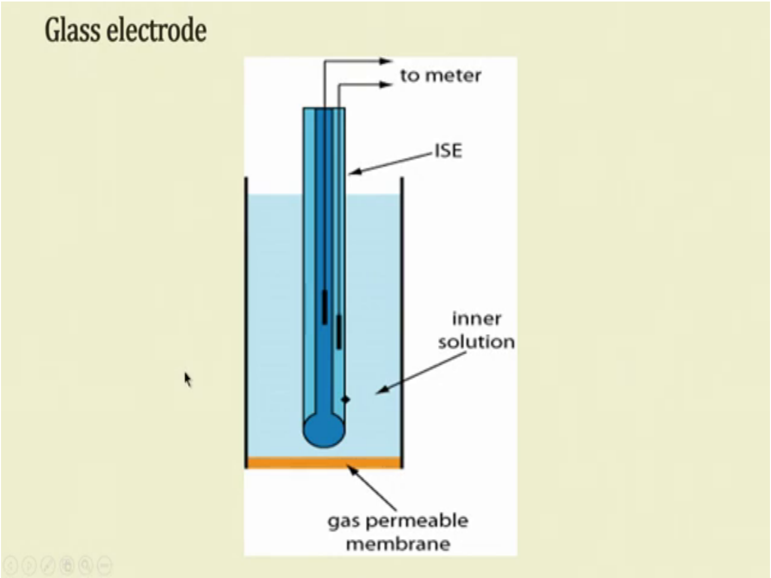
Glass electrode

So, this is the typical glass electrode I had shown you earlier its a fairly simple technique is not it, this we have seen earlier there is a bulb here and this bulb is the gas permeable membrane. And this in case of glass electrode it is permeable to hydrogen ions. You see at the bottom a red closing the electrode ok.

So, this whole electrode can be dipped in that and then there is an inner solution, here this blue color and then there is ion selective electrode here and then we can have a meter and then gas permeable membrane is also here. So, this could be for gas electrode.

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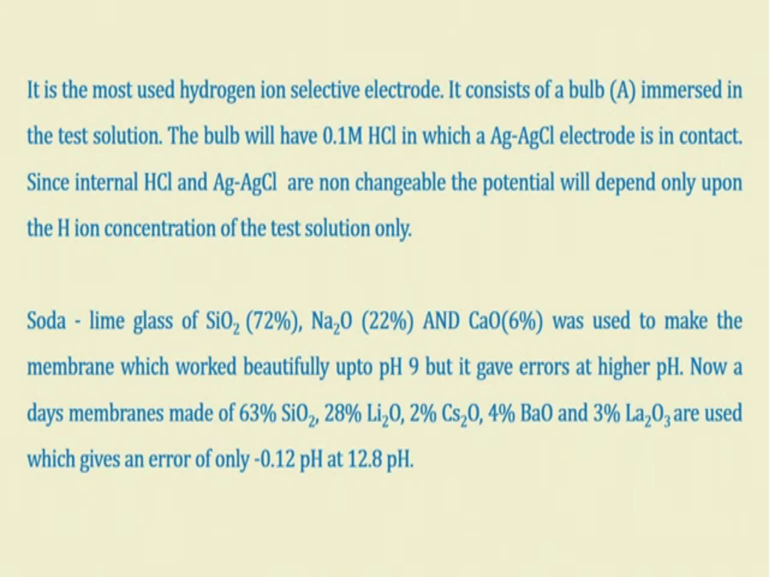

It is the most used hydrogen ion selective electrode. It consists of a bulb (A) immersed in the test solution. The bulb will have 0.1M HCl in which a Ag-AgCl electrode is in contact. Since internal HCl and Ag-AgCl are non changeable the potential will depend only upon the H ion concentration of the test solution only.

Soda - lime glass of SiO_2 (72%), Na_2O (22%) AND CaO(6%) was used to make the membrane which worked beautifully upto pH 9 but it gave errors at higher pH. Now a days membranes made of 63% SiO_2, 28% Li_2O, 2% Cs_2O, 4% BaO and 3% La_2O_3 are used which gives an error of only -0.12 pH at 12.8 pH.

So, its most used ion selective electrode is hydrogen ion selective electrode; because that hydrogen also is an ion only. So, the most used standard is a hydrogen ion selective electrode that is p H meter. So, p H meter you as you know it consists of a bulb is you must in the test solution. One is bulb is having point one molar HC l A g A g C l electrode this I have covered number of times. Since internal HC l and A g A g C l are non changeable in the potential; the potential will actually depend only upon the hydrogen ion concentration that is kept in the external solution outside the glass electrode.

So, soda lime glass that is S i O 2 approximately 72 percent and then sodium oxide and calcium oxide that is known as soda lime oxide glass. So, you can what is soda lime glass in your day to day experiences is, any glass that you come across which is heat not heat resistant, you heat it breaks. So, as usual glass is expected not to have a reproducible elasticity. So, it can expand unevenly and then break.

So, except some glasses like borosil or microwave glasses what you buy outside, now all other glasses if you heat them they will break. So, such glasses are known as soda lime glasses and their composition would be 72 percent silica, 22 percent N a 2 O 2 and N a 2 O sodium oxide followed by about 6 percent of calcium oxide. All these electrodes all these ions can be determined by ion selective electrode.

If I use the same glass electrode, I can determine these elements also with a slight modification in the electronics. So, the it we it make the membranes that work beautifully up to p H 9, but at higher p H there will be errors. So, its not very convenient to make a glass electrode containing a soda lime glass with S i O 2 for S i O 2 we can determine N a 2 O, we can determine and calcium oxide we can determine.

Nowadays, membranes made of 63 percent S i O 2, 28 percent lithium oxide, about 2 percent carbon disulphide oxide cc its not ccm its not carbon disulphide yeah it is ccm C s C s 2 O and then 4 percent barium oxide and 3 percent L a 2 O L a 2 O 3 its not L a 2 O 3 they are used with which gives an error of 0.12 p H to 12.8 p H.

So, what should be the architecture of silver silver chloride electrode? Very simple, I can have silver silver chloride dipped in HC l in a glass in test solution in KC l and containing saturated calomel electrode H g 2 C l 2 then mercury outside. So, when you want to make an electrode, the outermost membrane should be the outermost part of the electrode ions selective electrode.

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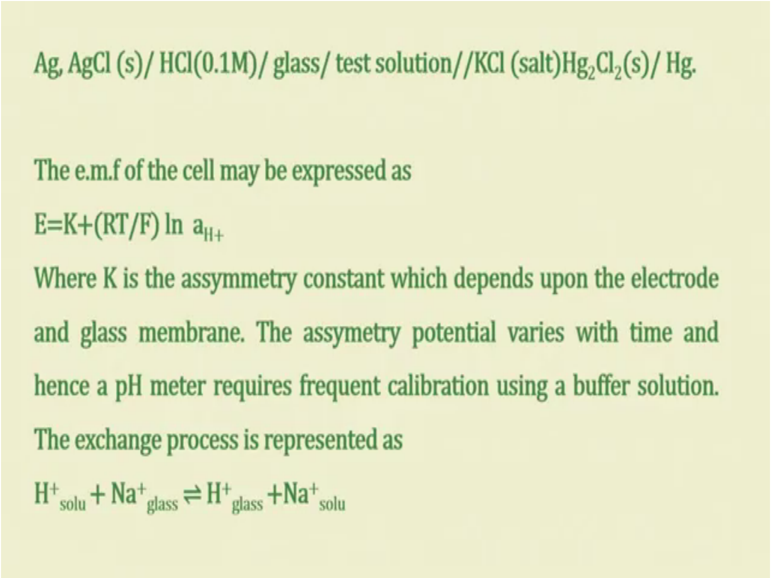

Ag, AgCl (s)/ HCl(0.1M)/ glass/ test solution//KCl (salt)Hg_2Cl_2(s)/ Hg.

The e.m.f of the cell may be expressed as

$E=K+(RT/F)\ln a_{H+}$

Where K is the assymmetry constant which depends upon the electrode and glass membrane. The assymetry potential varies with time and hence a pH meter requires frequent calibration using a buffer solution.

The exchange process is represented as

$H^+_{solu} + Na^+_{glass} \rightleftharpoons H^+_{glass} + Na^+_{solu}$

So, the emf of the cell maybe expressed as E is equal to K sum constant plus RT by n F l n a H plus where k is the assymmetry constant which depends upon the electrode and the glass membrane the assymmetry potential varies with time. And hence a p H meter requires a frequent calibration using a buffer solution this also we have covered earlier.

Now, with H plus solution and N a plus glass we have H plus glass and N a plus solution. So, here we make the change to convert it into sodium ion selective electrode.

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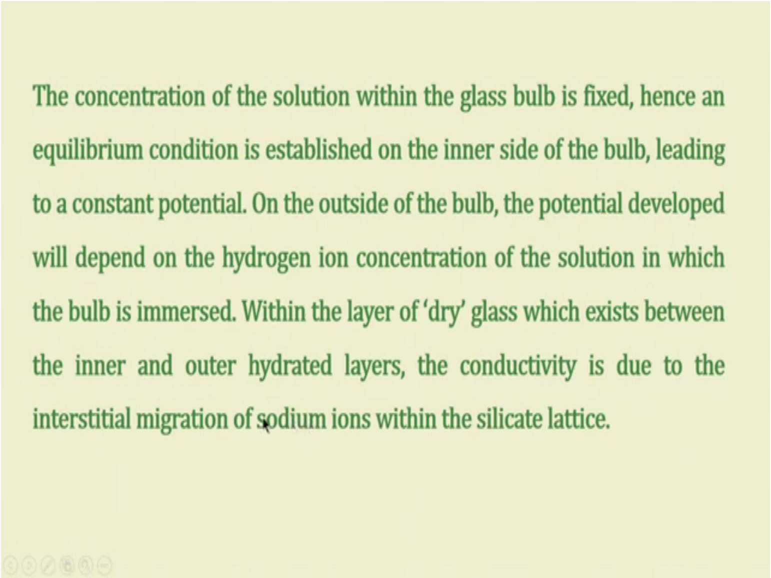

The concentration of the solution within the glass bulb is fixed, hence an equilibrium condition is established on the inner side of the bulb, leading to a constant potential. On the outside of the bulb, the potential developed will depend on the hydrogen ion concentration of the solution in which the bulb is immersed. Within the layer of 'dry' glass which exists between the inner and outer hydrated layers, the conductivity is due to the interstitial migration of sodium ions within the silicate lattice.

So, the concentration of the solution within the glass bulb is fixed. And hence an equilibrium condition is established on the inner side of the bulb leading to a constant potential. On the outside of the bulb the potential developed will depend upon the hydrogen ion concentration as usual in which the bulb is immersed.

So, within the layer of the dry glass, which exists between the inner and outer hydrated layers the conductivity is due to interstitial migration of the sodium ions within the silicate lattice; that is silicate lattice comes from the glass membrane. So, all these considerations take place when you want to make an alkaline electrode which is responsive you to sodium ions or silicate ions or borate ions.

So, the glass electrode can be used in presence of strong oxidants and reductants we had the no problem with that and then we can use it in viscous media that is also no problem and in presence of proteins and similar biological substances which may seriously interfere with other electrodes, but not the glass electrode. It can also be adopted for measurements with small volumes of solutions it may give erroneous results, when used with very poorly buffered solutions.

So, buffered solutions are near should be nearly neutral. So; obviously, the p H of buffer solution except in few cases would be neutral or acidic alkaline buffer solutions are very rare we do not need so much. But neutral and acidic buffers we need in day to day life or in scientific life.

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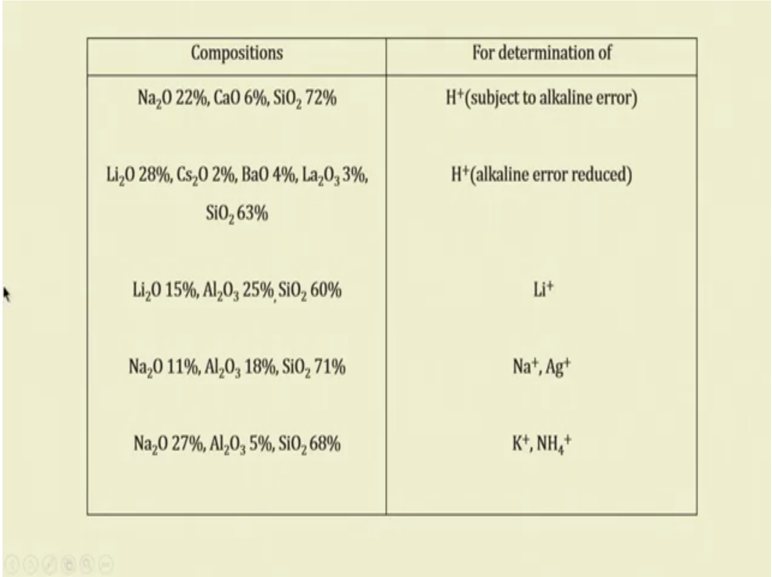

Compositions	For determination of
Na_2O 22%, CaO 6%, SiO_2 72%	H^+(subject to alkaline error)
Li_2O 28%, Cs_2O 2%, BaO 4%, La_2O_3 3%, SiO_2 63%	H^+(alkaline error reduced)
Li_2O 15%, Al_2O_3 25%, SiO_2 60%	Li^+
Na_2O 11%, Al_2O_3 18%, SiO_2 71%	Na^+, Ag^+
Na_2O 27%, Al_2O_3 5%, SiO_2 68%	K^+, NH_4^+

So, here are the compositions of the glasses, what are they? One is N a 2 O 22 percent, calcium oxide is 6 percent. S i O 2 is 20 72 percent and this would be used for the determination of H plus subject to alkaline error; alkaline condition we say do not use that is what I have been discussing so far. Then I can use lithium glass containing lithium oxide 28 percent C s 2 O 2 percent barium oxide 4 percent, lanthanum oxide 3 percent and S i O 2 63 percent; if I use this, I can still determine the this has a membrane.

What I am trying to say here on the left side is composition. So, if I use this kind of glass, I can still determine the H plus in alkaline region, but the alkaline error will be reduced quite a lot. Now, if I want to increase use the an electrode for some other elements for example, take the third one L i 2 O; it has 15 percent L i 2 O, A l 2 O 3 is 25 percent S i O 2 is 60 percent both these A l 2 or 3. And S i O 2 are not soluble in water.

So, a glass membrane made of aluminum and silicate containing lithium oxide up to 15 percent should be workable for lithium ion only because aluminum is not soluble, in water silicate is not soluble in water. Now, but I can make it a make a little change here instead of L i 2 O why not go for sodium oxide? Now, look at the sodium oxide content in the top one and in the bottom one in the third one. Here with the sodium atom or sodium ion would be approximately 15 percent of the top one is not it.

So, I can also prepare a an electrode containing N a 2 O and A l 2 O 3 and S i O 2 and this can work with respect to sodium and silver ion. And then N a 2 O I of course, I have to dope it with silver if I had to use it for silver ion. So, N a 2 O 20 percent A l 2 O 3, 5 percent and S i O 2 68 percent can be use for potassium and ammonium ions; they also would give certain amount of current that can be use for ion selective electrode.

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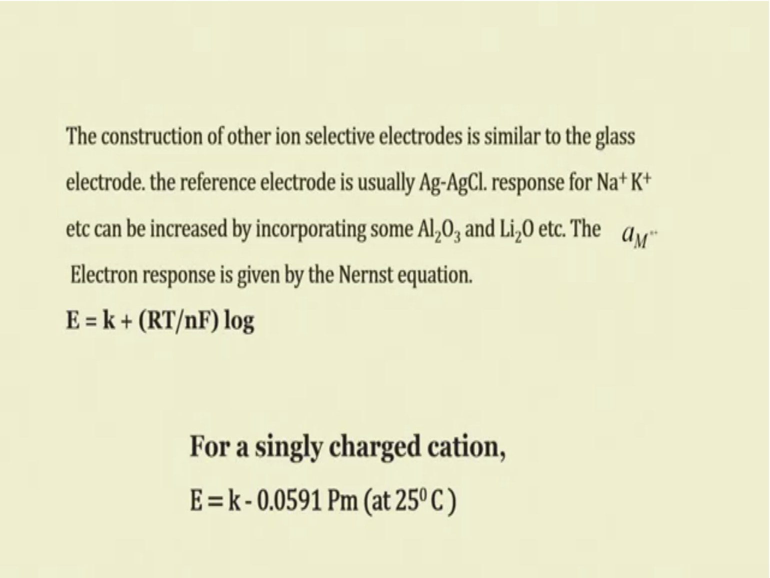

The construction of other ion selective electrodes is similar to the glass electrode. the reference electrode is usually Ag-AgCl. response for Na^+ K^+ etc can be increased by incorporating some Al_2O_3 and Li_2O etc. The a_{M} Electron response is given by the Nernst equation.

$E = k + (RT/nF) \log$

For a singly charged cation,

$E = k - 0.0591 \, Pm$ (at 25° C)

Then the construction of other ion selective electrodes is approximately similar to the glass electrode. So, how do I make a glass electrode? The glass electrode can be made into a bulb by take a glass make the glass composition make a tube and then blow it. So, when you blow the air the end of the tube will be blown like a bulb. So that is how I make the membrane glass membrane.

So, the reference electrode, in all these cases would be normally A g A g C l in all ion selective electrodes be why? Because, it is a very standard system, which can be easily made in any laboratory or it can be purchased also. So, the response for sodium and potassium can be increased by incorporating sum A l 2 O 3 and lithium oxide; we will have to do that you know addition or doping is a must.

So, the activity of the metal ion electron response is given by the Nernst equation. Here we do not write E is equal to E naught, but we simply write a proportionality constant and then we write RT by n F log of P m I kept it here open, because I can write many things here usually it is p metal ion. So, for a singly charged cation I can say E is equal to k minus 0.0591 P m that is metal ion; this P refers to negative log of concentration of the metal ion.

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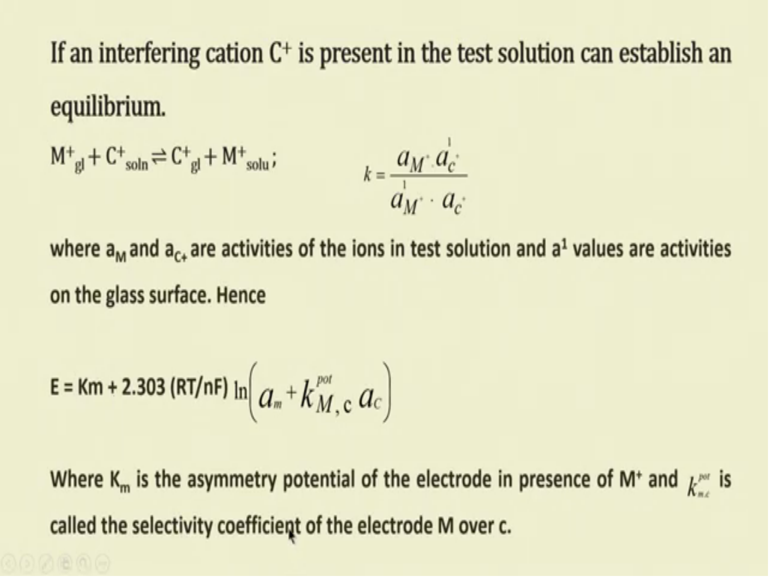

If an interfering cation C^+ is present in the test solution can establish an equilibrium.

$M^+_{gl} + C^+_{soln} \rightleftharpoons C^+_{gl} + M^+_{solu}$; $k = \frac{a_{M^+} \cdot a^1_{c^+}}{a^1_{M^+} \cdot a_{c^+}}$

where a_M and a_{C+} are activities of the ions in test solution and a^1 values are activities on the glass surface. Hence

$$E = Km + 2.303\,(RT/nF)\ \ln\left(a_m + k^{pot}_{M,c}\, a_c\right)$$

Where K_m is the asymmetry potential of the electrode in presence of M^+ and $k^{pot}_{m,c}$ is called the selectivity coefficient of the electrode M over c.

So, if an interfering cation C plus is present in the test solution, we can establish an equilibrium something like this metal in the glass plus concentration in solution. And then we have concentration in the glass that is equilibration followed by metal in the solution. So, for this reaction I can simply write the stability constraint, k is equal to equilibrium constraint I can write not stability.

So, it is a M into a c, a M into ac both are plus sign here. So, I put plus sign here is the this thing and single electron system so, it is raise to 1. So, you can write or leave it as such. So, a M and a C plus are the activities of the ions in the test solution and a 1 values are activities on the glass surface.

So, here I am writing a 1 no a 1 C and a 1 M. So, here it works out something like this then I can write E is equal to K m plus 2.303 RT by n F ln am plus a M potential into c a c where km is the asymmetry potential of the electrode, in presence of metal and the concentration and k pot mc is called selectivity coefficient of the electrode M over c.

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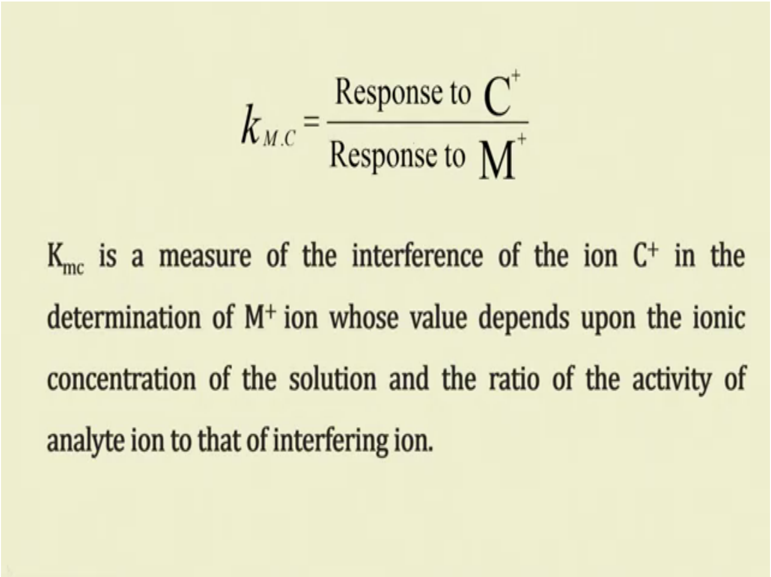

$$k_{M.C} = \frac{\text{Response to } C^{+}}{\text{Response to } M^{+}}$$

K_{mc} is a measure of the interference of the ion C^+ in the determination of M^+ ion whose value depends upon the ionic concentration of the solution and the ratio of the activity of analyte ion to that of interfering ion.

So, k MC is given by response to C plus divided by response to M plus; this is the standard ratio given for a particular manufacturing process. So, every time you buy an ion selective electrode, the manufacturer will tell you what is this k MC for each ion there they will give you a booklet containing those things. So, k MC is a measure of the interference of the ion C plus in the determination of M plus ion whose value depends upon the ionic concentration of the solution. And I hope you remember what is ionic concentration of the solution and the ratio of the activity of the analyte ion to that of the interfering ion.

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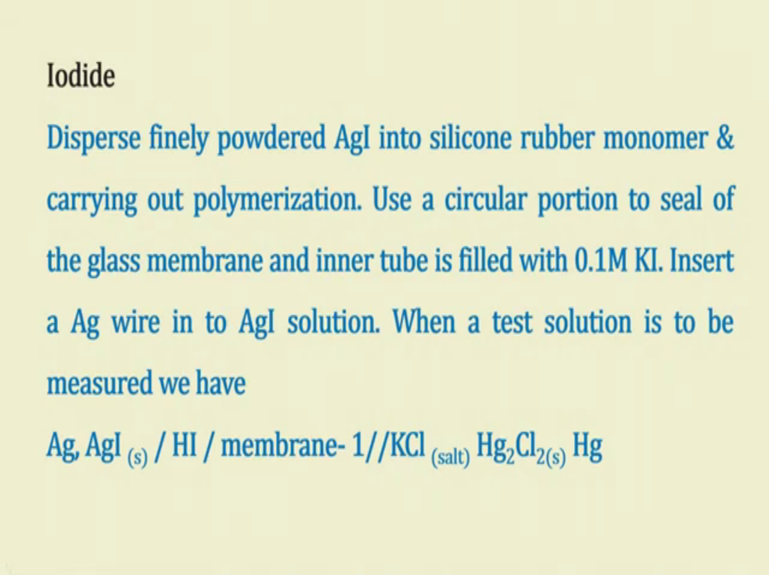

Iodide

Disperse finely powdered AgI into silicone rubber monomer & carrying out polymerization. Use a circular portion to seal of the glass membrane and inner tube is filled with 0.1M KI. Insert a Ag wire in to AgI solution. When a test solution is to be measured we have

$Ag, AgI_{(s)} / HI / membrane\text{-} 1 // KCl_{(salt)}\ Hg_2Cl_{2(s)}\ Hg$

So, now if I want to make a hydride iodide ion selective electrode, how would you go about doing it? There are different ways of preparing the membrane. Now, you see the whole problem of determining making an ion selective membrane is to make the membrane responsive.

So, I can do it by incorporating while melting and make the membrane will blowing glass blowing I had shown you earlier I have explained earlier or I can simply distribute these ions into a silicon rubber monomer and carry out the polymerization. So, the ions which are around on the membrane will be embedded in the polymer. So, the this finely powdered silver iodide can be dispersed into a silicon rubber monomer and polymerization should give me a silver iodide membrane.

So, silver iodide membrane should be useful for silver as well as iodide. So, I use a make a membrane and then cut a small piece, like this a small 1 centimeter this thing fit it into the ions selective electrode bottom layer and then outer layer is my test cell inner layer is a standard solution or saturated solution with silver silver chloride electrode as the reference electrode. So, the inner tube is filled with 0.1 molar KI solution in this case, if it is calomel electrode mercuring.

So, insert a silver wire into silver iodide that is our silver silver iodide electrode. So, when a test solution is to be measured, we have a silver silver iodide in the solid form that is the membrane that is the solid. And in contact with the hydrogen iodide that is in contact with the membrane. And then the whole thing is having a salt bridge separation double line like this, represents salt bridge separation.

And then KC l and then H g 2 C l 2 by H g so; that means, we are using a mercury saturated calomel electrode as a reference electrode; because A g A g C l I cannot use because there will be some problems with silver. So, best to when you want to use silver silver chloride, do not use A g A g C l electrode, but you can go for silver mercury chloride mercury electrode.

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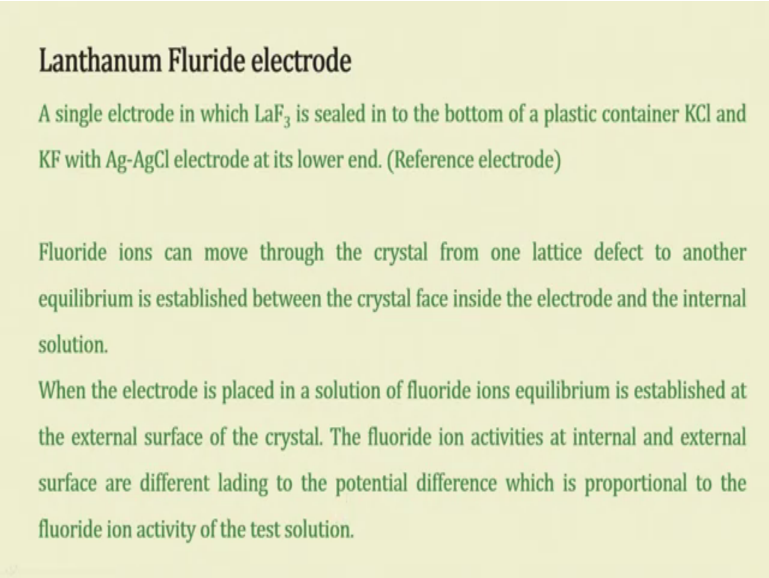

Lanthanum Fluride electrode

A single elctrode in which LaF_3 is sealed in to the bottom of a plastic container KCl and KF with Ag-AgCl electrode at its lower end. (Reference electrode)

Fluride ions can move through the crystal from one lattice defect to another equilibrium is established between the crystal face inside the electrode and the internal solution.

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 lading to the potential difference which is proportional to the fluoride ion activity of the test solution.

So, now, I want to describe a lanthanum fluride electrode. Here a single electrode in which lanthanum fluride is sealed into the bottom of a plastic container, containing KC l and KF with silver silver chloride electrode at its lower end. So, silver silver chloride would be the reference electrode. So, fluoride ions can move through the crystal from one lattice defect to another lattice defect in equilibrium. And equilibrium will be established between the crystal face inside the electrode and the internal solution.

So, when the electrode is placed in a solution of fluoride ions, equilibrium is established at the external surface of the crystal. And 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 solution. Now, I want to tell you there are many other electrodes, I am describing fluoride electrode for the first time here in this program.

Because fluoride is a very big contaminant and toxic element in the bore wells of the earth you know, you dig water and from the bore well it comes and everywhere there is fluoride nowadays and the fluoride is not good for health WHO prescribes 1 to 1.5 ppm of fluoride in drinking water. So, fluoride ion electrode is a very important activity or a very important gadget one can carry around if you want to determine fluoride.

So, we will discontinue our discussion in the next class about ion selective electrodes and then we will move on to sensors.

So, thank you very much.