Elementary Electrochemistry
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Electrolytic Solutions: Determination of Activity Coefficient

Welcome back to the course entitled elementary electrochemistry. In the previous class, we started discussing about how one can use the EMF measurement to get different physical quantities.

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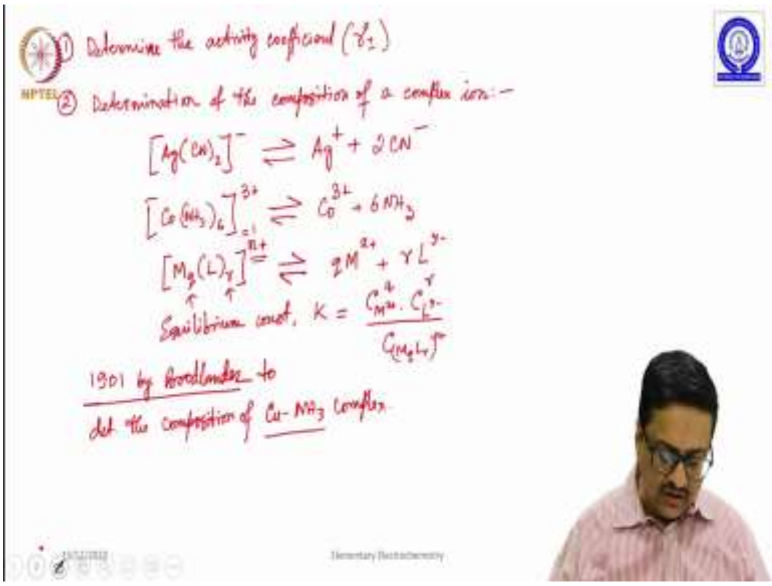

① Determine the activity coefficient ($\gamma_\pm$)

② Determination of the composition of a complex ion:-

$$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$$

$$[Co(NH_3)_6]^{3+} \rightleftharpoons Co^{3+} + 6NH_3$$

$$[M_q(L)_r]^{n\pm} \rightleftharpoons qM^{x+} + rL^{y-}$$

Equilibrium const, $K = \frac{C_{M^{x+}}^{q} \cdot C_{L^{y-}}^{r}}{C_{[M_qL_r]^{n\pm}}}$

1901 by Bodlander to det the composition of Cu-NH3 complex

So, in that in the first at the beginning, we have discussed how one can determine the activity coefficient that is the gamma plus minus of a particular ion undergoing a reaction in an electrochemical cell. So, now, in this class we will start by discussing a method which will be used to determine or determination of the composition of a complex ion. See in many chemical reactions, a cations form a complex ion with an anion or a ligand which may be neutral and the composition of that complex is different for different metal ligand systems.

So, for example, suppose if we have Ag CN whole 2 minus which is formed with the equilibrium of Ag plus plus 2 CN minus. Similarly cobalt hexamine complex 3 plus is formed when you mix cobalt 3 plus with ammonia. So, in general if you have a metal with q as its stoichiometric coefficient and some ligand L with the coefficient r and has some n plus or minus charge which essentially means that you should have qM and there should be the charge of the metal which may be x plus and r Ly minus such that the product and the difference results to a positive charge m plus.

So, when we try to write the corresponding equilibrium constant one has to write it using the concept of equilibrium constant. So, if I assume that this n is nothing but equal to 1 then this equilibrium constant K can be written as concentration of mx plus to the power q into concentration of Ly minus to the power r divided by the concentration of Mq Lr in suppose plus that is the charge that we have assumed.

So, in this context now we need to determine the values of q and r. So, one of the very early efforts made in 1909, in 1901 by Brodlander to determine the composition of copper ammonia complex as you all know as a chemist when you add ammonia in a solution of copper 2 plus the solution terms a deep blue in colour due to the formation of a copper ammonia complex. So, he wanted to know what is the composition of such complex.

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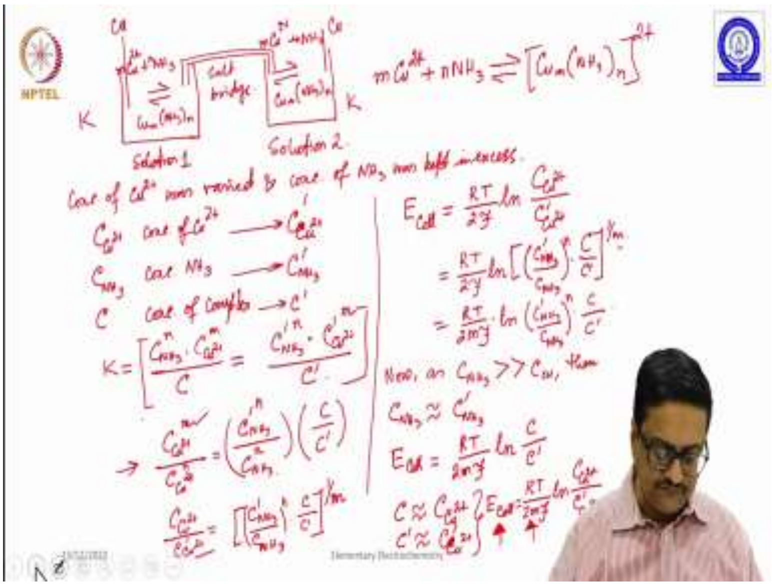

$mCu^{2+} + nNH_3 \rightleftharpoons [Cu_m(NH_3)_n]^{2+}$

Conc of Cu^{2+} was varied & conc of NH_3 was kept in excess.

$C_{Cu^{2+}}$ conc of $Cu^{2+} \longrightarrow C'_{Cu^{2+}}$

C_{NH_3} conc $NH_3 \longrightarrow C'_{NH_3}$

C conc of complex $\longrightarrow C'$

$$K = \left[\frac{C^n_{NH_3} \cdot C^m_{Cu^{2+}}}{C} = \frac{C'^n_{NH_3} \cdot C'^m_{Cu^{2+}}}{C'}\right]$$

$$\rightarrow \frac{C^m_{Cu^{2+}}}{C'^m_{Cu^{2+}}} = \left(\frac{C'^n_{NH_3}}{C^n_{NH_3}}\right)\left(\frac{C}{C'}\right)$$

$$\frac{C_{Cu^{2+}}}{C'_{Cu^{2+}}} = \left[\left(\frac{C'_{NH_3}}{C_{NH_3}}\right)^n \frac{C}{C'}\right]^{1/m}$$

$$E_{cell} = \frac{RT}{2F} \ln \frac{C_{Cu^{2+}}}{C'_{Cu^{2+}}}$$

$$= \frac{RT}{2F} \ln \left[\left(\frac{C'_{NH_3}}{C_{NH_3}}\right)^n \cdot \frac{C}{C'}\right]^{1/m}$$

$$= \frac{RT}{2mF} \cdot \ln \left(\frac{C'_{NH_3}}{C_{NH_3}}\right)^n \frac{C}{C'}$$

Now, as $C_{NH_3} >> C_{Cu}$, then

$C_{NH_3} \approx C'_{NH_3}$

$$E_{cell} = \frac{RT}{2mF} \ln \frac{C}{C'}$$

$$\left.\begin{array}{l} C \approx C_{Cu^{2+}} \\ C' \approx C'_{Cu^{2+}} \end{array}\right\} E_{cell} = \frac{RT}{2mF} \ln \frac{C_{Cu^{2+}}}{C'_{Cu^{2+}}}$$

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So, for that the methodology that he developed or used is that he took two solutions having copper plus ammonia forming a complex in equilibrium Cu m Mh3 n with MCo2 plus with n NH3 this is solution 1. And another solution of same thing where m Cu2 plus is mixed with ammonia forming this Cu m NH3 n complex solution 2. What we varied is the concentration of copper 2 plus in these two solutions was varied and concentration of NH3 was kept in excess. Which means that you have large amount of ammonia and whatever copper is there is almost in a complex state.

So, if C Cu2 plus CNH3 and simple C represent the concentration of Co2 plus in solution 1 concentration of ammonia in the first solution and concentration of complex in the first solution the corresponding values for the second solution he assumed to be Cu C Cu2 plus prime CNH 3 prime and C prime for the corresponding concentrations of copper ammonia and copper complex. And you remember that the equation is mCo2 plus reacting with n NH3 giving you Cu m NH3n with a charge 2 plus.

So, now, when we try to write down the equilibrium constant for this and that solution in terms of concentrations. Now, if we try to write down the values of equilibrium constant K for solution 1 and solution 2 one can write it like this CNH3 whole to the power n into CCu2 plus to the power m divided by C which is the concentration of the complex whereas CNH3 prime to the power n into CCo2 plus prime to the power m by C C prime.

Now by equating these two one can rearrange and write that CCu2 plus to the power m divided by CCu2 plus to the power n that is, I am taking this and that in one side and transferring the concentrations to the other side and one can write C prime to the power n NH3 divided by C to the power n NH3 that is the concentration part of ammonia and C by C prime the concentration part of your complex.

So, now, what he had done is he had then connected these two solutions using a salt bridge and used copper as electrode Cu on either side and then connected this to a potentiometer to determine the value of E cell. So, now, using the concept that we have learned in the previous class, you can calculate what should be the value of E cell in terms of these concentrations, where the concentration of copper and ammonia are different. We will come to that ammonia concentration can be made, thought to be equal.

So, by coupling these two solutions using a salt bridge, one can write down the E cell as equal to RT by 2F ln CCu2 plus divided by CCu2 plus prime. So, now, from this equation what you can get is that CCu2 plus by CCu2 plus prime is equal to C prime NH3 by CNH3 whole to the power n into C by C prime to the power 1 by m. So, when we replace this value here what we get is RT by 2F ln concentration of NH3 prime divided by concentration of NH3 whole to the power n into C by C prime to the power 1 by m.

So, now, we can take this 1 by m out of ln by writing it as RT by 2m into F ln CNH3 prime by CNH3 all to the power n into C by C prime. So, now, as CNH3 is much much greater than CCu then CNH3 can be considered to be equal as CNH3 prime because in both sides we have very large excess of ammonia and that large excess of ammonia is so, large compared to the corresponding copper 2 plus ion concentration they can be considered to be same. So, with this approximation you can write E sell as equal to RT by 2mF ln C by C prime.

Now, when we have ammonia in large excess, which essentially means that most of the copper 2 plus ions will remain complex in the form of copper and in complex. So, the concentration C is nothing but equal to the concentration of Co2 plus in the left solution and C prime is same as Cu concentration of Cu2 plus in the right solution. As a result, this equation can then be further simplified as E cell equal to RT by 2mF ln CCu by CCu 2 plus by CCu 2 plus prime.

So, now by just by measuring the concentration or fixing the concentration of Co2 plus in two solutions and by measuring the E cell using a potentiometer or by coupling it with some other half cell normally it is by a potentiometer one can easily determine the EMF of the cell and by knowing the concentration of Co2 plus one can determine the value of m and when you can determine the value of m using in this equation, the value of m concentration of copper and concentration of the complex one can easily determine the value of n as well. So, using this method one can determine the composition of a metal complex with a ligand.

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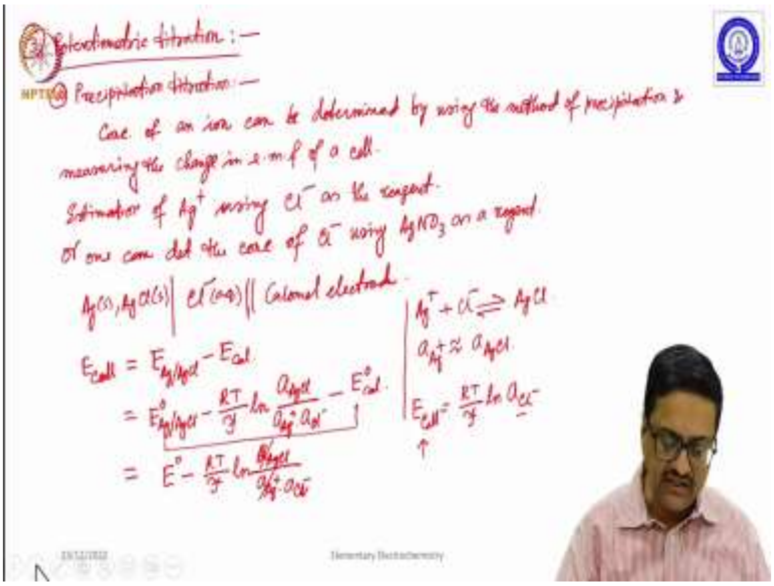

Potentiometric titration :-

(a) Precipitation titration :-

Conc. of an ion can be determined by using the method of precipitation & measuring the change in e.m.f of a cell.

Estimation of Ag^+ using Cl^- as the reagent.

or one can det the conc of Cl^- using $AgNO_3$ as a reagent.

$Ag(s), AgCl(s) | Cl^-(aq) || $ Calomel electrode.

$$E_{cell} = E_{Ag/AgCl} - E_{cal}$$

$$= \underbrace{E^0_{Ag/AgCl} - \frac{RT}{F} \ln \frac{a_{AgCl}}{a_{Ag^+} a_{Cl^-}} - E^0_{cal}}$$

$$= E^0 - \frac{RT}{F} \ln \frac{a_{AgCl}}{a_{Ag^+} a_{Cl^-}}$$

$Ag^+ + Cl^- \rightleftharpoons AgCl$

$a_{Ag^+} \approx a_{AgCl}$

$$E_{cell} = \frac{RT}{F} \ln a_{Cl^-}$$

$\uparrow$

The next application that wants to learn is the potentiometric titrations. So, it means that we will be doing some kind of titration experiments by measuring the potential of the cells that are is used during that particular electrochemical experiment. So, in potentiometric titration there are few different titrations we will discuss them one by one. Let us, first talk about a precipitation titration. So, from the name itself you can identify that this reaction or this titration involves precipitation of some of the ions present ions used during the titration.

So, here concentration of an ion can be determined by using the method of precipitation and measuring the change in EMF of a cell. So, one standard such experiment is the estimation of either estimation of Ag plus using Cl minus as the reagent or one can determine the concentration of Cl minus using AgNO3 as a reagent. In both the cases we will be using silver silver chloride electrode in combination with a calomel electrode or standard hydrogen electrode and determine the EMF of the cell while doing the titration.

So, we will demonstrate these experiments in the next week when you will see how these experiments are performed and then how the results are plotted and interpreted. So, for example today we will take this cell Ag solid with AgCl solid it is kept in connection with Cl minus in aqueous medium and it is coupled with a calomel electrode.

So, the E cell or EMF of the cell is nothing but E of Ag AgCl minus E calomel or one can write E0 Ag AgCl minus RT by F ln activity of AgCl divided by activity of Ag plus into activity of Cl minus minus E calomel. Calomel electrode is a standard electrode. So, one can further write the difference of E0 AgCl and E0 to for calomel. So, the E calomel is suppose at the standard state it is easy to calomel.

So, write the difference of this as E or simply E0 and it is RT by F ln activity of AgCl by activity of Ag plus into activity of Cl minus. So now, in this type of reaction what happens is as soon as you add any Ag plus to a solution which contains a large quantity of chloride almost everything gets precipitated as AgCl.

So, which essentially means, that activity of Ag plus is nearly equal to the activity of AgCl. So, then one can cancel this activity of Ag plus with AgCl and one can write the E cell equal to RT by F AgCl was down so, now, you take it up ln activity of Cl minus. So, now, what happens is that one can change the concentration of chloride ions and continuously determine the E cell value and do the experiment of determination of E cell with varying concentration of chloride.

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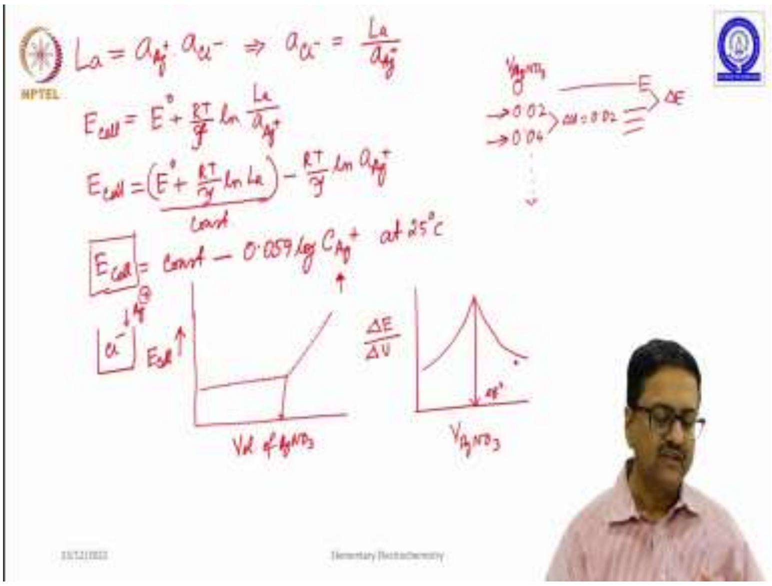

$L_a = a_{Ag^+}\, a_{Cl^-} \Rightarrow a_{Cl^-} = \frac{L_a}{a_{Ag^+}}$

$E_{cell} = E^\circ + \frac{RT}{F} \ln \frac{L_a}{a_{Ag^+}}$

$E_{cell} = \underbrace{\left(E^\circ + \frac{RT}{F} \ln L_a\right)}_{Const} - \frac{RT}{F} \ln a_{Ag^+}$

$\boxed{E_{cell}} = Const - 0.059 \log C_{Ag^+}$ at 25°C

But, then how do you know is that the activity product La is activity of Ag plus into activity of Cl minus. So, from this equation you can write activity of Cl minus is equal to La by activity of Ag plus. So, you can now again replace E cell equal to E0 which is the difference between silver silver chloride and calomel electrode plus RT by F ln activity of Cl is replaced by La by activity of Ag plus.

So, now, we again break it down E cell equal to E0 plus RT by f ln La plus RT or rather we should write, we should use a minus sign minus RT by F ln activity of Ag plus you see from numerator it has come to denominator. So, now this term is now a constant and one can write again E cell equal to constant minus RT by F ln can be converted to log at 25 degrees centigrade and the value you know that it is 0.059 log of concentration of Ag plus. So, activity is again replaced by concentration and it is at 25 degrees centigrade.

So, what is happening is now with increasing value of silver plus when the reaction is starting you have in a solution a certain amount of Cl minus and we are adding Ag plus to that and establishing that particular cell which I have written in the previous slide. So, with time this E cell will slowly change and beyond the neutralisation point when all this silver has consumed the entire amount of chloride then with increasing amount of, increasing amount of silver this value will keep on decreasing.

So, that we will have a change in the E cell. So, now, if I try to plot it in the form of a graph assuming that E cell is plotted in this direction and concentration of AgNo3 or in a better sense volume of AgNo3 added we will see that initially the EMF of the cell does not change significantly because it is not contributing anything and then after a while it will start increasing and the point of inflection is your endpoint.

So, this will indicate the endpoint of this particular titration. So, we will have to measure a number of points during this range when it is slowly precipitating the chloride and then after precipitation, we should continue the titration for around 10-15 readings and you will end up getting a plot like this. So, one can also plot delta E versus delta V, delta E by delta V versus V AgNo3. So, in that case, you will see that the graph increases like that and then again decreases length this.

So, with this we will get the corresponding equivalence point. So, this delta V means the difference in the volume between the 2 consecutive ratings. So, here suppose if your starting volume of AgNo3 is 0, then you have the next one 0.02, 0.04 like that if you are continuing, so, delta V is 0.02 and these delta E is the EMF measured for each of those values. So, delta E is the difference of that difference in EMF. So, this delta E by delta V is plotted against these values V to get this kind of plot.

So, in the next week when we demonstrate these experiments, I will explain this with a real data set. So, I will stop here in this class and we will continue from here in the next class, where we will discuss more of potentiometric titrations, which will always be, which will be demonstrated in the next week. Thank you.