Molecules in Motion

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Lecture – 25
Molecular Motion in Liquids (Contd.)

Welcome to another lecture on Molecules in Motion. In the last class, what we were talking about was how to determine the transport number.

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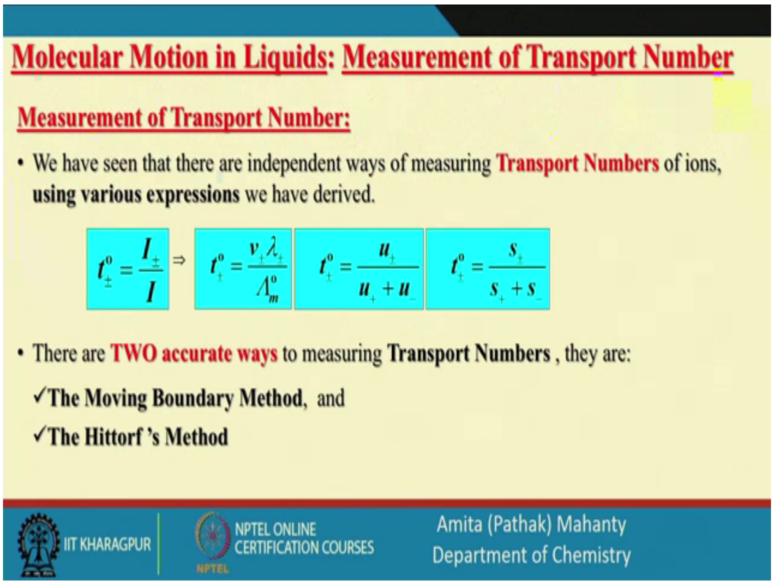

Molecular Motion in Liquids: Measurement of Transport Number

Measurement of Transport Number:

- We have seen that there are independent ways of measuring **Transport Numbers** of ions, **using various expressions** we have derived.

$$\boxed{t^{0}_{\pm} = \frac{I_{\pm}}{I}} \Rightarrow \boxed{t^{0}_{+} = \frac{\nu_{+}\lambda_{+}}{\Lambda^{0}_{m}}} \boxed{t^{0}_{+} = \frac{u_{+}}{u_{+} + u_{-}}} \boxed{t^{0}_{+} = \frac{s_{+}}{s_{+} + s_{-}}}$$

- There are **TWO accurate ways** to measuring **Transport Numbers**, they are:

✓**The Moving Boundary Method**, and
✓**The Hittorf 's Method**

Transport number as you remember is defined as the fraction in which we express the amount of ion current carried by each of the ion. So, we have seen from the independent migration of ions if we apply that Kohlrausch’s law the; the measuring of the transport number can be used by using various expressions. So, we have seen how the transference number or transport number can be expressed as a ratio of the fraction of current carried by the positive ion, by the total current pass through the system.

Similarly, if we have also seen that the transport number can be also given by the, this is the number stoichiometry number the formula unit of the electrolyte, which is going to give rise to the number of formula or cation or anion for a particular electrolyte system; that into the ionic conductivity divided by the molar ionic conductivity of the electrolyte that is another method of finding out the transport number.

So, and also we have seen that if you take the ratios of the ionic mobility of any of the ions divided by the ionic mobility of both the ions present in the system; we were essentially talking about electrolyte, one type of electrolyte where we can generate one type of cation and another type of anion. We are not talking about any mixed system where we have the electrolyte dissociated 2 type of electrolyte dissociated what 3 type of electrolyte dissociated giving rise to a number of cations and anions in the system.

We have also seen that the transport number can be given by the ratio of the drift speed of the cation or the anion divided by the drift speed of the total ions, cations and anions present in the system. And if you remember this transport number we have associated with the condition; with the concentration is approaching 0; that means infinite dilution.

So, the plus minus sign essentially is clubbed together it is can be separated for individual contributions. So, for convenience we have written plus minus if this is plus this is; obviously, going to be plus this is; obviously, going to be plus and this is; obviously, going to be plus for all the numerators. Similarly, if we have the subscript minus; that means, corresponding to the anion; then it will be the current carried by the anion here, it will be the ionic mobility of the anion and the number of anions generated per mole of the electrolyte.

Here will be the mobility ionic mobility of the anion; so, will be the ionic speed. So, this is the ratio and we are you essentially going to use the ratio of the; we are going to find out the fraction of the current carried by the individual ions. And since the number of electrolyte we are dealing with is 1; so, the fraction of current carried by the anion and the fraction of the current carried by the cation; if they are added should be always equal to 1, they are the fractions; so, the total should be always 1.

We have talked about how to do go about the measurements of the transport number for electrolyte system in the last class in the previous lecture 24; we have discussed the moving boundary method. In today’s lecture, we are going to take up another method; in fact, this was the method which we began with to find out the transport number it was the Hittorf’s it is the Hittorf’s method.

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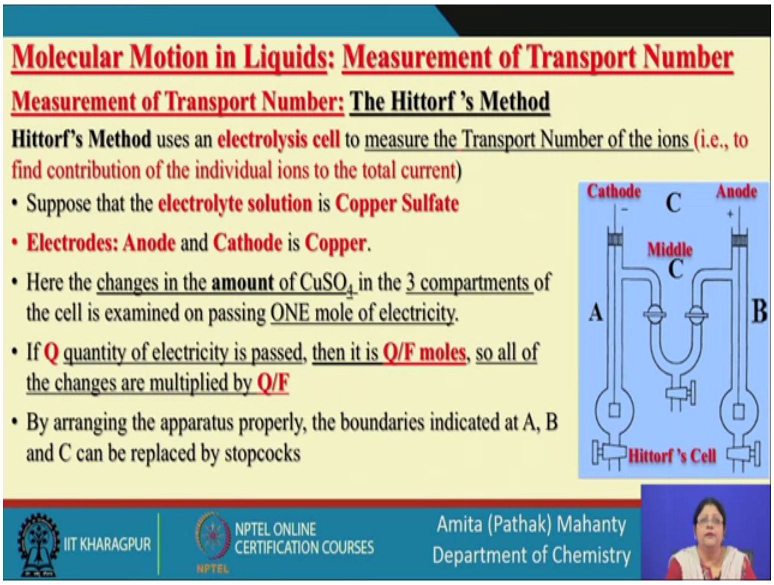

Molecular Motion in Liquids: Measurement of Transport Number

Measurement of Transport Number: The Hittorf 's Method

Hittorf's Method uses an **electrolysis cell** to measure the Transport Number of the ions (i.e., to find contribution of the individual ions to the total current)

- Suppose that the **electrolyte solution** is **Copper Sulfate**
- **Electrodes: Anode** and **Cathode** is **Copper**.
- Here the changes in the **amount** of $CuSO_4$ in the 3 compartments of the cell is examined on passing ONE mole of electricity.
- If Q quantity of electricity is passed, then it is Q/F moles, so all of the changes are multiplied by Q/F
- By arranging the apparatus properly, the boundaries indicated at A, B and C can be replaced by stopcocks

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And Hittorf was the first person to put forward the measurement of the transport number for a particular system even before Kohlrausch's law was establishing in independent migration of ions were established in full form.

So, the Hittorf's method if you can see this is the Hittorf's cell which we are talking about. In this Hittorf's method unlike the moving boundary method where you had 2 types of solution the lead solution and the indicator solution. And what we had discussed in that class that we had a common anion a 2 salts were used, 2 electrolytes were used one was composing the lead solution and another salt was composing the indicator solution. But both these electrolytes had a anion common and if we had anion common; we have it actually determining the transport number of the cation.

Unlike that what we have in this Hittorf's method is a electrolysis cell; this is the electrolysis cell we have. And we measure the transport number the contribution of the current carried by in each of the cation and anion in the system of the total current. We do is through the Hittorf's cell ok; what you have? We have a electrolyte system suppose the electrolyte system which we have is copper sulfate ok.

And the cathode and the anode which we have here we have; if you see this system of the electrolysis cell, you have the cathode here you have the anode here. This portion is known as the C we can a nomenclated C, we have nomenclated this part as A and this part as B.

Now, what we have? We have electrodes which are made of copper and the electrolyte we are using is copper sulfate. What we are going to monitor? See if you see the Hittorf's cell very carefully, we have compartmentalized the cell into 3 parts A, B and C. A is the cathode compartment, B is the anode compartment and C is the middle one.

So, what we have? We have 3 compartments now we see and each of the compartment will have the electrolyte copper sulfate. So, now, what we are going to see is the change in the amount of copper sulfate in each of the 3 compartments on processing of one mole of electricity.

Now, according to the definition of the current passed or electricity passed, if Q is the quantity of electricity passed then Q by F; F is the Avogadro a faraday constant is the moles and all of these changes which we are going to see for the amount of copper sulfate in each of the compartment hence should be multiplied by Q by F ok.

So, the moles which is going which is changing is Q by F; when Q amount of electricity is passed right. So, Q by F is the fraction of the mole which is the mole which is generated when you have Q amount of electricity passed. So, the change is whatever you see in the amounts of copper sulfate for each of the compartment should be multiplied by Q by F to get per moles or the moles of the changes in the moles of the amount of copper sulfate.

So, this is to simplify the whole thing. So, that you have an all in one unit in moles and if Q is the amount of electricity; then Q by F; F is the Faraday constant amount of moles which is bringing about the change. So, we have to multiplied Q by F for each of the changes which we see for the amount of copper sulfate clear.

Now, what we see in this? That by arranging the apparatus properly the boundaries between A B C can be replaced by the stop cork. See in previously we had a boundary generated by the mobilities of the ions and the densities of the electrolyte solution. Here what we have? We have separated out the 3 compartments you see for the compartment 1; I have put a stop cork.

And so this, whatever solution concentration is there I can monitor here. Similarly, for the anode compartment we have a stop cork; so, all of the solutions in this is going to be retained in this we can change see the changes in the concentration of copper sulfate here. And then you have this section which is the middle one; which is having the electrolyte copper sulfate and we have stopped, the separated the compartment by a stop cork.

So, I have 3 distinct boundaries differentiated by using a stop cork. So, that each of the portions I can have amount of the electrolyte taken out from this or this or this and find out the amount of copper sulfate that has changed. That means what I need to know? We need to know the amount of copper sulfate was which was initially present. So, that; obviously, can be done because we are making the solution. So, we are putting the electrolyte into the Hittorf's cell; so, the initial concentration of copper sulfate should be known to us.

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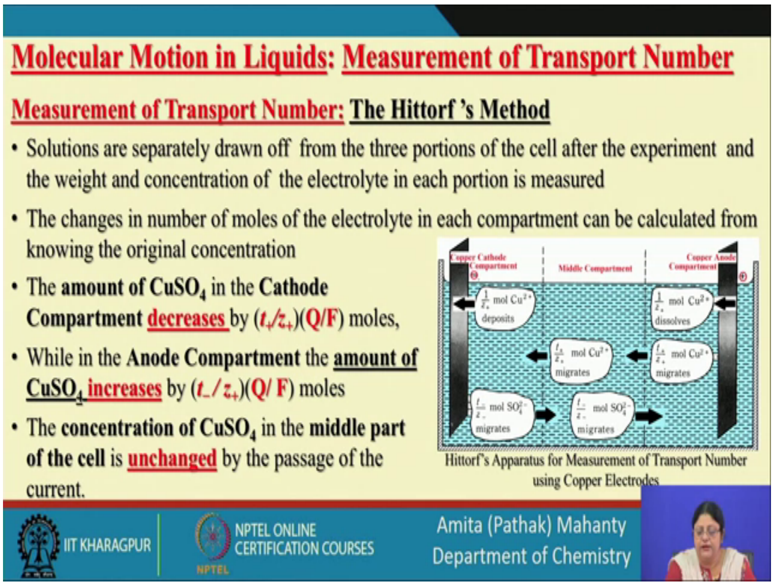

Molecular Motion in Liquids: Measurement of Transport Number

Measurement of Transport Number: The Hittorf 's Method

- Solutions are separately drawn off from the three portions of the cell after the experiment and the weight and concentration of the electrolyte in each portion is measured
- The changes in number of moles of the electrolyte in each compartment can be calculated from knowing the original concentration
- The **amount of $CuSO_4$** in the **Cathode Compartment** decreases by $(t_+/z_+)(Q/F)$ moles,
- While in the **Anode Compartment** the **amount of $CuSO_4$** increases by $(t_-/z_+)(Q/F)$ moles
- The **concentration of $CuSO_4$** in the **middle part of the cell** is unchanged by the passage of the current.

Hittorf's Apparatus for Measurement of Transport Number using Copper Electrodes

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Now, as you see we are going to look into what is happening; you have the anode compartment, a cathode compartment you have the anode compartment and both of them are made the electrodes are made up of copper. So, the solutions are separately drawn from each of the 3 portions after the experiment is done and either we weigh or find out the concentration of the electrolyte in each portion and then analyze our data. The change in the changes in the number of moles of the electrolyte in each compartment can be; obviously, known from the knowledge of the original concentration of copper sulfate in each of the compartments.

So, what we have here? You just see we have the deposit in the cathode section; we have deposition of the copper ion. What is happening in anode? Anode in the you have this as the copper electrode, here what happens? The copper ions get dissolved in the electrolyte solution and here what you have? The copper ion present in the electrolyte solution is deposited onto the electrode.

So; obviously, you see what happens when you see the 3 compartments? Here you have a deposition, here you have a dissolution. So, the if I have 3 compartments like this is the compartment A, this is the compartment B and this is the compartment C; what should happen in this compartment A. If you look at it very closely since the amount of copper is getting deposited.

So, what should happen? There should be a depletion of the amount of copper sulfate in the compartment which is having a cathode right because we have a deposition here. So, the amount of copper sulfate which is present is getting deposited so; obviously, the amount of the copper sulfate concentration the in this compartment should decrease.

And what happens to this part the cathode anode part anode part is what is happening? There is a dissolution of the copper. So, the copper ions from the copper electrode is dissolved into this compartment. So, as we pass as the experiment proceeds what we expect is the compartment which is cathode to have a depletion in amount of copper sulfate in this compartment. While the compartment which is anode should have a increase in the concentration of copper sulfate in the after passage of current or passage of electricity on performing the experiments.

So, and we have seen that if to if we want to find out what is the change of mole, if Q amount of electricity is passed we want to see the changes in mole. So, whatever we have said in the just now that each of the changes which whichever we are saying; the amount of copper sulfate in the cathode compartment, this is the cathode compartment where you will have a depletion decreases by how much amount?

This should be; this fraction should be multiplied by in both a cathode and anode compartment Q by F gives you the moles; so Q by F moles into what? I know there is transport number divided by the z i. So, if z plus t plus is the transport number, transference number whatever you call per the cation charge of the cation z; this is the if this is multiplied by Q by F gives you the amount which is now present in the compartment which is a decreased amount which is present in the compartment cathode.

While what happens in the anode sorry this should be a negative sign. So, the anode compartment what happens? You have an increase in concentration for what happens 1 by z plus moles of copper plus 2 ion dissolved. So, what is the total change in moles? This into the transference number that is that the t plus ions into divided by the say the charge of the plus 2 ion; into the moles of the electric; if Q moles of electricity is Q amount of electricity is passed to find out the mole change in moles we have to multiply by Q by F.

So, we have this for the in the anode cathode compartment, we have this for the anode compartment. Now, what happens in the middle of the middle compartment? If you just have a look at it this is a zone where the migrations are taking place. Here in this portion you will have a amount of copper ion migrating from the anode to the cathode. And here you have this is sulfate ions where you have the sulfates sulfate ion migrating from the cathode to the anode.

So, virtually what you should have that the copper sulfates concentration in this middle section should not have any change; until you have a transference which is generated. So, you have a look at this what we have seen?

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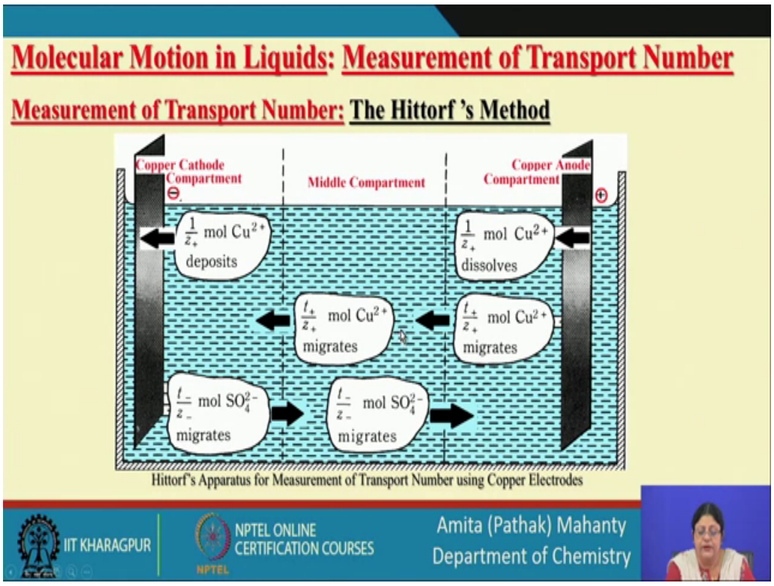

Molecular Motion in Liquids: Measurement of Transport Number

Measurement of Transport Number: The Hittorf 's Method

Hittorf's Apparatus for Measurement of Transport Number using Copper Electrodes

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We are saying how many moles of the copper is dissolved? We say if the charge of the ion is z then 1 by z moles of copper is dissolved and 1 by z plus moles of copper is deposited; the same amount should be should is expected to be deposited in the cathode compartment.

And this amount 1 by z a moles of coppers 2 salt should be dissolved in the anode compartment. And what happens to the anion? The anion which is you see it is getting deposited the; so, you have a copper sulfate system where you have copper plus 2 ions and the sulfate ions. Now the copper is getting deposited; so, the excess we have to maintain the charge neutrality.

So, to maintain the charge neutrality what you have? The sulfate ions which should be becoming excess in this compartment should start moving from the cathode compartment towards the anode compartment. Because you see here you have generated more of copper to ions and not sufficient amount of sulfate and the present to maintain the charge neutrality in the entire electrolysis cell; we have to have a migration of the anions from the cathode compartment to anode compartment.

So, what virtually is happening? We are having a cation movement from anode to the cathode and we have a anion movement from the cathode to the anode. And this is like a platform through which each of the ions is changing from one compartment to other right.

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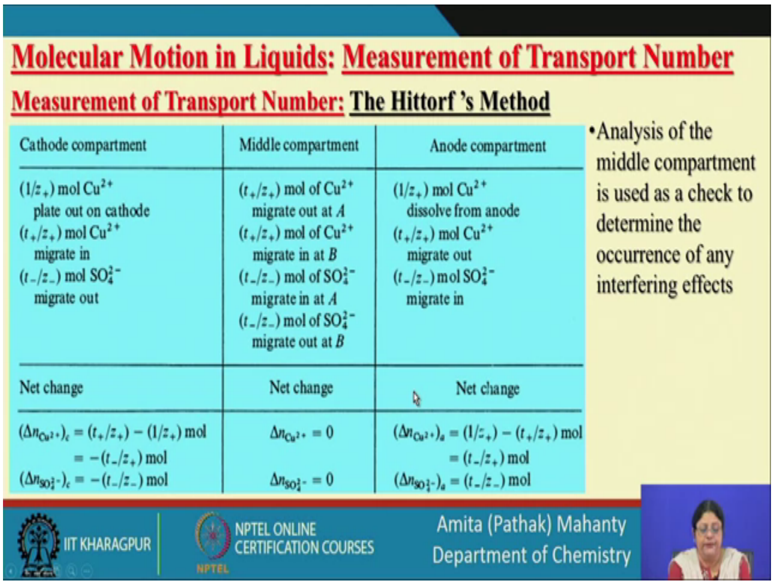

Molecular Motion in Liquids: Measurement of Transport Number

Measurement of Transport Number: The Hittorf 's Method

Cathode compartment	Middle compartment	Anode compartment
$(1/z_+)$ mol Cu^{2+} plate out on cathode (t_+/z_+) mol Cu^{2+} migrate in (t_-/z_-) mol SO_4^{2-} migrate out	(t_+/z_+) mol of Cu^{2+} migrate out at A (t_+/z_+) mol of Cu^{2+} migrate in at B (t_-/z_-) mol of SO_4^{2-} migrate in at A (t_-/z_-) mol of SO_4^{2-} migrate out at B	$(1/z_+)$ mol Cu^{2+} dissolve from anode (t_+/z_+) mol Cu^{2+} migrate out (t_-/z_-) mol SO_4^{2-} migrate in
Net change	Net change	Net change
$(\Delta n_{Cu^{2+}})_c = (t_+/z_+) - (1/z_+)$ mol $= -(t_-/z_+)$ mol $(\Delta n_{SO_4^{2-}})_c = -(t_-/z_-)$ mol	$\Delta n_{Cu^{2+}} = 0$ $\Delta n_{SO_4^{2-}} = 0$	$(\Delta n_{Cu^{2+}})_a = (1/z_+) - (t_+/z_+)$ mol $= (t_-/z_+)$ mol $(\Delta n_{SO_4^{2-}})_a = (t_-/z_-)$ mol

- Analysis of the middle compartment is used as a check to determine the occurrence of any interfering effects

So, if I want to see; so what is happening? So, let us see in each of the portions of the compartment cathode, anode and the middle section. What is happening? What is happening is we are in cathode compartment we are having 1 by z plus, z is the charge of the cation which we are dealing with.

So, n 1 by z plus moles of copper ions a plated is deposited or plated on the cathode ok. And in the anode compartment we have 1 by z plus ion that is z is the charge of the ion which is cation, which is getting dissolved from the anode. This is what; what is happening and what is happening here?

The fraction of the current which is carrying when you are passing Q amount of electricity then this into the fraction of the transport number, the fraction carried a current carried by each of the cation and anion has to be multiplied and multiplied. So, this is the fraction which is multiplied with into the total charge which is carried 1 by z; it gives you the moles into, it has to be multiplied by Q by F to get the total moles.

So, z t t plus by z plus is the number of moles of copper ion which is migrated from B to the compartment A ok. Now, what happens here? Again what we have see in the compartment in the cathode compartment what is happening?

That means, if this is the fraction of current carried by the cation, then t plus that is the transport number of the cation into 1 by z should be the moles of the copper ion which is migrated to the section A; that is the cathode compartment. And to maintain the charge neutrality; the fraction of the current which is carried by the anion t minus into 1 by the charge of the anion that many moles of the sulfates ion should migrate from the cathode compartment to the anode compartment; this is the thing which I am talking about.

So, this is going to be this is the amount which is going to be transported in and this is the amount which is going to be transported out right. So, what should happen in the compartment; middle compartment? Middle compartment you will see that if you look at this what is happening?

These many 1 by z plus the cation of the which is migrated into the fraction of the current carried by the cation that is the transport number of the cation into z plus t plus into 1 by z plus of moles of copper will migrate from the anode to the cathode passing through this place.

Similarly, since 1 by z minus is the charge of the anion which is present in the cathode. And the fraction of the current which is if you pass electricity; the fraction of the current which is carried by the anion is t minus into 1 by z minus will be the moles of the sulfate ion which is present in the in excess in the compartment ion in compartment A should be migrating to compartment B.

So, if you see this is the portion which is this side is migrating to this cation is migrating to the left side and anions are migrating to the right side. So, you can write down this as moles of the cations migrated out at A and moles of copper to migrated in migrated in at B ok.

So, the sulfate ions are going to be migrating from A to B and the anions are going to be migrating out of the B. So, the total anode concentration which we are going to be looking we are saying that 1 by z amount of charge is dissolved. So, what will happen if total current is carried by that t plus ion then t plus by into 1 by z of moles is migrating out of the anode compartment and t minus by z the total current carried by the anion that is the sulfate ion is moving into the compartment anode that is the B.

So, now we see take the note of what are the changes which has happened. We have the how much is deposited and how much is migrated of the cations and anions. And now take the take note of what are the changes which has made; which has been which has happened due to the electrolysis in the cell.

If you understand this is the platform in section C or middle portion is the section we do not expect any amount of accumulation of ions in this section because this is only a platform through which the cations are moving from say anode compartment to the cathode compartment and anions are moving from the cathode compartment to the anode compartment. So, this is virtually a place through which it is passing.

So, analysis of the middle portion is only done to check if there is any interference effect generated; if the if there is interference effect; obviously, you will not get the correct amount of the charge which you are expecting. Because interference can be accumulation of ions or some other form of problems in the migration.

So, what you see here now let us see the changes in the moles of the copper ion at the cathode ok. So, what we have, we have t plus the fraction of 1 by z minus 1 by z moles which is this is the amount which is migrating in and how much is deposited this is the deposition amount.

So, we have this many ions, if you do the 1 minus t plus t the transport number of the ion plus the transport number of anion should be 1, from that expression you get a expression like this. Have a look at it, please try to do is along with what I am just now showing. I am not writing it since it is already there in the slide, but I hope you understand that why I can write t minus here.

Because t minus is nothing, but because t plus and t minus is totally sum it up is equal to 1. So, I can write down t plus minus 1 in terms of minus t of the anion. So, we have similarly we can see the changes in the sulfate ions. Sulfate ions also should be having the same changes transference number of the anion into 1 by the charge of the anion.

The changes in cation and anions concentration in this middle portion should be 0 because we should not be expecting any sort of concentration effects or interference effect in this portion. If you have that then we have to correct it with the change of current. And in the anode compartment what we have? We have this many amount which is having dissolved.

And how much is migrating out? The migrating the total amount which is migrating is a fraction of the current carrying carried by the cation divided by a multiplied by the 1 by the charge of this. So, this gives the moles which is getting moving out and this is what is generated in the compartment; the difference should give the changes in the number of moles in the of the copper ion in the compartment anode; so, this is going to be how it is going to be represented.

So, if I know this then I can find out what is the change in the concentration of the sulfate ion. This is going to be a transport number of the sulfate divided multiplied by 1 of 1 by the charge of the sulfate ion. So, if I have these all these monitored in each of the experiment what I have?

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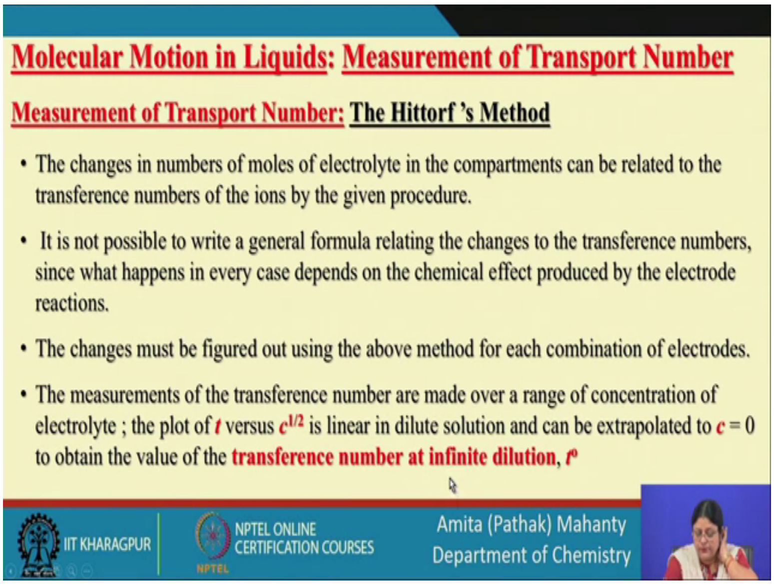

Molecular Motion in Liquids: Measurement of Transport Number

Measurement of Transport Number: The Hittorf 's Method

- The changes in numbers of moles of electrolyte in the compartments can be related to the transference numbers of the ions by the given procedure.
- It is not possible to write a general formula relating the changes to the transference numbers, since what happens in every case depends on the chemical effect produced by the electrode reactions.
- The changes must be figured out using the above method for each combination of electrodes.
- The measurements of the transference number are made over a range of concentration of electrolyte ; the plot of t versus $c^{1/2}$ is linear in dilute solution and can be extrapolated to $c = 0$ to obtain the value of the **transference number at infinite dilution, t°**

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The changes in the number of moles of the electrolyte in each compartment, we can be related to the transfer transference number of each of the ion by given the procedure which we have just now taken. It is possible to write down it is generally not we cannot have a equation; it is not possible to write down a general formula relating the changes in the transference number.

Since whatever is happening in each case depends on the chemical if changes that is occurring in the electrode compartment or the electrode reactions which are taking place. Changes must be figured out using the method which we have just now established for each of the compartment. The measurement of the transport number are made over a large number of concentrations of the electrolyte, then what we do?

We do measurement whatever value of t we calculate for each concentration that we plot against the concentration square root of the concentration and in a linear dilute solution. And from extrapolation to a condition where C equal to 0; we obtain the transfer number at infinite dilution.

So, at each concentration, from each compartment we are finding out what is the concentration change. And from that concentration change we are trying to correlate the concentration change with the transport number. And those transport number which we have calculated for each set of concentration of the electrolyte; we are plotting it versus unless the c square, c under root concentration under root of the concentration of the electrolyte. And from extrapolation to of that graph which is going to be a linear plot at c equal to 0; we obtain this transport at infinite dilution.

Thank you so much.