Microsystem Fabrication with Advanced Manufacturing Techniques

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Lecture – 11

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Microsystems Fabrication by Advanced Manufacturing Processes- Lecture 11

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Hello and welcome back to this eleventh lecture of Microsystems fabrication by advanced manufacturing processes. So, so far we were looking into the mechanical processes like: abrasive jet machining, powder blasting, also USM ultrasonic machining. And we did those processes from a fundamental stand point and then also modeled very various important issues like: material removal rate or surface average, surface roughness etcetera.

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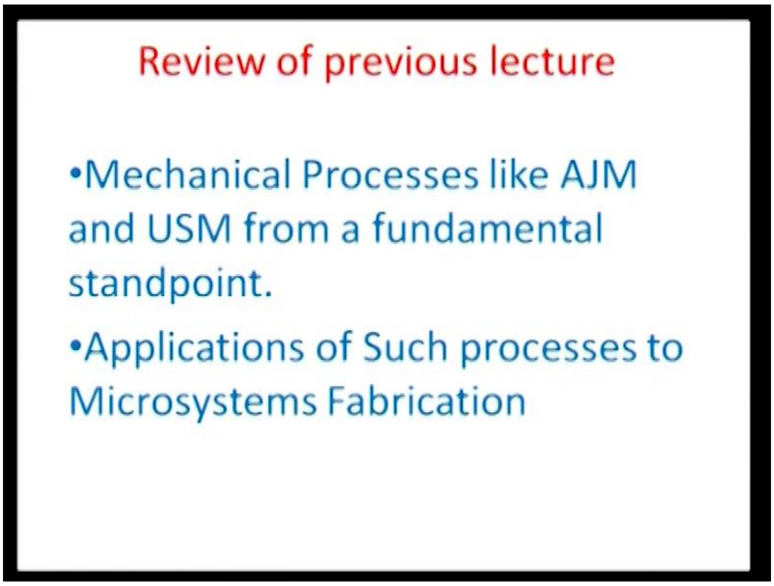

Review of previous lecture

- Mechanical Processes like AJM and USM from a fundamental standpoint.
- Applications of Such processes to Microsystems Fabrication

Then, we also tried to understand the direct applications of such processors in the Microsystems business, where micro-devices are manufactured from these mechanical so called energy processes. Today, we will be looking into a slightly different aspect; into the electrochemical machining, that is another very important nonconventional machining process or fabrication process, very widely used again in the Microsystems fabrication. And as the name suggests, electrochemical has a component of electricity and is also related to the chemical aspect, which means: essentially it is a ion transport.

So, as any other electrochemical process would be, this machining also involves the transport, the material removal getting removed by means of displacement through ions into an electrolyte solution. You need conducting surfaces for such machining operations. And then the idea is that instead of depositing on the tool side, if supposing the ions that emanate out of the work piece material, they can be somehow precipitated into a state which is undissolvable.

So, they can be like debri and by circulating the electrolyte, you can carry away those materials away from the main work zone and that way you can do bulk micromachining, by using electrochemical operations. So, let us look this process, at this process from a fundamental standpoint as we always normally do.

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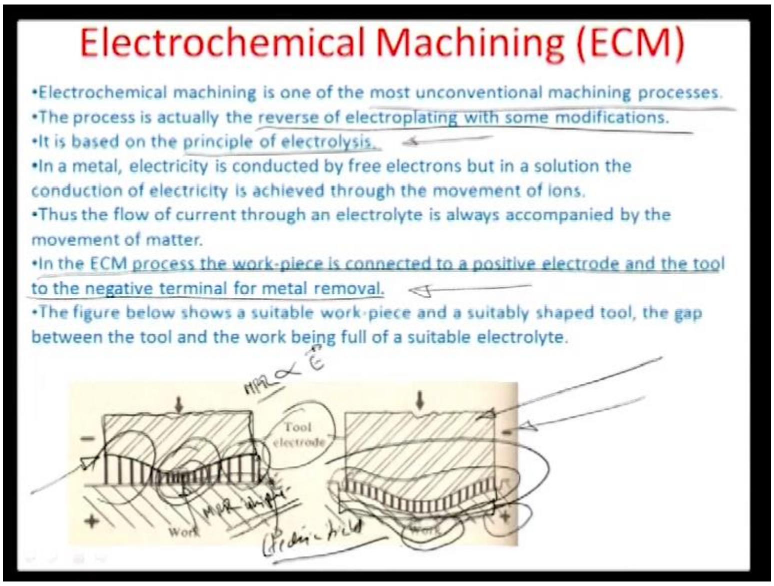

Electrochemical Machining (ECM)

- Electrochemical machining is one of the most unconventional machining processes.
- The process is actually the reverse of electroplating with some modifications.
- It is based on the principle of electrolysis.
- In a metal, electricity is conducted by free electrons but in a solution the conduction of electricity is achieved through the movement of ions.
- Thus the flow of current through an electrolyte is always accompanied by the movement of matter.
- In the ECM process the work-piece is connected to a positive electrode and the tool to the negative terminal for metal removal.
- The figure below shows a suitable work-piece and a suitably shaped tool, the gap between the tool and the work being full of a suitable electrolyte.

So, it is one of the again. Electrochemical machining is one of the most sort of wanted unconventional processes that are existing. The processes are reverse of electroplating with some minor modifications. And again it is a based on the principle of electrolysis that can be seen from the way that the processes described. So, as you already know that in a metal, in a piece of metal, electricity is typically conducted by free electrons. But in the solution, the electricity actually gets converted or the electricity gets carried by ions.

So, in metal, on 1 side the electrons are kind of bound within the clutches of the nucleus, formulating sometimes part of a large cloud, electron cloud which moves around the various orbital’s. But in solution, the major current comes out of the ions and the mobility of those ions in the solutions, that is the major charge carrier, positive ions or negative ions, cat ions and anions in a solution.

So, the flow of a current in an electrolyte, always is accompanied by movement of matter as opposed to what typically would happen in metallic conductors, where it is really the electron of the hole vacancy which is moving around and that results in the current. And somehow, this movement of a current on an external circuit should be somehow balanced to the movement of a charge carriers or ions in the solution, for creating a continuous process or continuous state of operation.

So, electrochemical machining is to establish that kind of a continuous operation. But charge carriers on the solutions are kind of a neutralized by the electrons and holes carried from the in the external circuit of such a process. So, as you can see here back in the slide; in the ECM process, the work piece is connected to the positive electrode, so it is made the anode. And the tool to the negative terminal for the metal removal, so that is conventionally followed in some of these processes, so tool is the cathode and the work piece is the anode as we can see in this figure here.

And 1 good point that I would like to mention here is that, it is a dye sinking process meaning thereby; that whatever is the profile of the tool; however, complicated the profile of the tool may be, is kind of impinged or impregnated into the work piece surface eventually, because of the of the improper distribution of the electric field to begin with.

So, electric field as you all are aware, is basically the gradient of potential. And the distances as you can see between this and this is quite large. So, the sides here of the tool are at a much higher distance, thereby meaning; that the electric field here is lower and the electric field here is very high, as can always be illustrated by this field lines. You can see the density of the lines closer to the interface which is closer of the tool surface in comparison to the sides.

So, therefore, it is obvious to assume that, if by Faraday's principle we assume the material removal rate MRR to be proportional to the electric field somehow. The field vectors are very high at the center and sort of trace amounts at the sides which means thereby; that the MRR from the central portion of the work piece would be highest. So, MRR is highest, where the tool is closest. And the MRR is subsequently is lower as you move to the sides.

Therefore, it is obvious to assume that the work piece would kind of achieve a shape after a while, where the electron electric field kind of get homogenized. And beyond which the whole shape the negative of the shape of the tool electrode, is impregnated and the ECM process gets carried out after that in the same shape, as once this full impregnation in shape of the tool is embedded on to the work piece surface. So, that is what the beauty of this ECM processes, that it is a dye sinking process. So, whatever shape you want to generate, you create a negative of that shape as a tool and automatically impregnates that shape finally on the work piece.

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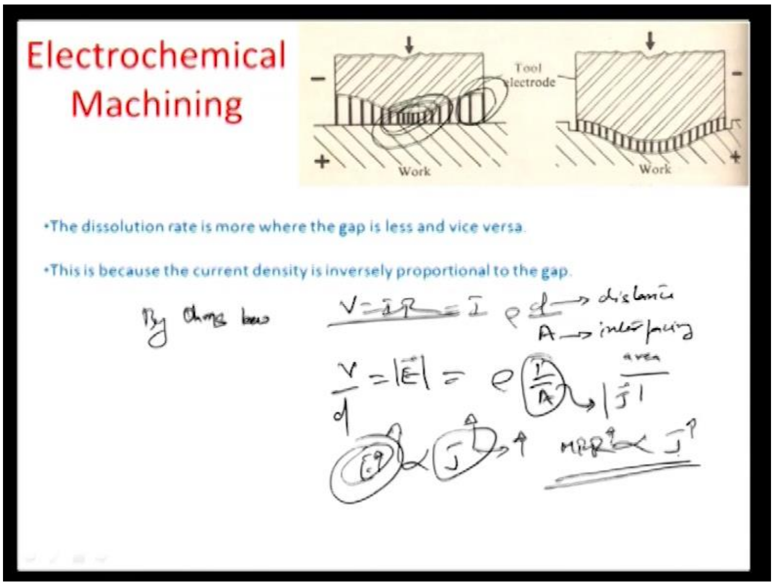

Electrochemical Machining

- The dissolution rate is more where the gap is less and vice versa.
- This is because the current density is inversely proportional to the gap.

By Ohms law $V = IR = I \rho \frac{d}{A}$

d → distance

A → interfacing area

$\frac{V}{d} = |\vec{E}| = \rho \frac{I}{A} \rightarrow |\vec{J}|$

$E \uparrow \propto J \uparrow$ $MRR \uparrow \propto J \uparrow$

So, this can be also sort of more mathematically represented by the Ohms law. So, which is actually followed here; V equal to IR, potential is current into resistance. And here, we just sort of modify this is rho d over A, where d is the distance between the 2 electrodes and A is the interfacial area between the 2 electrodes. And so therefore, we can easily find out that v by d which is nothing, but the electric field on the magnitude of the electric field is actually equal to rho times of the current density. So, this actually is the magnitude of the current density.

So, therefore, electric field is proportional to the current density, meaning thereby; that if current density is more, the electric field would be higher and vice versa. So, the current density definitely is more here in comparison to here because, you have more amount of current travelling for more amount. So, because of the increased electric field has can be seen here.

So, you have more amount of current density at the center because, the e field is high and less amount of current density at the sides because, e field or the electric field is lower. And MRR of course, as I told you before is proportional to the current density. So, therefore, if e field is high meaning thereby; the current density is high, the MRR also is high and vice versa. So, that is how electrochemical machining is really performed.

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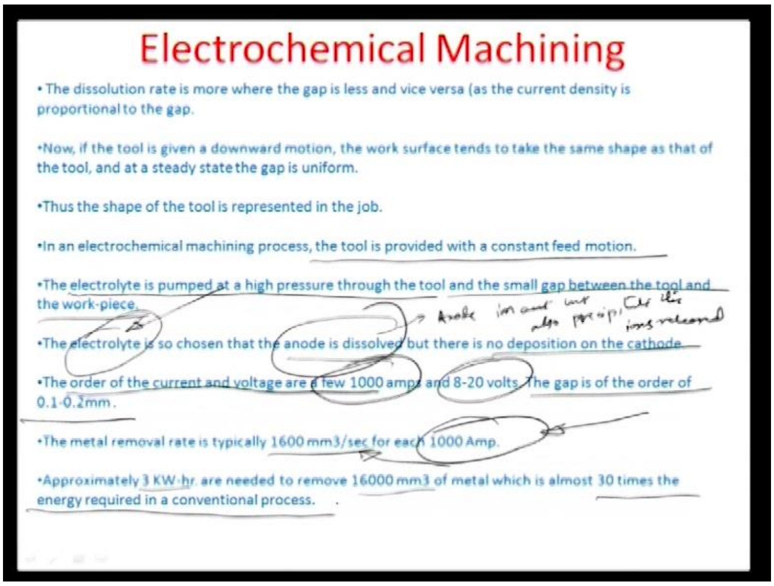

Electrochemical Machining

- The dissolution rate is more where the gap is less and vice versa (as the current density is proportional to the gap.
- Now, if the tool is given a downward motion, the work surface tends to take the same shape as that of the tool, and at a steady state the gap is uniform.
- Thus the shape of the tool is represented in the job.
- In an electrochemical machining process, the tool is provided with a constant feed motion.
- The electrolyte is pumped at a high pressure through the tool and the small gap between the tool and the work-piece.
- The electrolyte is so chosen that the anode is dissolved but there is no deposition on the cathode.
- The order of the current and voltage are a few 1000 amps and 8-20 volts. The gap is of the order of 0.1-0.2mm.
- The metal removal rate is typically 1600 mm3/sec for each 1000 Amp.
- Approximately 3 KW-hr. are needed to remove 16000 mm3 of metal which is almost 30 times the energy required in a conventional process.

→ Anode ion out but also precip. all the ions released

And that is how, you know in the dye sinking nature of the ECM comes. So, there are certain basic fundamentals about this ECM electrochemical machining process. 1 of them is that the tool is provided with a constant feed motion. And as I already mentioned before, that the whole idea is to somehow be able to precipitate, whatever comes out of the work piece of the anode. And that precipitate can be circulated outside the work zone by means of the electrolyte, which is a flowing or a moving electrolyte. That way the debri removal would mean that machining rule happens.

So, the electrolyte has to be therefore, circulated. So, it is pumped at a high pressure through the tool and the small gap between the tool in the work piece. And the electrolyte so chosen is such that, the anode is dissolved, but there is no deposition in the cathode meaning thereby; that whatever properties the electrolyte has would, let the anode ion out, but also precipitate the ions released.

So, a fundamental choice in any ECM system is, to first be able to identify what electrolyte would do that with what pair, with what paired electrode which would be the tooling ton. So, the order of current and voltage that a normally found in such processes, are a few 1000 amps current and about 8 to 20 volts, voltage in the gap of the ECM, where the ECM is conducted between the tool. And the work piece is typically about, 100 to 200 microns 0.1 to 0.1 0.2 millimeters. Typical material removal rates can be about 1600 millimeter cube per second for about 1 kilo amp current.

So, this is how highly energy, its high energy process typically. Energy density is a very high, specific energy of the material is very high. And just some other factors figures approximately 3 kilo volt hour of power are needed to remove about 16000 millimeter cube of metal and this is about 30 times the energy required in any conventional process. So, in general we, what we are seeing when we did these mechanical processes or even now in electrochemical processes is that, these nonconventional advanced machining processes are very highly energy intensive. So, the question is why do we use them?

So, the first reason the, although the processes are low yield is that, you can more accurately do surface finishing. And also, if you can somehow constrain the operations to a very small zone, you can do micromachining very wonderfully. Particularly let us say for example, the modality involved in the ECM process would make it amenable to crevices or cornets, which may not be otherwise, get machine or be able to get machine by a conventional process as such, which involves a metal to metal cutting.

So, if supposing the ship complexity of the final, you know product that you want to make is huge, somehow this nonconventional processes are really better choices over the conventional processes; even though the fact that the yield is low, even though the fact that the energy density which is needed for removing a certain volume of metal may be very high, energy required may be very high and the energy density maybe higher.

So, still do, people do use because of shape complexities, because of surface finishes. Particularly in Microsystems design sometimes, very complex shape needs to be fabricated and there is no other choice left part from some of these nonconventional ways and means of fabricating. So, that is the reason why nonconventional processes go hand in hand with manufacture of Microsystems or micro-machine systems so on so forth. So, let us look at some of the other aspects of ECM as we have already illustrated here.

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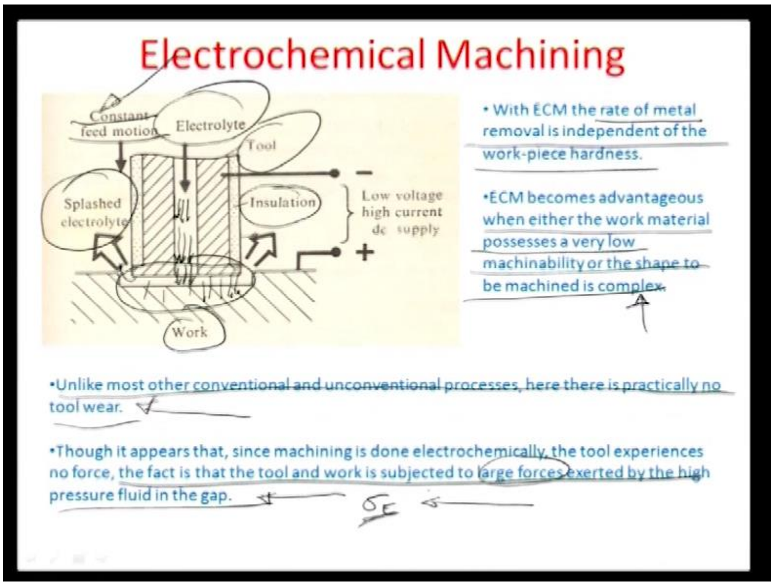

Electrochemical Machining

- With ECM the rate of metal removal is independent of the work-piece hardness.
- ECM becomes advantageous when either the work material possesses a very low machinability or the shape to be machined is complex.
- Unlike most other conventional and unconventional processes, here there is practically no tool wear.
- Though it appears that, since machining is done electrochemically, the tool experiences no force, the fact is that the tool and work is subjected to large forces exerted by the high pressure fluid in the gap.

σ_E

The electrolyte has to be flow somehow between the tool and the work piece. The best way to do that is to sort of coaxially move the electrolyte, as you can see here. This electrolyte is being move through this coaxial tool, which is actually present at the center of the tool. And there also needs to be provided some insulation at the sides of the tool, to ensure that the machining is not done sideways. The machining is only done in this vertical manner and then of course, this tool should have constraint feed motion.

So, there has to be a precise control on the feed motion of the tool and then of course, the electrolyte which is splashed, needs to be collected and circulated back into the pumping system, so that the debri which is moves along with it can also go and enter clock, the gap, the very small gap between the work piece and the tool. So, with the ECM, the advantages are that the rate of metal removal is independent of the work piece hardness.

So, the work piece may be of any hard hardness value, there is no scribing as such which is involved or there is no plowing action which is involved. So, it is not mechanical and therefore, the dissolution is really a property which is electrically dependent. You need not have a higher force, typically to remove the material which may happen in conventional processes. So, hardness does not matter here. Any kind of hardness is can be machine amenably, because the basic principle is dissolution; dissolution because of ions coming out of the surface.

So, it becomes advantageous when either the work material processes very low machinebility or the shape machine to be machined is complex. So, this I have emphasized greatly in the last slide. And unlike most other conventional and unconventional processes, here there is practically no tool wear. Although that is not true really, because sometimes great pressures get generated into this small gap here, which may be a reason for tool deformation even if not wear, but the idea is that because, there is no deposition on the tool as such or there is no change in the characteristic of the tool as such. Whatever comes out of the work piece goes into the solution and gets precipitated and this precipitate is getting carried away.

So, the tool should be left alone by enlarging by this process. And the wear of the tool is not is min cube actually. So, though it appears that since machining is done electrochemically, the tool experiences no force. The fact is; that the tool and work are subjected to large forces. And we will do some design problems later, when we will try to find out whether these forces are inconsonance with the ultimate flow stress sigma the tool side, which would give you a feasibility or non-feasibility of the process on question. So, we will do some of these design examples when we discuss this in some more details later: an electrochemical machining.

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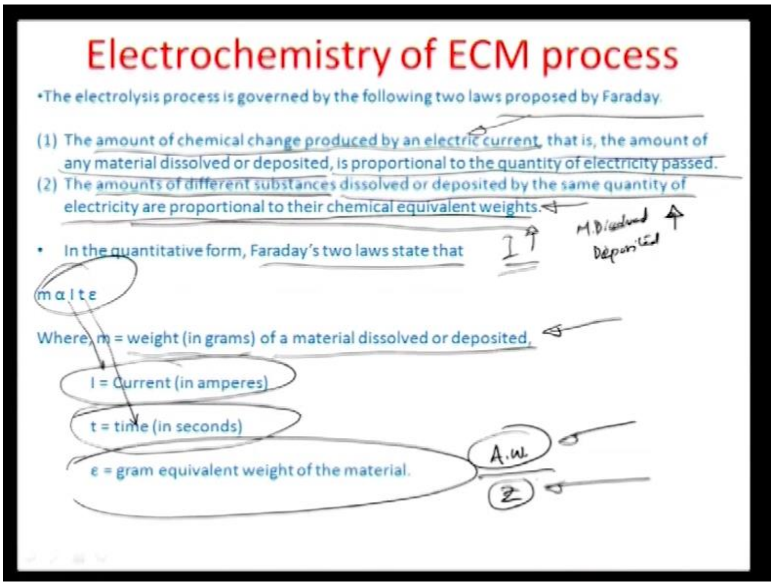

Electrochemistry of ECM process

- The electrolysis process is governed by the following two laws proposed by Faraday.

(1) The amount of chemical change produced by an electric current, that is, the amount of any material dissolved or deposited, is proportional to the quantity of electricity passed.
(2) The amounts of different substances dissolved or deposited by the same quantity of electricity are proportional to their chemical equivalent weights.

- In the quantitative form, Faraday's two laws state that

$m \propto I t \varepsilon$

Where, m = weight (in grams) of a material dissolved or deposited,

I = Current (in amperes)

t = time (in seconds)

ε = gram equivalent weight of the material.

So, let us now look at a little bit of modeling, about how you know material removal in such a ECM process electrochemical machining process, can be predicted. And so the basic theory theories which come to our mind or the basic formulations which come to our mind are the Faradays laws of electrolysis. So, let see what those 2 laws are. So, fundamentally which govern this whole machining processes this is as could as any other electrochemical business. So, the faradays laws are pretty much valid in the machining also.

So, 1: the first Faradays law says that the amount of chemical change produced by an electric current, that is the amount of any material dissolved or deposited. So, that is essentially what the current is going to do; either carryout ions or deposit ions to the electrodes, that is proportional to the quantity of electricity that is passed. So, if current is higher, current that is passed is higher, the amount of chemical change produced by the electric current will also be higher, which typically means; the material dissolved or the material deposited would also be higher.

So, that is the first law. And the second Faradays principle law of electrolysis says; that the amount of amounts of different substances dissolved or deposited by the same quantity of electricity, is proportional to their chemical equivalent weights. And this chemical equivalent weight as we will just see a little bit later is basically a function of the total atomic weight and also the function of the valiancy state in which it has to be moved.

So, if it is moving by plus 2, the chemical equivalent weight would be the atomic weight by 2 so on so forth. So, it is a function of the valiancy, at which the ion is coming out and also a function of the atomic weight. So, the amount of different substances dissolved or deposited by the same quantity of electricity are proportional to their chemical equivalent weights.

So, in quantitative form, the Faradays 2 laws can be stated here; that the mass, the weight in grams of a material dissolved or deposited is proportional to the current in amperes. So, I is from here at the time for which this current flows time in seconds and this gram equivalent epsilon weight of the material, which is actually equal to the atomic weight per unit the valiancy of the material.

So, atomic weight can be obtained from the periodic table and this valiancy states can be multifarious, there can be plus 2 plus 3 plus 1 states or maybe you know minus 1 minus 2 states. And so basically 1 has to be aware of, at what stage this is electrochemical dissolution is happening, is it a divalent association, etcetera trivalent or those kind of things have to be taken care of, while doing electrochemical machining.

So, let us actually look at the little slightly different aspect of this theory. And what I would like to now go ahead and workout is, how ions or how solutions would behave at the interface of or interfacial boundary of a solid and a solution. So, whenever there is a solid which is immersed in a solution, there is almost always the formulation of a certain layer of charges, which is also known as the dual layer of charges.

So, automatically by tendency, you know by the natural tendencies, the metal which were immersing in a solution would tried to bleed out ions and it would retain electrons, and there would be ion electron pair which is thus generated with the ion floating in the solution and the electron on the electrode. And then there is going to be a very thin layer of a dielectric, high dielectric like water is separating both these ions and electrons are not allowing them to intermingle again, once they have been liberated.

So, each ions that is formulated as a bunch of water molecules around it. And it does not let the ion go back and take the electron from the metal surface. So, it is very important to somehow see the characteristics of such ions may be positive and negative, in solution and how they are transported. And such a transport theory was for the first time proposed by you know which came as Debye hackle theory of ion transport.

So, basically we want to look into that aspect before starting with electrochemical machining, because a corollary of that which is the zeta potential of any surface, is very important for the process of electrochemical machining.

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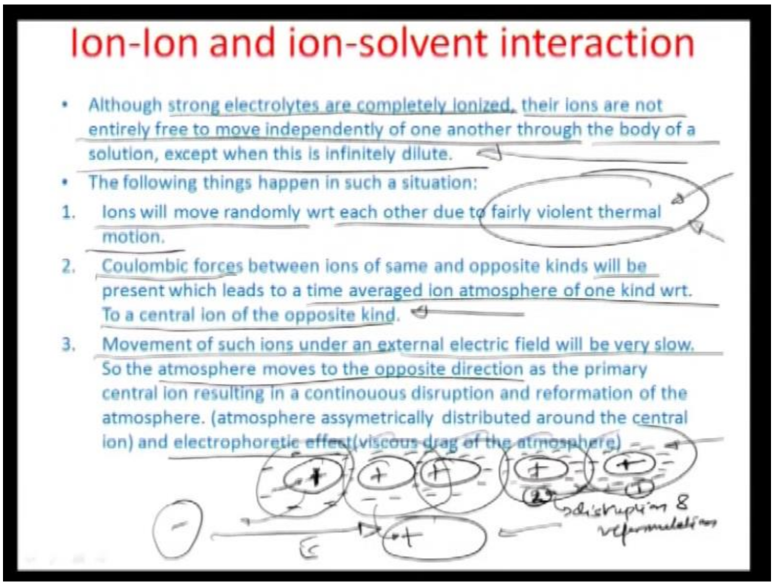

Ion-Ion and ion-solvent interaction

- Although strong electrolytes are completely ionized, their ions are not entirely free to move independently of one another through the body of a solution, except when this is infinitely dilute.
- The following things happen in such a situation:

1. Ions will move randomly wrt each other due to fairly violent thermal motion.
2. Coulombic forces between ions of same and opposite kinds will be present which leads to a time averaged ion atmosphere of one kind wrt. To a central ion of the opposite kind.
3. Movement of such ions under an external electric field will be very slow. So the atmosphere moves to the opposite direction as the primary central ion resulting in a continouous disruption and reformation of the atmosphere. (atmosphere assymetrically distributed around the central ion) and electrophoretic effect(viscous drag of the atmosphere)

So, let see what happens when strong electrolytes are completely ionized and their ions are not entirely free to move independently of 1 another, through the body of a solution, except when this is infinitely dilute. So, the following situations may happen. So, let us say there are positive ions in this and there are bunch of different negative ions. And each of this, positive ions are formulating a cloud of negative ions around it, something like this. So, these are cloud of negative ions around it.

So, the first effect that 1 can imagine intuitively that is, the ions will move randomly with respect to reach other due to fairly violent thermal motion. So, this is also the Brownian movement, that the ions would move due to their ambient thermal energy, which is a function of the temperature state, at which they are in they would actually move randomly with respect to each other. And then there are going to be columbic forces between opposite kinds of ions. Like for example, in this case it is the positive charge centers in the negative cloud around it, of negative ions around it, there are going to be columbic forces of attraction, which would lead essentially to the assembly of these charge clouds around the positive central charge systems or vice versa.

So, in this kind of leads to time averaged ion atmosphere of 1 kind, with respect to a central ion of the opposite kind. In this case it is the positive central ion and the time average atmosphere is the negative ion. And this is the distribution which will almost always happen; when you pore you know such a ion pair, or an ionic solid into dragoman by columbic forces into a solution. Like N a C l in water. So, N a plus and C l minus and then water comes in between.

So, water molecules kind of because, they are hi dielectric, they get into hence in gulf the N a plus and the C l minus. And they do not they send along them to come together. But then what can happens is because, there is an overall positive charge center in the N a plus and overall negative charge center in the C l minus there can be a assembly in a manner. So, that there is an average atmosphere of C l minus around n a plus or vice versa. So, that is what we are meaning by this columbic forces.

Then, supposing you make an external electric field applied to such a system, where this let us say is the positive side, this is the negative side. So, all the negative ions will start moving in the positive end and the positive ions of course, will start to move in the negative side. And therefore, movement of such ions under an external electric field, first of all would be very slow and the atmosphere starts moving in the opposite direction. As in this case you can see, the negative ion atmosphere moves to the positive side and the positive center ion starts moving to the opposite, that is the negative side of this field or potential, which is created by 2 electrodes.

So, therefore, there would be a continuous disruption and reformulation in the ion atmospheres with respect to the central ions. So, for example, when they start moving, these negative ions are going to get reformulated into cloud of this second positive ion right. From first positive ion it moves to the second positive ion so on so forth. So, therefore, there is an assemblage of charges, which kind of disrupted from the ionic environment of ion 1 into the ionic environment of ion 2 and vice versa and so that happens all way throughout the solution.

So, therefore, there may be many effects like electrophoretic effect, which is essentially the movement of the charges across a medium, over a potential externally applied to the system. And there can be also viscous drag of the atmosphere because; mind you these all moieties charge moieties are present in solution. So, therefore, if the positive center is moving ahead and the negative center is trying to move in the opposite direction, it is obvious that there would be viscous effects or there would be shear between the layers of the solution which is containing these ions in turn.

So, there would be viscous drag, which is associated with the forward motion of the ion through this whole so called atmosphere. So, all these parameters need to be included in a model, where we can really estimate what would happen to the layer of moiety which is formulated across a metal electrode. So, let us look at how we will be able to in a simplified manner, model such a situation in a solution. So, let us look into the formulation of this sort of ion transport equation.

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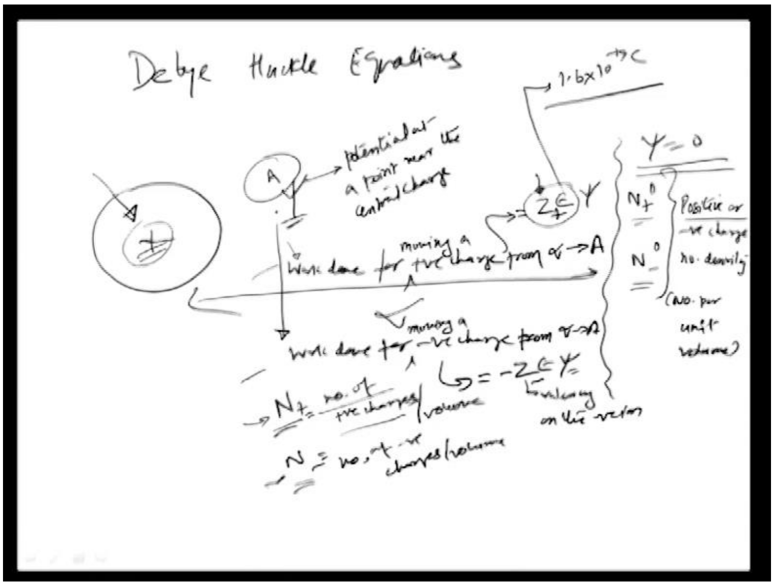

Also known as the Debye hackle equation. So, let us suppose. So, there is a positive charge and single positive charge and it has a environment made up of both positive and negative charges. And at a distance of at an infinite distance from this charge, the charge density of the positive the number density of the positive or the negative charges of, the environment of this positive charge are n plus 0 n minus 0 per unit volume right. So, this is the positive or negative charge number density, meaning thereby; number per unit volume of this ion of interest central ion of interest which is a positive charge.

So, supposing if we want to find out a point a here in the near vicinity of this positive charge the central positive charge of interest here, the amount of work that and let us say, at particular A there is existing potential psi defined by a function. So, this psi is the potential at a point near the central charge. So, the work done for a positive by the system, for let us say moving a positive charge is actually given by the charge itself. Let us say the charge is a valiancy z plus.

So, z plus times of electronic charge epsilon. This epsilon as you all know is 1.6 10 to the power of minus 19 coulomb electronic charge right. So, the total charge on the ion times, of the potential; similarly, the work done for moving a negative charge from distance infinity, where psi is 0 actually all the way to this point A. So, from for moving a positive charge from infinity to A, negative charge moving a negative charge form infinity to A, would then be given by minus z minus epsilon psi, psi is the potential at A, z minus is the valiancy on the negative ion and e of course, as you know as the electronic charge.

So, that is the amount of work which is done in case of a positive charge or negative charge, it comes from infinity to the point A close to the central ion of interest. Now, if we look at… So, therefore, there would be a possibility of h r distribution at the point A, which can now be given as N plus and N minus. And these mind you, are numbers per unit volume; number of positive charges per unit volume, number of negative charges per unit volume.

So, we are concluding here that the ion which is the central ion of interest, its assembling its own charge atmosphere around it and at a point A, a numbers are N plus and N minus of positive and negative charges per unit volume. Assuming that at point in space which is infinite distance from the central ion, the distribution of the positive and negative ions are N plus 0 and N plus N minus 0 in terms of numbers of charges per unit volume.

So, and we already know what is the work done for moving 1 charge of a certain value of a certain charge from infinity to A. So, there is a correlation which exist and I am not going into the details of that correlation between you know the numbers which are add the point A to the numbers which are far away or at infinite distance from the point A. So, that correlation actually emanates out of the Boltzmann distribution.

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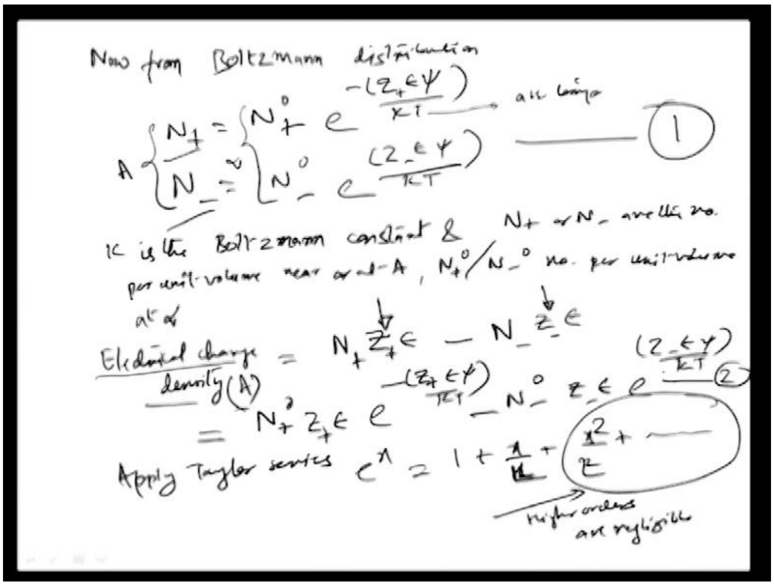

Now from Boltzmann distribution

$$A\begin{cases} N_+ = N_+^0 \, e^{\frac{-(Z_+\epsilon\psi)}{KT}} \\ N_- = N_-^0 \, e^{\frac{(Z_-\epsilon\psi)}{KT}} \end{cases} \xrightarrow{} \text{all charge} \quad \text{———} \; ①$$

∞

K is the Boltzmann constant & N+ or N- are the no. per unit volume near or at A, N_+^0/N_-^0 no. per unit volume at ∞

$$\text{Electrical charge density (A)} = N_+ Z_+ \epsilon - N_- Z_- \epsilon$$

$$= N_+^0 Z_+ \epsilon \, e^{\frac{-(Z_+\epsilon\psi)}{KT}} - N_-^0 Z_- \epsilon \, e^{\frac{(Z_-\epsilon\psi)}{KT}} \quad ②$$

Apply Taylor series $e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \text{——}$

higher orders are negligible

So, from Boltzmann distribution, the N plus 0 number density near the point A is actually equal to N plus zeroth at infinity times, of exponential to the power of minus the total amount of work which is done. So, z plus epsilon psi by K t and this is also a function of the absolute temperature, in which the system is installed. And similarly, the N minus add the point A. Mind you these are number densities at point A, these are number densities at infinity point infinity. So, N minus 0 e to the power of z minus epsilon phi psi by K t.

So, K is the Boltzmann constant and N plus or N minus are the numbers per unit volume near or at A, n plus 0 n minus 0 numbers per unit volume at infinity or at infinite distance. So, the total electrical density, the total electrical charge density near A or at A, can be given as the numbers per unit volume at A times of the amount of, charges let us assume the charge on 1 ion is z plus epsilon minus the number of negative charges per unit volume times the, value of the charge z minus e on the negative ion.

If, we substitute the values of N plus and N minus from this set of equation 1 earlier, we can get this as N plus 0 z plus epsilon times of e to the power of minus z plus epsilon psi by K t minus of N minus 0 z minus epsilon times of e to the power of z minus epsilon psi by K t. So, that is the electrical charge density at the point A. And if we just apply Taylor series here and just assume that the higher orders are negligible x square by factorial 2 plus so on so forth. And we assume that the higher orders because of the low value of x are negligible. We can write this equation number 2 in the following manner.

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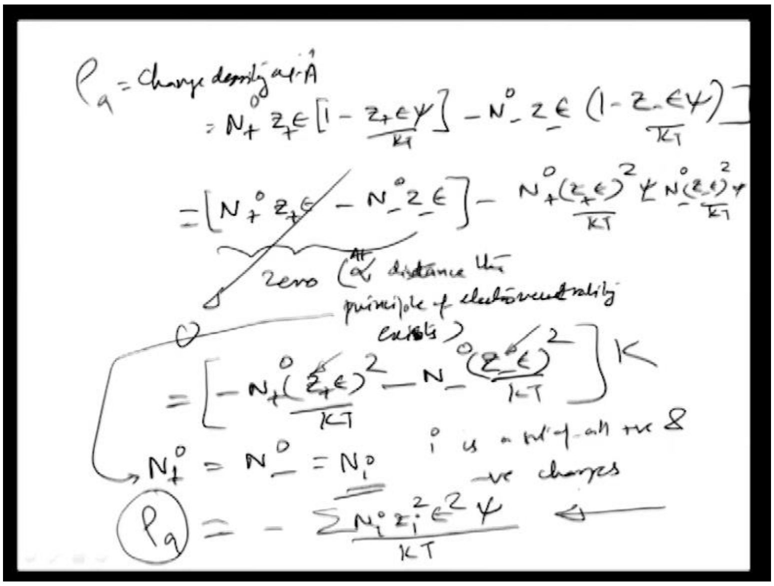

ρ_a = Charge density at A

$$= N_+^0 z_+ \epsilon \left[1 - \frac{z_+ \epsilon \psi}{KT}\right] - N_-^0 z_- \epsilon \left(1 - \frac{z_- \epsilon \psi}{KT}\right)$$

$$= \left[N_+^0 z_+ \epsilon - N_-^0 z_- \epsilon\right] - \frac{N_+^0 (z_+ \epsilon)^2 \psi}{KT} - \frac{N_-^0 (z_- \epsilon)^2 \psi}{KT}$$

zero (At ∞ distance the principle of electroneutrality exists)

0

$$= \left[-\frac{N_+^0 (z_+ \epsilon)^2}{KT} - \frac{N_-^0 (z_- \epsilon)^2}{KT}\right] K$$

$N_+^0 = N_-^0 = N_i^0$ i is a set of all +ve & -ve charges

$$\boxed{\rho_a} = -\frac{\sum N_i^0 z_i^2 \epsilon^2 \psi}{KT}$$

So, you have rho at a the overall charge density at A written as N plus 0 z plus epsilon times of 1 minus z plus epsilon psi by K t minus of N minus 0 z minus epsilon 1 minus z minus epsilon psi by K t. And therefore, this can further be written down as N plus 0 z plus epsilon minus N minus 0 z minus epsilon minus of N plus 0 z plus epsilon square psi by K t minus of N minus 0 z minus epsilon square psi by K t.

So, this of course, 0 because at infinite distance, we can assume the principle of electro neutrality to exist and this becomes 0. And so the other term, which can be taken care of is basically minus N plus 0 z plus epsilon square by K t minus N minus 0 z minus epsilon square by K t times of psi. So, if you assume that the charge density is of the positive and negative kinds are same at infinity, which is are actually the true because of again the principle of electro negativity, electro neutrality coming into existence and this we assume to be equal to let us say N i.

So, we formulate a system where i is a set of all positive and negative charges. Let us say i varying between 1 and N, meaning thereby; if it is exactly half 1 to N by 2 can be the positive charges and by 2 to N can be the negative charges so on so forth. So, therefore, we can write down this charge density equation rho a as in a very simplistic manner a sigma N i z i square. Now, I am actually getting rid of all these pluses and minuses in the subscripts and representing them by i's.

So, N i z i square call of epsilon times of potential function psi by K t. So, that is the density of the charges, the overall charges at a point A in space close to the simple ion of interest. So, we somehow need to be able to derive the potential function, which exist at A near that central ion of interest, owing to the charge density which is around it. And in the next step, what we are going to do is to utilize the Poison's equation in the space coordinates and try to find out that, at least in the CGS system; the gram centimeter second system, how this equation can be used for determining the electrical field at a point A because of the complete amount of positive and negative charges with densities N N i, where i varies between all the positive and negative charges close to the central ion of interest. So, the electrostatic potential and charge density.

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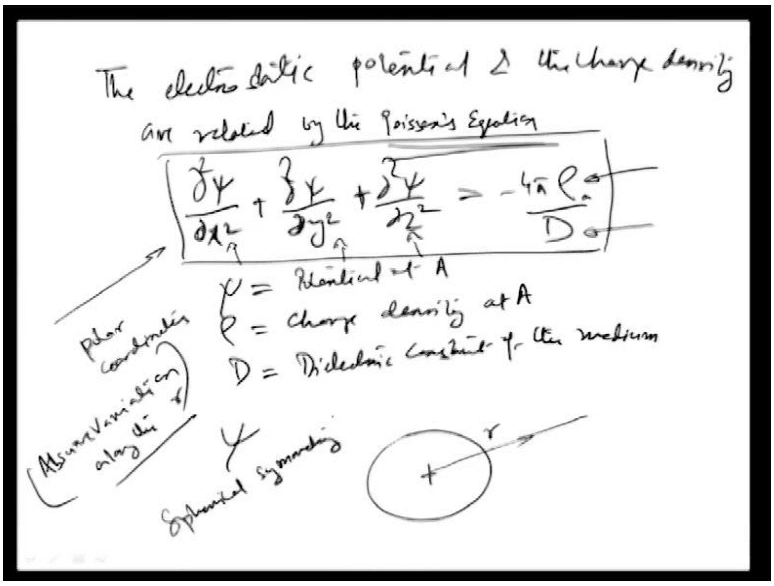

The electrostatic potential & the charge density are related by the Poisson's Equation

$$\frac{\partial\psi}{\partial x^2} + \frac{\partial\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} = -\frac{4\pi\rho}{D}$$

ψ = Potential at A

ρ = Charge density at A

D = Dielectric constant for the medium

polar coordinates

(Assume variation along the r)

ψ Spherical symmetry

Are related by the Poisson's equation as del 2 psi by del x 2 plus del 2 psi by del y 2 plus del 2 psi by del z 2, this is the special all second derivatives space derivatives and that is actually equal to minus 4 pi charge density, which is actually the charge density at a rho at a by the dielectric constant. Here psi is the potential at a rho is the charge density at a and d is the dielectric constant of the medium.

So, we want to somehow be able to solve for this equation, to find out a relationship between psi and all these other terms like: charge, density, dielectric constant and of course, this space term. So, that you know psi can come as a function of the special variation and also the variation of the charge density between different shells around the central ion of interest.

So, what we will try to do is to just use a simple conversion technique, to convert this whole you know equation into polar coordinates. So, here what we assume is because, there is a central ion and you know potential function really varies as a function of distance r from the central ion and. So, somehow we have to convert this whole equation into polar coordinates a spherical coordinates. And then assume only variation along of the radius vector r or we assume spherical symmetry. So, I am not going to go into the derivation of it, but the approach can be represented here.

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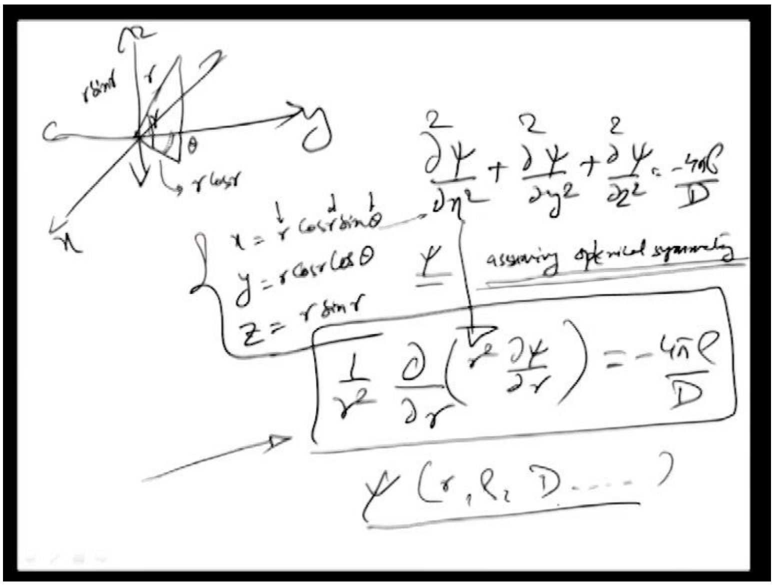

Let us say you have a cuts in coordinate system x y z and you have a radius vector here r. So, you have the first projection of the radius vector as on the x y plane. So, this can be projected by let us say an angle gamma. So, this component here is r cos gamma and this component here is r sin gamma. And then if you rotate this at an angle let us say theta. So, the x component can out come out to be r cos gamma sin theta and y component can come out to be r cos gamma sin theta r cos theta cos theta and then of course, you know that the z component is already r sin gamma.

So, if you want to change this whole form of Poisson’s equation into polar coordinates, you will have to just represent psi by differentiating with respect to r gamma and theta using the chain rule. And then assume spherical symmetry. So, the variation that you are assuming is only on an r. So, this whole equation now gets converted or changed into the form 1 by r square del by del r times of square of r times del 2 r del psi by del r and this is equal to minus 4 pi rho by d.

So, this is the spherical coordinates or you know this is the equation is spherical coordinates or polar coordinates assuming, that there is spherical symmetry and there is no variation along the angle gamma or theta. The only variation is along the radius vector r. So, we want to now be able to solve this, so that psi comes as a function of r rho dielectric constant d so on so forth. And it is very amenable for us to now, try to find out what is the work done by a charge at infinity, to come very close to the surface in question, which is actually a where the potential is psi. So, here let us try to solve this differential equation which has been obtained.

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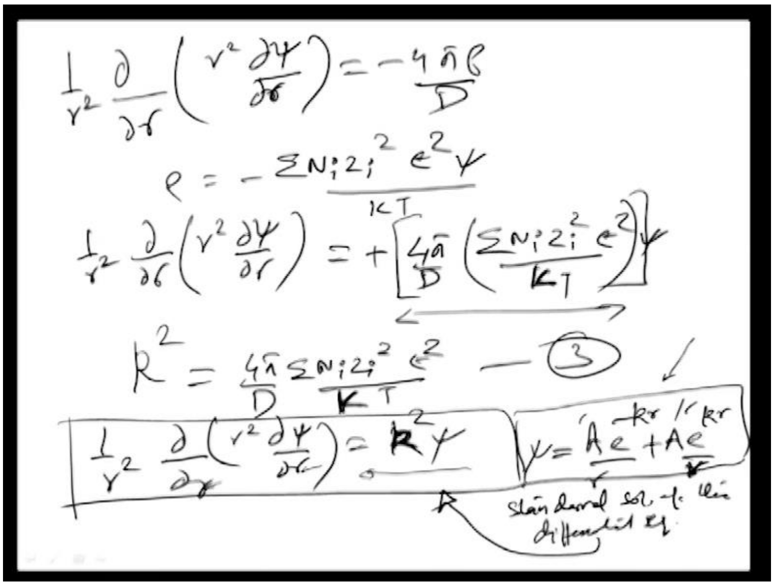

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) = -\frac{4\pi\rho}{D}$$

$$\rho = -\frac{\sum N_i z_i^2 e^2\psi}{KT}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) = +\left[\frac{4\pi}{D}\left(\frac{\sum N_i z_i^2 e^2}{KT}\right)\right]\psi$$

$$K^2 = \frac{4\pi \sum N_i z_i^2 e^2}{D\,KT} \quad — ③$$

$$\boxed{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) = K^2\psi} \qquad \boxed{\psi = A\frac{e^{-kr}}{r} + A'\frac{e^{kr}}{r}}$$

Standard sol. to this differential eq.

1 by r square del by del r times of square of r del psi by del r equal to minus 4 pi rho by d and we already know that, the rho has been illustrated before in an equation which you formulated earlier as minus N i z i square square of epsilon potential function psi by K t. So, therefore, this can be represented as 1 by r square del by del r times of or del by del r of r square del psi by del r is minus 4 pi by d and the minus goes away N i z i square epsilon square psi by K t.

So, if you want to just take this portion stand alone and consider this to be square of k, the K of course, here as you are seeing as the Boltzmann constant. So, we will not go into that with the k. So, the k square can be represented as 4 pi d sigma N i z i square epsilon square by Boltzmann constant K times of t. Let this be equation 3. And we can represent this equation 1 by r square del by del r of r square del psi by del r as square of k times of potential function psi.

So, this of course, is a standard equation with the standard solution and this also a you know general differential equation. It is not partial anymore because, only 1 variable has involved. And the solution to this standard solution to this comes out as psi equal to some constant A times of e to the power of minus k r by r plus to some constant a dash times of e to the power of k r by r. So, that is how the standard solution of this equation comes out as. So, we will take the solution and try to investigate, what these values of A and A dash r A prime r based on the boundary conditions, that are imposed to 1 to us through this problem. So, here the first condition that, we can actually think of is that.

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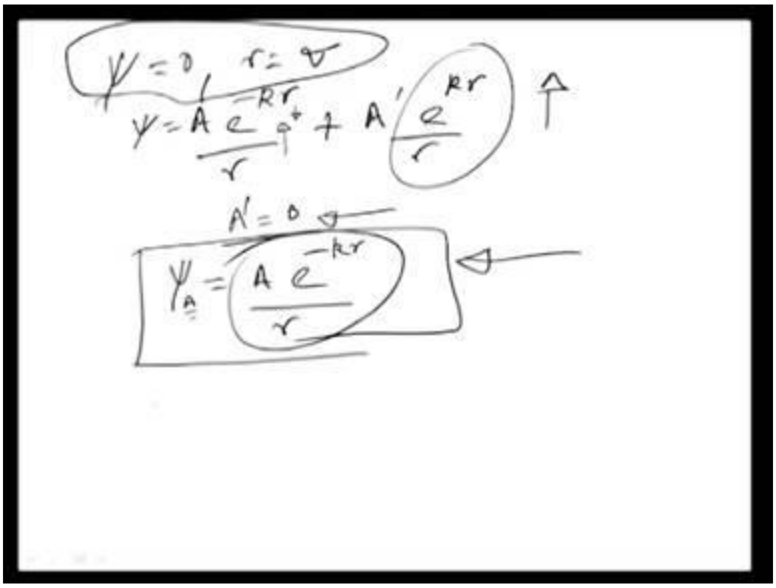

The potential function psi is actually 0 at r equal to infinity right. And therefore, so psi infinity is 0. So, if you consider psi to be equal to A e to the power of minus k r by r plus A dash e to the power of plus k r by r, meaning thereby; that if supposing this whole psi equal to 0 be true at r equal to infinity A dash automatically becomes 0, otherwise this term will you know be undefined by undefined. Of course, here because it is e to the power minus k r as r increases to infinity, this term goes very small. And so therefore, overall the equation can be 0.

So, therefore, A dash is 0 from the boundary conditions and psi becomes equal to the constant A to the power of or e to the power of minus k r by r. So, that is the solution for the potential function at A, close to the central ion of interest, which is A e to the power of minus k r by r. So, we already know that, from the previous equation, the charge density had been earlier defined.

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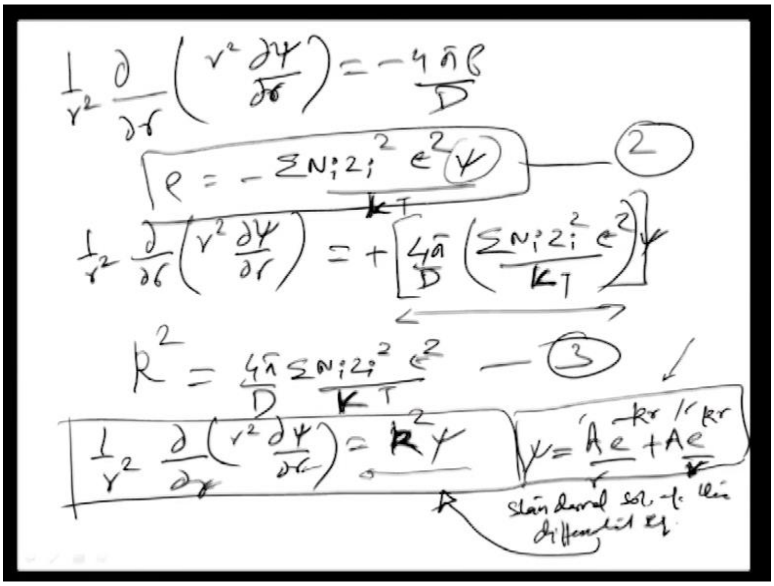

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) = -\frac{4\pi\rho}{D}$$

$$\boxed{\rho = -\frac{\Sigma N_i z_i^2 e^2 \psi}{kT}} \text{ --- } ②$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) = +\left[\frac{4\pi}{D}\left(\frac{\Sigma N_i z_i^2 e^2}{kT}\right)\right]\psi$$

$$k^2 = \frac{4\pi}{D}\frac{\Sigma N_i z_i^2 e^2}{kT} \text{ --- } ③$$

$$\boxed{\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) = k^2\psi} \quad \boxed{\psi = \frac{Ae^{-kr}}{r} + \frac{A'e^{kr}}{r}}$$

Standard sol. to the differential eq.

As a function of N i z i square epsilon square psi, the potential function by Boltzmann constant k times of t. And so we can actually substitute the value of psi that we have obtained here.

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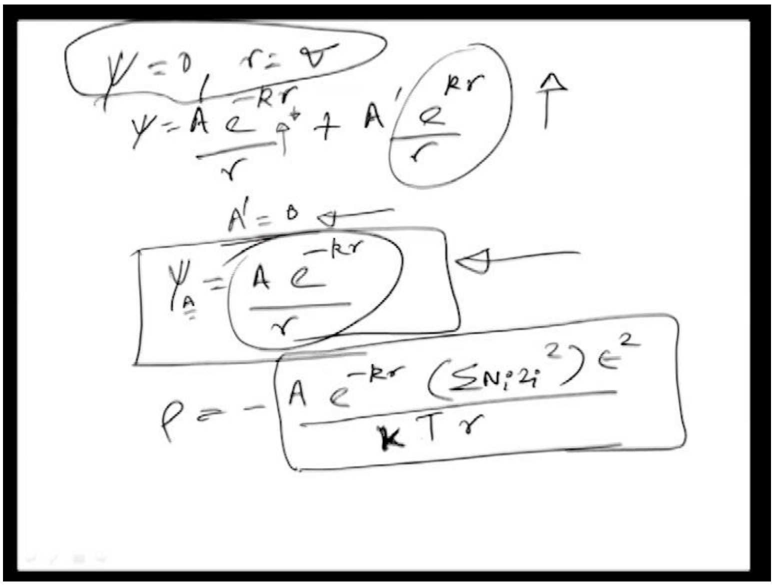

$$\boxed{\psi = 0, \quad r = \infty}$$

$$\psi = \frac{A e^{-kr}}{r} + A' \frac{e^{kr}}{r}$$

$$A' = 0$$

$$\boxed{\psi_A = \frac{A e^{-kr}}{r}}$$

$$\rho = -\boxed{\frac{A e^{-kr} \left(\Sigma N_i z_i^2\right) \epsilon^2}{k T r}}$$

To obtain the charge density at space close to that point A as minus A e to the power of minus k r sigma N i z i square epsilon square divided by Boltzmann constant k times of absolute temperature T times of r it, just a substitution. So, that is what the charge density value comes out to be. Or in other words, if we were to involve k in to picture you know that.

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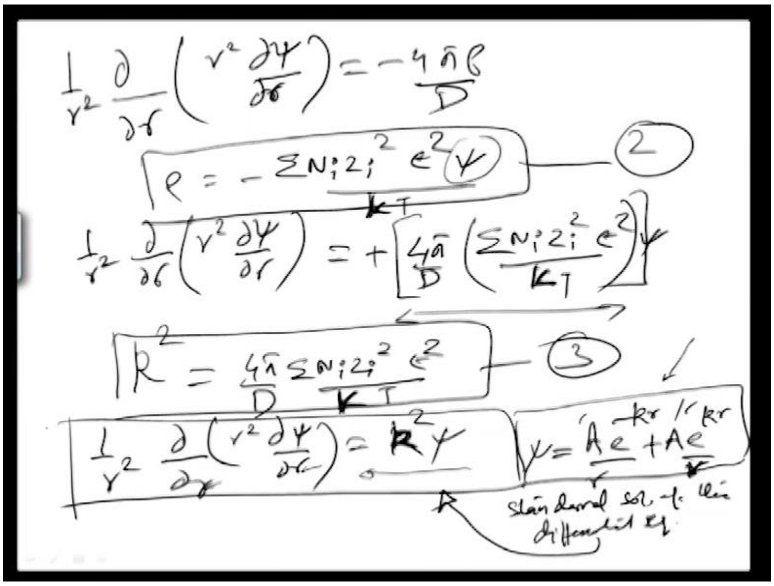

$$\frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) = -\frac{4\pi\rho}{D}$$

$$\boxed{\rho = -\frac{\Sigma N_i z_i^2 \epsilon^2 \psi}{kT}} \quad \text{(2)}$$

$$\frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) = +\left[\frac{4\pi}{D}\left(\frac{\Sigma N_i z_i^2 \epsilon^2}{kT}\right)\right]\psi$$

$$\boxed{k^2 = \frac{4\pi \Sigma N_i z_i^2 \epsilon^2}{D\, kT}} \quad \text{(3)}$$

$$\boxed{\frac{1}{r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial \psi}{\partial r}\right) = k^2 \psi} \quad \boxed{\psi = \frac{A e^{-kr}}{r} + \frac{A' e^{kr}}{r}}$$

Standard sol. of the differential eq.

k was defined by equation 3 here.

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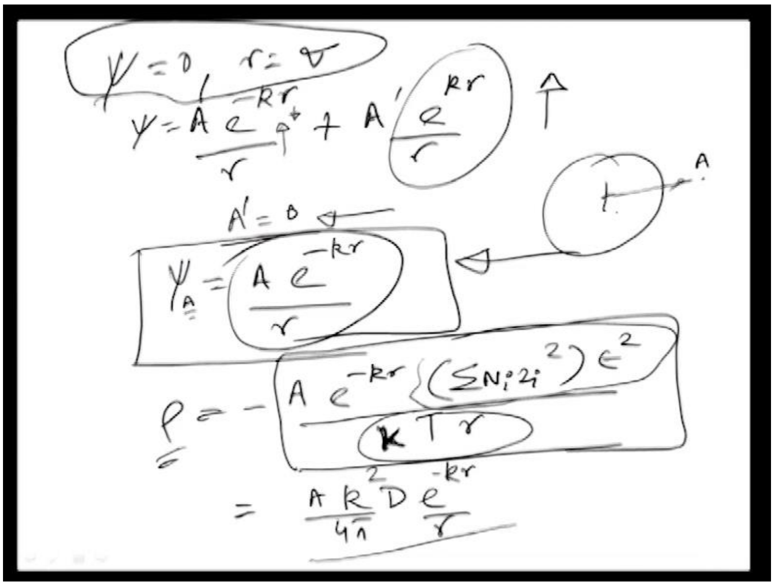

So, therefore, we can say that this whole term, can be written down as A k square by 4 pi times of D e to the power of minus k r by r. So, this way you can actually get rid of this whole complex sigma by k t r. So, that is how, the charge density would equate to close to the central ion of interest. Add a point A very close to it. We will try to now find out. So, we kind of are kindling at the end of this lecture.

But, in the next lecture, we would try to find out, what is the value of A, which we would like to investigate and finally, the potential function will come out once the value of A comes from a certain condition that, we would do in terms of principle of electro neutrality of charges, around the central ion of interest. So, with this we close today’s lecture. And we will try to solve this or take it up and solve this further in the next lecture.

Thank you.