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E-Notes

COURSENAME: PHYSICAL CHEMISTRY-I

CODE:FCH53

UNIT-IV ELECTROCHEMISTRY - I

Metallic and Electrolytic Conductors-Faraday's Laws-Electro plating Specific conductance and Equivalent conductance - Measurement of equivalent conductance - Variation of Equivalent Conductance and Specific Conductance with Dilution Kohlrausch Law and its applications - Ostwald's Dilution Law and its Limitations - Debye-Huckel's theory of Strong Electrolytes - Onsagar equation (No derivation) - Verification and Limitations Wien effect, Falkenhagen effect. Ionic Strength - Migration of ions - Ionic Mobility - Ionic Conductance - Transport Number and its determination - Hittorff's method and Moving Boundary method.Effect of Temperature and Concentration on Conductance.

Learning Objective:To impart knowledge about variation of conductivity with dilution, measurement of conductivity and concept of Transport Number and its determination.

Learning Outcome: To understand Conductors Electrochemistry and application..

ELECTROCHEMISTRY:

Electrochemistry is the study of electron movement in an oxidation or reduction reaction at a polarized electrode surface. Each analyte is oxidized or reduced at a specific potential and the current measured is proportional to concentration. This technique is a powerful methodology towards bioanalysis.

Electrochemistry-I

SpecificandEquivalentConductance

• Bothmetallicandelectrolyticconductorsobeyohm's law, Accordingtoohm's law,

$$I = \frac{E}{R}$$

WhereIis intensityofcurrent,

Eispotentialdifferent,

Ris resistance,

• Theresistance(R)ofanyconductorsisdirectlyproportionaltoitslength(*l*)andinversely proportional to uniform area of cross-section (a),

$$R \propto^{l} \frac{1}{a}$$

 $R = \frac{\rho l}{a}$

Where ρ is specific resistance (or) Resistivity obtained by 1cm length and 1cm² area of cross-section of conductor.

$$\rho = \frac{a}{l} \times R$$

When l=1 cm and a=1 cm², then

$$\rho = R$$

*ρ*isexpressedinOhm.cm

SpecificConductance(*k*):

 \circ Thereciprocalofspecificresistanceisknownasspecificconductance. It is denoted by k

$$k = \frac{1}{\rho}$$

$$k = \frac{1}{k} \text{(or)} R = \frac{1}{ka}$$

Unitofkisohm⁻¹cm^{-(or)}mhocm⁻¹

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EquivalentConductance(λ):

o Itisdefinedasthespecificconductanceandthevolumeofthesolutioncontaininggram- equivalent of electrolyte.

 $\lambda = k \times v$

Where λ is Equivalent conductance,

kisspecific conductance,

*v*isvolumeofthe solution

Itisfurtherexpressedas



WherecisNqrmalityofsolution.

Unitof λ iso $hm^{-1}cm^2gmeq^{-}(or)mhocm^2gmeq^{-1}$

Molarconductance:

• Itisdefinedasthespecificconductancemultiplebythevolumeof thesolution containing one mole of the electrolyte.

 $\mu = k \times v$

Where *µ* is molar conductance

Unitof μ isohm⁻¹cm²mol⁻(or)mhocm²mol⁻¹

Determination of Specific conductance (k) and Equivalent conductance (λ):

- 1. By measuring the resistance of the solution using **KohlrauschBridge** (wheat stone's bridge). k and λ values are determined.
- 2. The solution whose resistance to be determined taken in a conductivity cell.
- 3. The conductivity cell made with two parallel *Pt* electrodes coated with Pt –black. The distance between the two electrodes is not changed during the experiment because they are fixed in position.
- 4. The conductivity cell is connected with Kohlrauschbridge circuit
- 5. The AC current is used to overcome the emfproduced by polarisation in solution.
- 6. Afterconnectingthecell, the jackeyisadjust (between *A*&*B* point)togetapoint inwhich the minimum sound is heard.
- 7. Thelengths $l_1(AC)$ and $l_2(BC)$ are measured and following equationistaken.

$$\frac{ResistanceinCell_ResistanceintheBox}{BC}$$
Theresistanceinthecell=Resistanceinthebox×^{AC}

$$R = \frac{l_1}{EC}$$

 l_2

8. Thecellconstantisnotdeterminedprecisely, but any particular cellwould be constant is called cell constant that is measured from solution of known *k* values (*likeKCl*)

$$k = \overset{l}{\underset{a}{\times}} R$$

$$\frac{l}{a} = R \times k$$

9. If there sistance (*R*) of the solution and cell constant

areknown,the**specific**

conductance(*k*)canbecalculated.

$$k = \overset{l}{\underset{a}{\times}} R$$

10. Once knowing *k*values and concentration of the solution; the **Equivalent conductance** canbe determined.

$$\lambda = \frac{k \times 10^3}{c}$$

11. All the experiment proceed using conductivity water.

Variation of Specific conductance (k) and Equivalent conductance (λ):

- 1) In general, the conductivity of electrolyte solution is increases with dilution which is due to the number of ions are produced by dissociation of its solution.
- 2) The conductance is depended upon the number of ions insolutions othat conductivity increase with dilution.
- Ondilution,specificconductivity(k)isdecreasedwhileEquivalent(λ)andmolar(μ) conductivityisincreased.
- 4) Thespecificconductivity is reciprocal of specific resistance¹ that depends upon the number

of ions per concentration of the solution. On dilution, although the total number of ions increases, the number of ions per concentration decreases. So that *k* value decreases.

- 5) But $\lambda = k \times v$ value is increased because of decrease in k value is compensated by increasing v value on dilution. So the λ is depending on total number of ions and their mobility.
- 6) When the electrolyte solution is progressively diluted, Equivalent conductivity (λ)will be increaseduntilmaximumorlimiting value, onfurther dilutionit kept constant, this maximum or limiting conductance is known as λ_∞.
- 7) Based on variation of equivalent conductance with dilution, electrolytes are two types, they are
 - a) Strongelectrolyte
 - b) Weak electrolyte
 - a) <u>Strongelectrolyte:</u>
 - Itisfullyionised insolution,
 - Itsequivalentconductanceisrelativelysmallandeasilyreachlimitingvalue experimentally.

Ex:*OH*,*NaCl*,*KOH*,*KCl*,*HCl*,*HNO*₃,*etc*.,

- b) <u>Weakelectrolyte:</u>
 - Itisslightlyorpartiallyionizedinsolutionandbehavedifferentlywhenitis diluted.
 - Itsequivalentconductancevarywithdilution.
 - Evenatvery high dilutions their λ do not become constant.

Ex:₃*COOH*,*NH*₄*OHetc.*,

Ostwalddilutionlaw

o Itgives lawofmassactiontopartial dissociation of Arrhenius theory.

Consideraweakelectrolyte inequilibrium,

$AB \stackrel{k}{\blacksquare}$	€ A	+ B
Initial Co <u>nc</u> . c	0	0
eq. concentration $1 - \alpha$	α	α
$c(1-\alpha)$	сα	сα

Where c is concentration

 $c\alpha$ isdegree of dissociation

• Therateofreaction(or)equilibriumconstantkis

$$r \propto^{d[\frac{A^{+}][B^{-}]}{d[AB]}}$$

$$r = k^{d[\frac{A^{+}][B^{-}]}{d[AB]}}$$

$$\therefore [A^{+}] = ; [B^{-}] = c \alpha$$

$$[AB] = c(1 - \alpha)$$

$$k = \frac{[A^{+}][B^{-}]}{[AB]}$$

$$k = \frac{[A^{+}][B^{-}]}{[AB]}$$

$$k = \frac{a^{2\alpha^{2}}}{(1-\alpha)}$$

• Forweakelectrolyte \propto is very small, so(1- α) = 1

 $k = c\alpha^2$



 \circ Dissociation constant k for weak acid and base is k_a and k_b respectively

$$\alpha = \sqrt{\frac{k_a}{c}} \frac{-}{c}$$
$$\alpha = \sqrt{\frac{k_b}{c}} \frac{-}{c}$$

• Oswalddilutionlawisusefultocalculatethedissociationconstantofweakacidsandweak bases.

Limitations:

• WeakelectrolytesobeyOstwalddilutionlawbutitfailscompletelyforstrong electrolytes.

$\label{eq:experimental} Experimental verification of Oswald dilution law$

- 1. Theresistanceofvariouselectrolyteconcentrationisdeterminedbyconductometrically.
- 2. Fromthatkand λ valuesare determined

$$k = {}^{k} \times {}^{l}_{R} \operatorname{isspecific conductance taken as dissociation constant katinfinite dilution.}_{R} \lambda = {}^{k \times 10^{3}}_{c} \operatorname{is equivalent conductance taken as total concentration}(\lambda c) of electrolyte.$$

- $\label{eq:constant} 3. \ It is found that the kvalues are constant for weak electroly team disnots of or strong electroly team.$
- 4. At infinite dilution λ_{∞} values can be calculated by using Kohlrauschlaw.

$$\lambda_{\infty} = \lambda_{+} + \lambda_{-}$$

5. Therefore∝is

$$\alpha = \sqrt{k \frac{1}{c}}$$

AccordingtoKohlrauschlaw

$$\alpha = \frac{\lambda_c}{\lambda_o}$$

Debye-Huckel'stheoryofstrongelectrolyte

- 1. The equivalent conductance is decreased with increasing the concentration of weak electrolyte that is due degree of ionisation is decreased.
- 2. The above concept cannot be applied to strong electrolytes because the ions exist in their solid state.
- 3. To account for that variation, Debye and Huckel in 1923 proposed the interionic attraction theory.
 - Theyare suggested that λ is increased with dilution instrongelectrolytes is due to increase in the mobilities of ions rather than increase in the degree of ionisation.
- 4. According to their theory, each ions in solution is surrounded by oppositely charged ionic atmosphere and they are spherically and symmetrically distributed in the absence of an applied electric field.
- 5. When a potential is applied across the solution, the ions move towards oppositely charged electrodes. As a result certain effects and changes takes place in ionic atmosphere which results decrease in the speeds of the ions,
- 6. Debye-Huckelpointedoutthefollowing effects.
 - i. RelaxationeffectorAsymmetryeffect:
 - ii. Electrophoreticeffect:
 - iii. Viscouseffect:

i. RelaxationeffectorAsymmetryeffect:

- 1. The central ion and its ionic atmosphere are oppositely charged. When a central ion is positively charged the atmosphere is negative and vice-versa.
- 2. The force of attraction between central ion and its atmosphere is uniform in all directions and balanced out. Hence it retains symmetrical structure in absence of applied electric field.
- 3. But the ions get greater force behind in its than front when electricity is passed, Consequently the symmetry of atmosphere is distorted and the ions experiences a **retarding force** that is opposite direction to its motion, so that the mobility or motion of ion is slow down. This effect is known as **asymmetry effect**.



ii. Electrophoreticeffect:

- 1. The central ion as well as its atmosphere is associated with solvent molecule by solvation.
- 2. These solvent molecules carries them in opposite direction to applied field. Thus the ions are forced to move towards the respective electrodes through solvent medium results **counter current**.
- Consequently, this counter current reduce the velocity (mobility/motion) of ions. This effect is known as Electrophoretic effect.

iii. Viscouseffect:

- 1. This effect is arises from viscous drag of the solventonions mobility.
- 2. The ionstendtomove inthe direction of applied field but the electric force is opposed by the frictional viscous drag exerted by the solvent.
- 3. Stokeslawgivesthe frictionalviscousdragvaluesis

 $f = 6\pi a\eta v$

Where *f* is frictional force

aisradius of the ion

 η is viscous coefficient of solvent

visvelocityoftheion

OnsagarEquation

1. Onsagartookintoconsiderationthethreeeffects(asymmetry,electrophoreticandviscous effects)

- 2. And He derived an quation for the concentration dependent of the equivalent conductance in dilute solution.
- 3. Forauni-univalent electrolyte, the equation is

$$\sum_{c} \lambda = \lambda - \left[\frac{82.42}{(DT)^{1/2} \eta} + \frac{8.204 \times 10^5}{(DT)^{3/5}} \lambda \right] c_{\infty} \sqrt{2}$$

Where Disdielectric constant of the medium,

 η isviscositycoefficientofthe medium,

Tisabsolutetemperature,

cisconcentrationinequivalentsperlitre.

Significance:

- 1) TheOnsagarequationaccountsforthedifferencebetween λ_c and λ_{∞} .
- 2) itisevidentthat $\lambda_c < \lambda_{\infty}$. This is due to electrophoretic effect and a symmetry effect.
- 3) The first term in the bracket gives electrophoretic effect value and the second term gives asymmetry effect.
- 4) For a given solvent and a tagiven temperature, the above equation may be written as,

 $\lambda_c = \lambda_\infty - [A + B\lambda_\infty] \sqrt{ccc}$

Where *A* and *B* are constants for a given solvent and dependon viscosity and dielectric constant of the solvent.

- 5) The Onsagar equation is verified by plotting a graph with λ against \sqrt{c} the extrapolation gives λ_{∞} is compared with λ_{∞} value obtained by equation.
- 6) It gives best resultatlow concentrations but fails at more concentrated solutions.



7) At infinite dilutions, the second term on the right hand side of the equation becomes negligible and λ_c approaches λ_{∞}

Limitations:

- 1) It gives good results for dilutes olutions of uni-univalent electrolytes.
- Butitfailswhenappliedtoconcentratedsolution(C>0.01M)andpolyvalent electrolytes solution.

KOHLRAUSCHLAWANDITSAPPLICATIONS

Kohlrauschlaw:

- 1) Kohlrausch investigated the λ_{∞} values for various electrolytes and find out an interesting relationship amongst these values.
- He concluded that each ion contributes a definite value to the total conductivity of the electrolyte at infinite dilution and this value is independent to the other ion present in the solution.
- 3) Hestates, the independent migration of ions is

"The equivalent conductivity of an electroly teat infinite dilution is the sum of both cation and an ion".

$$\lambda_{\infty} = \lambda_c + \lambda_a$$

ApplicationofKohlrauschlaw:

- 1) Calculation of λ_{∞} values for weak electrolytes:
 - i. λ Value of a weak electrolyte does not become constant even at very high dilutions. Therefore it is not possible to determine the λ_{∞} values.
 - ii. ButKohlrauschlawhelpstocalculate λ_{∞} values by indirect method.
 - iii. Suppose we have to find out the λ_{∞} for a ceticacid, the equivalent conductivities of *CH*₃*COONa*, *Cl*, and *HCl* are determined at infinite dilution. It is possible because these are strong electrolytes.
 - iv. From these values, the λ_{∞} for CH_3COOH can be calculated. $\lambda_{\infty}CH_3COOH = \lambda_{\infty}CH_3COONa - \lambda_{\infty}NaCl - \lambda_{\infty}HCl$

AccordingtoKohlrauschlaw,

$$\lambda_{\infty} CH_{3}COOH = \lambda_{\infty} CH_{3}COO + \lambda_{\infty} Na - \lambda_{\infty} Na - \lambda_{\infty} CI - \lambda_{\infty} H + \lambda_{\infty} CI$$
$$\lambda_{\infty} CH_{3}COOH = \lambda_{\infty} CH_{3}COO + \lambda_{\infty} H$$

2) Calculation of degree of dissociation and dissociation constant of weak electrolytes:

i. The degree of dissociation of weak electroly te is given by

$$\alpha = rac{\lambda_c}{\lambda_\infty}$$

- ii. λ_c is equivalent conductance at a given concentration which is determined experimentally.
- iii. λ_{∞} is equivalent conductance at infinite dilution that can be calculated using Kohlrausch law. $\lambda_{\infty} = \lambda_c + \lambda_a$
- iv. Similarly α values for various concentrations of electrolyte is determined, the α values and corresponding cvalues are substituted in the Ostwald's dilution law equation.

$$k = \frac{C\alpha^2}{(1-\alpha)}$$

fromabove expression, the degree of dissociation and dissociation constant of a weak electrolyte can be calculated with help of kohlrausch law.

3) Calculationofionicconductances:

By combiningKohlrauschlawandthetransportnumbermeasurementresults, it is possible to calculate the ionic conductance values using the following equations,

$$\lambda c = n c \lambda_{\infty}$$

$$\lambda_c = n_a \lambda_\infty$$

Theionicconductanceis veryusefultocalculatethefollowing

- i. Calculating λ_{∞} for weak electrolytes
- ii. Calculatingabsolutevelocityofionswhichisrelated withionic conductance as Absolute ionic velocity = $\frac{Ionic conductance}{Ionic conductance}$

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iii. TocalculateionicproductofH₂O

iv. SolubilityofSparinglysolublesaltscanbedetermined.

Migrationofions-ionicmobility

Migration of ions:

- Whencurrentpassedthrough the electroly tesolution, the ions moves towards oppositely charge electrodes is known as **Migration of ions**.
- Duringthismigration
 - Ionsmovingatdifferent speed
 - Butamountofions(cation&anion)dischargedatelectrodesare equivalent.
 - Changesinconcentrationaroundtheelectrodeisalsodifferent.

Experiment:



1) Utube is filled with agar-agar KCl dilutes olution and small phenolph thale in

2) Adropof dil. HCl and NaOH is added in left and right sideres pectively (a).

- 3) Sothat leftsideiscolourlessandrightsideispink colour.
- 4) The Utube is cooled inice-bath for few minutes to set agar-agarlike jelly.
- 5) $HClandCuCl_{2}$ solution is added on right side and NaOH on left side (b).
- 6) Currentispassed byinserting metalelectrodesateachside.
- 7) The*H*+and Cu^{2} +ions movetowardsleft sidethat is indicated by **disappearanceofpink by** *H*+ions and formation of blue colour by Cu^{2} +ions.
- 8) While *OH*⁻movestowardsrights ide that is indicated by appearance of pink colour on left side.

Ionicmobility

• Itisdefinedasthe**distancetravelledbyanion**persecondunder**1Voltpotentialgradient** per cm.

Potentialgradient=potentialdifferentappliedattheelectrodes distancebetweenthetwoelectrodes.

In mathematics

 \therefore AbsoluteionicvelocityorIonicmobilityis=

Determinationofionicmobility:



1) Itcanbeexplainbymovingboundary

2) If needtodeterminetheionicmobility of K^+ ion,twoelectrolyteKCl(principleelectrolyte)and $CdCl_2$ (indicatorelectrolyte)areused.

3) *KCl*is placed over*CdCl*₂both having decinormal solution, it is taken in tube of uniform holes contains two electrodes.

4) If current is passed through the solution, K⁺ ionsmovestowardscathode followedby Cd²⁺ionssothat

theboundarymovesupward.

5) Letboundarymoveadistancex cmintime(t)secatappliedelectricalfield(E)voltcm⁻¹.

 \therefore ThemobilityofK⁺ionisgivenby

$$\int_{+}^{+} U = \frac{x}{t \times E} \operatorname{cm}^{2} V^{-1} \operatorname{s}^{-1}$$

TransportNumberanditsdetermination Transport

Number:

- 1) From the **Hittorff's discussion**, the number of ions discharged at electrodes depends onsum of the ionic mobility of the ions (+Ve& Ve)
- 2) Accordingtofaraday'sllaw, the number of ions discharged at electrodes are proportional to the quantity of current passed through the solution.

÷	the Quantity of current pass through thesolution }	∝ sumofthe mobilityofions	sumof mobility	
. .	the Quantity of current carried out bya particular ion }	$\propto \frac{mobility of that}{particularion}$	obilityofth articulario	

"Thefractionoftotalcurrentcarriedbyeachioniscalledthetransport number."

Let U+andU-be themobility of cation and an ion respectively.

t+andt-istransportnumberofcationandanionrespectively

Therefore,

Transportnumberofcationis=

currrentcarriedbycation totalcurrent

 $t_+ = \frac{U_+}{U_+ + U_-}$

Similarly,

$$t_{-} = \frac{U_{-}}{U_{+}+U_{-}}$$

Further,

$$t_{+}+t_{-}=1$$

Determinationoftransportnumber(Hittorffmethod) Principle:

 Thefallofconcentrationaroundtheelectrodesisproportionaltothevelocity(or mobility) of the ion that moves a way from it.

 $\begin{array}{l} \underbrace{Mobility of cation \cup_{+}}_{fall of con. around an ode} \\ \underbrace{Mobility of an ion \cup_{-}}_{fall of con. around cathode} \\ \\ \underbrace{transport number}_{of cation} \} t_{+} = \underbrace{\underbrace{\cup_{+}}_{\cup_{+} + \cup_{-}}}_{fall of con. around an ode} \\ = \underbrace{fall of con. around an ode}_{[fall of con. around an ode]} \\ = \underbrace{fall of con. around an ode}_{total fall of concentration} \end{array}$

2) If the concentration is measured in terms of grame quivalent then,

$$t_{+} = \frac{No.ofgm.eq.lostinanodecompartment}{totalno.ofgm.eq.lostinbothcompartments}$$

 But,totalno.ofgramequivalentlostatbothcompartmentsisequaltotheno.ofgram equivalents deposited on each electrode,

 $t_{+} = \frac{No.ofgm.eq.lostinanodecompartment}{No.ofgm.eq.depositedoneachelectrode}$

 According to Faraday's II law, the no. of gram equivalents deposited on each electrodeis equal to the no. of gram equivalents of copper deposited in copper coulometer for the same quantity of current.

$$:t_{+} = \frac{No.ofgm.eq.lostinanodecompartment}{No.ofgm.eq.ofcopperdepositedincoulometer}$$

Experiment:

1. Hittorff's apparatus consist of two vertical glass tubejoined togetherby using U type of tube, in order to avoid mixing of two solution (cathode & anode)



- 2. The anode compartment is filled with known concentration of $AgNO_3$ (electrolyte) with Agelectrode (actas an anode) connected with battery, ammeter rheostat.
- 3. The cathode compartment is connected with coulometer (actasa cathode)

4. A current of 0.01 to 0.02 ampere is passed through the circuit for 3-4hr. so that the solution from the anode and cathode compartments are run into separate flasks and analysed and also weigh of coulometer is calculated.

Movingboundary method:

- 1. In this method, the migration of ions in an electric field is directly observed and more precious.
- 2. Let us consider the determination of transport number of H^+ ions in HCl
- 3. The apparatus consist of long vertical tube filled with $HClandCdCl_2$
- 4. The concentration of *HCl* should be higher than that of *CdCl* solution so that the *HCl* solution floats over *CdCl* solution.
- 5. *HCl*istheprincipalelectrolyte, $CdCl_2$ is the indicator electrode that for masharp boundary between two solutions, because of Cd^2 + is less immiscible than that of H^+

Indicatorelectrolyteisselectedbasedonfollowingfacts

- The cation inits hould not move faster than that the cation whose transport number is to be determined.
- o Itshouldhavethesameanionasintheprincipalelectrolyte.



- 6. APtcathodedipped at top and*Cd*anodeat bottom.
- 7. A small currentis passed through the conductivity cell, +ionsmove towards cathode followed by Cd^{2+} ions. The boundary also moves upwards.

 ${\it Let} {\it l} is the distance moves by boundary in {\it cm}$

Aisarea ofcrosssectionoftubeincm

$.: The volume of the liquid that moved up is = lAcm^3$

LetconcentrationofHCliscingm. Equ/litre

 $\therefore \text{No.ofgm.equi.ofH}^+\text{ions}_{\text{carredtowardscathodeis}} = \frac{lAC}{1000}$

Onegramequivalentcarries1faradayelectricity,

$$::\frac{lAC10}{00}$$
 gmequicarries $\frac{lAC}{1000}$ faraday

Thetotalquantiyofcurrent measuredbycoulometeris }=Qfaraday

 $\therefore t_{H^+} = \frac{Current carried by H^+ ions}{Total current passed}$



PRACTICE QUESTIONS:

- 1. Define Metallic and Electrolytic Conductors
- 2. Explain Kohlrausch Law and its applications
- 3. Discuss about Ostwald's Dilution Law and its Limitations
- 4. Explain Ionic Mobility and Ionic Conductance -
- 5.Discuss about Debye-Huckel's theory of Strong Electrolytes

Reference Books :

1. Principles of Physical Chemistry - B. R. Puri, Sharma and Madan S. Pathania, 78 Vishnal Publishing Co., - 2013.

2. Text Book of Physical Chemistry - P. L. Soni, O. P. Dharmarha and U. N Dash - Sultan Chand & Co., - 2006.

- 3. Physical Chemistry Negi and Anand Eastern Wiley Pvt.Ltd..
- 4. Physical Chemistry Negi and Anand Eastern Wiley Pvt.Ltd..
- 5. Physical Chemistry Kundu and Jain S. Chand & Co.

Web source :

- 1. <u>https://www.pdfdrive.com/modern-electrochemistry-e34333229.</u>
- 2. http://xrayweb.chem.ou.edu/notes/symmetry.html.
- 3. http://www.uptti.ac.in/classroom-content/data/unit%20cell.pdf.