Unit 3

Electrochemistry

One mark questions

1. ***What is an electrolyte?***

   An electrolyte is a compound which conducts electricity either in its aqueous solution or in its molten state.

   e.g Acids HCl, CH_3COOH, HNO_3

   Bases NaOH, NH_4OH

   Salts $CuSO_4$, NaCl etc

2. ***Define conductivity of an electrolytic solution.***

   Conductivity of a solution of an electrolyte is the conductance of a solution placed between two electrodes each of one square meter area kept at a distance of 1 meter apart.

3. ***Write the S.I unit for conductivity.***

   SI unit for conductivity is Sm^{-1}.

4. ***Give the S.I unit for molar conductivity.***

   $Sm^2\ mol^{-1}$

5. ***State Kohlrausch Law.***

   The limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte.

6. ***Define electrode potential.***

   The potential difference developed between the electrode (metal) and the electrolyte (solution containing its own ions) when both the metal and the solution are in equilibrium is called electrode potential.

7. ***Define standard electrode potential.***

   Standard electrode potential is the electrode potential when the concentrations of all the species involved is unity (1M) and if a gas is involved its pressure should be 1 bar.

8. **Write Nernst Equation.**

$$E_{(M^{n+}/M)} = E^{o}_{(M^{n+}/M)} - \frac{0.059}{n} \log_{10} \frac{1}{[M^{n+}]}$$

9. ***State Faradays second law of electrolysis.***

   The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights.

10. ***Define cell potential.***
Cell potential is the potential difference between the two electrodes of the galvanic cell.

11. ***Define EMF of the cell.***
It is the difference between the electrode potential of the cathode and anode when no current is drawn through the cell.

12. ***What is Fuel cell?***
Galvanic cells that are designed to convert the energy of combustion of fuels like hydrogen, methane etc directly into electrical energy are called fuel cells.

13. ***Give a method to prevent rusting.***
Rusting may be prevented by barrier protection like painting, metal plating etc.

14. ***Write the relationship between cell potential and Gibb's energy***

$$\Delta_r G^o = -nFE^o{}_{cell}$$

15. ***Write the relationship between equilibrium constant and E^o_{cell}***

$$E^o{}_{cell} = \frac{0.059V}{n} \log K_c$$

2 mark questions

1. ***What are redox reactions? Give an example.***
Reactions in which both oxidation and reduction taken place simultaneously are called redox reactions.
e.g $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$
In this Zn is oxidised to Zn^{2+} Cu^{2+} is reduced to Cu

2. ***Mention any two factors on which the conductivity of an electronic conductor depends.***
The electronic conductance depends on
(i) The nature and structure of the metal
(ii) The number of valence electrons per atom.
(iii) Temperature (it decreases with increase in the temperature) (any two)

3. ***Mention any two factors on which the conductivity of an electrolytic conductor depends.***
The conductivity of electrolytic solution depends upon
(i) The nature of the electrolyte
(ii) Size of the ions produced and their solvation.
(iv) The nature of the solvent and its viscosity.
(iv) Concentration of the electrolyte and
(v) Temperature (increases with increase in temperature (any two)

4. ***Give two difference between the conductivity of an electronic conductor and electrolytic conductor.***

   1. On passing direct current composition of electronic conductor does not change but that of electrolytic conductor changes.
   2. On increasing the temperature in case of electronic conductor conductivity decreases in case of electrolytic conductor conductivity increases.

5. ***What is a strong electrolyte? Give an example.***
   A strong electrolyte is an electrolyte that dissociates completely into ions at moderate concentrations of its aqueous solution
   Ex: acids HCl, H_2SO_4, HNO_3
   Base NaOH, KOH
   Salts NaCl, $CuSO_4$ (any salt)

6. ***What is a weak electrolyte? Give an example.***
   A weak electrolyte is an electrolyte that dissociates partially into ions in its aqueous solution.
   Ex: CH_3COOH, NH_4OH

7. ***Define molar conductivity. How is it related to conductivity?***
   Molar conductivity of a solution at a given concentration is the conductance of the volume V of a solution containing one mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length.
   It is represented by λ_m

λ_m = kv where k is conductivity and v is volume of the solution containing 1 mole of the electrolyte

or

If λ_m is in Sm^2mol^{-1} and k in Sm^{-1}

$$\lambda_m = \frac{k}{1000C}$$ where C is conc. in mol L^{-1}

or

When λ_m is in S cm^2mol^{-1} and k is in Scm^{-1}

$$\lambda_m = \frac{1000k}{C}$$

8. ***How does conductivity of a solution change with change in concentration of the solution? Give reason.***

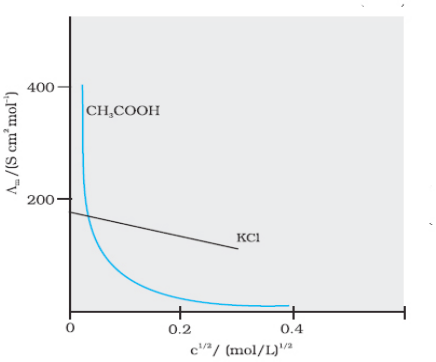
   Conductivity of a solution decreases with decrease in concentration of the solution due to decrease in the number of ions per unit volume of the solution.

9. ***Define limiting molar conductivity. Write the relationship between molar conductivity and limiting molar conductivity.***

   Limiting molar conductivity is the molar conductivity of a solution when concentration approaches zero or molar conductivity at infinite dilution.

   $\lambda_m = \lambda^o_m - AC^{\frac{1}{2}}$ **where λ_m is molar conductivity and λ^o_m is limiting molar conductivity, C is concentration in mole/L and A is constant which depends on nature of the electrolyte, solvent and temperature.**

10. ***Draw a graph of molar conductivity verses square root of the molar concentration for KCl and CH_3COOH mentioning clearly each.***



11. ***How is limiting molar conductivity for a strong electrolyte found out by extrapolation method?***

    Prepare four solutions of given strong electrolyte of different concentrations. Measure the conductivities of each solutions using conductivity cell and calculate the molar conductivities of each solution. Plot a graph of molar conductivity verses square root of the molar concentration for these solutions. A straight line is obtained which is to be extrapolated back so as to touch the vertical axes .This point of intersection on the vertical axes gives the limiting molar conductivity.

12. ***State and illustrate Faradays first law of electrolysis.***

    The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte either through its aqueous solution or molten state.

    If w is the mass of the substance deposited and Q is the current passed in coulombs

    $w \propto Q$

    But $Q = I\,t$ where I is the current strength in ampere and t is time in seconds.

13. ***Conductivity of 0.01 M NaCl solution is 0.12 Sm^{-1}. Calculate its molar conductivity.***

$$\lambda_m = \frac{k}{1000C} = \frac{0.12}{1000 \times 0.01} = 1.2 \times 10^{-2}\, Sm^2 / mol$$

14. ***The molar conductivity of 0.1M nitric acid is 630 S cm^2 /mol. Calculate its conductivity.***

$$\lambda_m = \frac{1000k}{C}$$
$$630 = \frac{1000k}{0.1}$$
$$\therefore k = \frac{630 \times 0.1}{1000} = 0.063\ Scm^{-1}$$

15. ***A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of nickel is deposited at the cathode? (Mol mass of Ni = 58.7)***

Q = I t

= 5×20×60 = 6000C

$$Ni^{2+} + 2e^- \longrightarrow Ni$$
$$2 \times 96500C \qquad 58.7g$$
$$193000C$$

For 193000C of electricity mass of nickel obtained = 58.7g

For 6000C of electricity $\frac{6000 \times 58.7}{193000} = 1.812g$

16. ***How long it will take for the deposition of 0.2g of silver when silver nitrate solution is electrolysed using 0.5 ampere of current (Mol mass of Ag = 108)***

$$Ag^+ + e^- \longrightarrow Ag$$
$$96500C \quad 108g$$

For 108g of silver to be deposited current required is 96500C.

For 0.2g of Ag

But Q = I t $\frac{0.2 \times 96500}{108} = 178.7C = Q$

$$t = \frac{Q}{I} = \frac{178.7}{0.5} = 357.4\ se$$

17. ***The cell in which the following reaction occurs*** $2Fe^{3+}_{(aq)} + 2I^-_{(aq)} \longrightarrow 2Fe^{2+}_{(aq)} + I_{2(s)}$ ***Has E^o_{cell} = 0.236V at 298K. Calculate the standard Gibb's energy and the equilibrium constant for the cell reaction.***

n = 2

$\Delta.G^o$ = -nFE^o

= - 2×96500×0.236

= - 45548 J

$$E_{cell} = \frac{0.059}{n} \log K$$

$$0.236 = \frac{0.059}{2}\log K$$

$$\log K = \frac{2 \times 0.236}{0.059} = 8$$

Taking the antilog K = 10^8

18. ***Write the reaction taking place at cathode and anode when aqueous solution of copper sulphate is electrolysed using copper electrodes.***

$$At\ \textbf{anode}\ \ Cu_{(s)} \xrightarrow{oxdn} Cu^{2+}{}_{(aq)} + 2e^-$$

$$At\ \textbf{cathode}\ \ Cu^{2+}{}_{(aq)} + 2e^- \xrightarrow{redn} Cu_{(s)}$$

Thus copper from anode dissolves and an equivalent amount of pure copper is deposited on cathode. This technique is used in electrolytic refining of crude copper.

19. ***Write the reaction taking place at anode and cathode when molten NaCl is electrolysed.***

When molten sodium chloride is electrolysed using inert electrodes

$$At\ \textbf{anode}\ 2Cl^- \xrightarrow{oxdn} Cl_2 + 2e^-$$

$$At\ cathode\ Na^+ + e^- \xrightarrow{redn} Na$$

Thus chlorine gas is liberated at anode and Sodium metal is formed at cathode.

20. ***Write the reaction taking place when aqueous solution of NaCl is electrolysed.***

When aqueous solution of NaCl is electrolysed,

$$NaCl \longrightarrow Na^+ + Cl^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

The reaction taking place at cathode is

$$H^+{}_{aq} + e^- \longrightarrow \frac{1}{2}H_{2(g)}$$

The reaction taking place at anode is

$$Cl^-{}_{aq} \longrightarrow \frac{1}{2}Cl_{2\,aq} + e^-$$

21. ***What is a primary battery/cell ?Give an example.***

Primary battery is one in which reaction occurs only once and cannot be recharged. Eg Dry cell or Leclanche cell and Mercury cell

22. ***What is a secondary battery/cell ? Give an example.***

Secondary battery is one which can be recharged by passing current through it in opposite direction,so that it can be Reused.

Eg: Lead storage battery and Nickel cadmium cell.

23. ***E^o_{Cu} = +0.34V and E^o_{Zn} =-0.76V. Daniel cell is obtained by coupling these two electrodes.***
(i) represent the cell symbolically
(ii) calculate the EMF of the cell

(i) Daniel cell can be represented as

$$Zn/\ Zn^{2+}{}_{(aq)} \,||\, Cu^{2+}{}_{(aq)}/Cu$$

(ii) EMF of Daniel cell E^o cell = $E^o_R - E^o_L$

$= E^o_{Cu} - E^o_{Zn} = 0.34-(-0.76)$

$= 1.10V$

24. Calculate the molar conductivity of a solution of $MgCl_2$ at infinite dilution given that the molar ionic conductivities of $\lambda^o_{(Mg^{2+})} = 106.1\ Scm^2 mol^{-1}$ and $\lambda^o_{(Cl^-)} = 76.3\ Scm^2 mol^{-1}$

$$\lambda^o_{MgCl_2} = \lambda^o_{Mg^{2+}} + 2\lambda^o_{Cl^-}$$
$$= 106.1 + 2(\ 76.3)$$
$$= 258.7\ Scm^2 mol^{-1}$$

25. The resistance of a conductivity cell containing 0.001 M KCl solution at 298K is 1500Ω. What is the cell constant if the conductivity of 0.001M KCl solution at 298K is $0.146\times10^{-3}\ Scm^{-1}$?

Cell constant G*= Rk

=resistance × conductivity

$=0.146\times10^{-3}\ Scm^{-1}\times1500S^{-1}$

$= 0.219\ cm^{-1}$

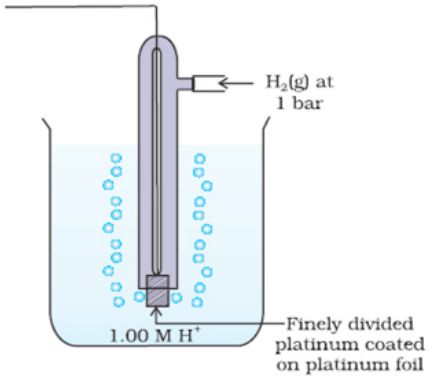
Question carrying 3 or 4 marks

1. ***Explain the construction of Daniel cell. Write the reaction taking place at anode and cathode and the net cell reaction. (3 mark)***

To prepare Daniel cell get a zinc electrode by dipping zinc rod in 1M $ZnSO_4$ solution. Get a copper electrode by dipping a copper plate in 1 M $CuSO_4$ solution. Couple these two electrodes using a salt bridge to get Daniel cell. Reactions taking place

$$At\ \text{anode} \qquad Zn \xrightarrow{oxdn} Zn^{2+} + 2e^-$$
$$At\ \text{cathode} \qquad Cu^{2+} + 2e^- \xrightarrow{redn} Cu$$
$$Net\ cell\ reaction\ Zn_{(s)} + Cu^{2+}{}_{(aq)} \longrightarrow Zn^{2+}{}_{(aq)} + Cu_{(s)}$$

2. ***With a labeled digram explain standar hydrogen electrode. Represent it symbolically. Write the reduction reaction at the anode. What is its electrode potential? (4 marks)***



: *Standard Hydrogen Electrode (SHE).*

It consists of a platinum electrode coated with platinum black. The electrode is dipped in 1M HCl. Pure hydrogen gas is bubbled through it under a pressure of 1 bar. S.H.E is represented as

$$Pt(s)\ |H_{2\,(g)(1bar)}|H^+_{(aq)(1M)}$$

The reduction reaction taking place is

$$H^+(aq) + e^- \longrightarrow \frac{1}{2}H_2(g)$$

S.H.E is assigned an electrode potential of 0.0 V at all temperatures.

3. ***Explain the use of standard hydrogen electrode in measuring the standard electrode potentials of copper and zinc electrode (4 mark)***

Construct a standard electrode of the given metal by dipping the pure metal in 1M solution of its own ion at 25^o C Couple this standard electrode with SHE using a salt bridge to get galvanic cell. Measure the emf of the cell using suitable instrument like potentiometer.

$E^o = E^o_R - E^o_L$

One of the electrodes of the cell is SHE and its electrode potential is 0.0V. So the electrode potential of the given electrode will be the emf of the cell in magnitude. If reduction takes place at the given electrode its E^o will be +ve but if oxidation takes place at the given electrode is E^o will be –ve.

e.g if SHE is coupled with standard copper electrode reduction takes place at copper electrode cell can be represented as

$Pt_{(s)}\ |H_{2(g.\ 1bar)}|H^+_{(aq1M)}||Cu^{2+}_{(aq.1M)}|Cu$

$$E^o_{cell} = E^o_{Cu^{2+}/Cu} - E^o_{H^+/H_2}$$

$$0.34 = E^o_{Cu^{2+}/Cu} - 0 \quad \therefore E^o_{Cu^{2+}/Cu} = 0.34V$$

If SHE coupled with standard zinc electrode oxidation takes place at zinc electrode. Cell can be represented as

$$Zn^{2+}{}_{(aq.1M)} / Zn_{(s)} \mid |Pt_{(s)}|H_{2(g.1bar)}|H^{+}{}_{(aq.1M)}$$

$$E^{o}cell = E^{o}{}_{H^{+}/H_2} - E^{o}{}_{Zn^{2+}/Zn}$$

$$0.76 = 0 - E^{o}{}_{Zn^{2+}/Zn} \qquad \therefore E_{Zn^{2+}/Zn} = -0.76V$$

4. ***How is Kohlrausch law helpful in finding out the limiting molar conductivity of a weak electrolyte? (3 m)***

Let us try to calculate $\lambda^{o}{}_{m}$ for a weak electrolyte CH_3COOH. Select three strong electrolytes whose $\lambda^{o}{}_{m}$ can be found by extrapolation method in such a way that if we subtract $\lambda^{o}{}_{m}$ for one electrolyte from the sum of $\lambda^{o}{}_{m}$s of the remaining two electrolyte $\lambda^{o}{}_{m}$ for CH_3COOH can be obtained. The three electrolytes to be selected are CH_3COONa, HCl & NaCl

$$\lambda^{o}{}_{CH_3COOH} = \lambda^{o}{}_{CH_3COONa} + \lambda^{o}{}_{HCl} - \lambda^{o}{}_{NaCl}$$

5. ***The values of limiting molar conductivities ($\lambda^{o}{}_{m}$) for NH_4Cl, NaOH and NaCl are respectively 149.74; 248.1 and 126.4 Scm^2mol^{-1}. Calculate the limiting molar conductivity of NH_4OH (3M)***

$$\lambda^{o}{}_{NH_4OH} = \lambda^{o}{}_{NH_4Cl} + \lambda^{o}{}_{NaOH} - \lambda^{o}{}_{NaCl}$$

= 149.74+248.1-126.4

= 271.44 Scm^2 mol^{-1}

6. ***Calculate the equilibrium constant for the reaction at 298K*** $Cu_{(s)} + 2Ag^{+}(aq) \longrightarrow Cu^{2+}{}_{(aq)} + 2Ag_{(s)}$

Given that E^{o} Ag^{+}/Ag = 0.80V and $E^{o}(Cu^{2+}/Cu)$ = 0.34V

$$E^{o}{}_{cell=} \frac{0.059}{n} \log K_c$$

$$\therefore \log K_c = \frac{nE^{o}cell}{0.059}$$

$$E^{o}{}_{cell} = E^{o}{}_{(Ag^{+}/Ag)} - E^{o}{}_{(Cu^{2+}/Cu)}$$

=0.80-0.34=0.46V

$$\log K_c = \frac{2 \times 0.46}{0.059} = 15.59$$

Taking the antilog $K_c = 3.92 \times 10^{15}$

7. ***In Leclanche cell (dry cell) what are anode and cathode? What is the electrolyte used? Write the reactions at each electrode. What is the role of zinc chloride?***

It consists of a zinc container as an anode. A graphite rod surrounded by a mixture of manganese dioxide and carbon powder is cathode.

The space between the electrodes is filled with electrolyte a moist paste of ammonium chloride and zinc chloride

Reaction taking place

$$At\ anode\ Zn_{(s)} \longrightarrow Zn^{2+} + 2e^-$$

$$At\ cathode\ MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$$

NH_3 produced in the reaction forms a complex with Zn^{2+} to form $[Zn(NH_3)_4]^{2+}$.

8. ***What are the anode and cathode of lead acid battery? What is the electrolyte? Write the reactions taking place at anode and cathode and the overall reaction during discharging of the battery. (3 M)***

It consists of lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode.

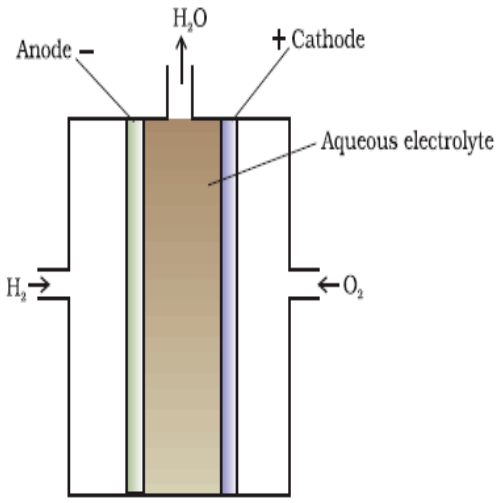
Electrolyte is 38% solution of sulphuric acid. The reactions taking place when the battery is in use are

$$Anode\ \ Pb_{(s)} + SO_4^{2-}{}_{(aq)} \longrightarrow PbSO_{4(s)} + 2e^-$$

$$Cathode\ \ PbO_2(s) + SO_4^{2-}{}_{(aq)} + 4H^+{}_{(aq)} + 2e^- \longrightarrow PbSO_{4\ (s)} + 2H_2O_{\ (l)}$$

The overall reaction is $Pb_{(s)} + PbO_{2\ (s)} + 2H_2SO_{4\ (aq)} \longrightarrow 2PbSO_{4\ (s)} + 2H_2O_{\ (l)}$

9. ***In Hydrogen oxygen fuel cell (i) Draw the schematic diagram mentioning the anode and cathode. What is the electrolyte? Write the reaction taking place at each electrodes and the net cell reaction. (4M)***



In this hydrogen and oxygen gases are bubbled through porous carbon electrodes into concentrated aqueous sodium hydroxide solution. Catalyst like finely divided platinum or palladium is incorporated into the electrodes for increasing the rate of electrode reaction

Reaction taking place are

$$Cathode\quad O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq)}$$

$$Anode\quad 2H_{2(g)} + 4OH^-_{(aq)} \longrightarrow 4H_2O_{(l)} + 4e^-$$

Overall reaction is

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$$

10. ***What is corrosion? During rusting of iron write the anodic and cathodic reactions. Give the composition of rust. (3M)***

When a metal is exposed to the atmosphere it is slowly attacked by the constituents of the environment as a result of which the metal is slowly lost in the form of its compound . This is called corrosion.

Reaction taking place are

$$\text{At Anode} \quad 2Fe_{(s)} \longrightarrow 2Fe^{2+} + 4e^-$$

$$\text{At Cathode} \quad O_{2(g)} + 4H^+(aq) + 4e^- \longrightarrow 2H_2O_{(l)}$$

H^+ are produced from H_2CO_3 formed due to dissolution of carbon dioxide from air into water The Fe^{2+} ions are further oxidised by atmospheric oxygen to ferric ion which are ultimately converted to hydrated ferric oxide called rust. Composition of rust is ($Fe_2O_3.xH_2O$).

11. A conductivity cell when filled with 0.01M KCl has a resistance of 747.5 ohm at 25^oC. When the same cell was filled with an aqueous solution of 0.05M $CaCl_2$ solution the resistance was 876 ohm. Calculate

(i) Conductivity of the solution

(ii)Molar conductivity of the solution (given conductivity of 0.01M KCl = 0.14114 sm^{-1}) (3M)

Cell constant G* = Rk

= 747.5×0.14114

=0.105.5m^{-1}

$$\text{Conductivity } k = \frac{\text{cell constant}}{R} = \frac{105.5m^{-1}}{876\ ohm} = 0.1204Sm^{-1}$$

$$\text{Molar conductivity } \lambda_m = \frac{k}{1000C} = \frac{0.1204}{1000 \times 0.05} = 0.00241sm^2\ mol^{-1}$$

12. The electrical resistance of a column of 0.05M NaOH solution of diameter 1cm and length 50cm is 5.55×10^3 ohm. Calculate its

(i) resistivity

(ii) conductivity

(iii) molar conductivity ***(3M)***

Cell constant $G^o = \frac{l}{a}$

l = 50 cm

Diameter = 1 cm $\therefore$ radius = 0.5 cm

Area of cross section A = $\pi r^2 = 3.14\times(0.5)^2 = 0.785\ cm^3$

$$G^* = \frac{50}{0.785} = 63.694\ cm^{-1}$$

$$\text{Resistivity } \rho = \frac{1}{k} = \frac{1}{1.148 \times 10^{-2}} = 87.135\ \Omega$$

$$\text{Molarconductivity } \lambda_m = \frac{1000k}{C}$$

$$= \frac{1000 \times 1.148 \times 10^{-2}}{0.05}$$

$$= 229.6\ S\ cm^2\ mol^{-1}$$

13. ***Calculate the emf of the cell in which the following reaction takes place.***

$$Ni_{(s)} + 2Ag^{+}(0.002M) \longrightarrow Ni^{2+}(0.160M) + 2Ag_{(s)}$$

Given that E^{o}_{cell} = 1.05V

$$E_{cell} = E^{o}_{cell} - \frac{0.059}{2}\log_{10}\frac{[Ni^{2+}][Ag_{(s)}]^2}{[Ni_{(s)}][Ag^{+}]^2}$$

But [M] for any element is taken as unity

$$E_{cell} = E^{o}_{cell} - \frac{0.059}{2}\log_{10}\frac{[Ni^{2+}]}{[Ag^{+}]^2}$$

$$= 1.05 - \frac{0.059}{2}\log\frac{0.160}{(0.002)^2}$$

= 0.914V