CHAPTER

17

Electrochemistry

Key Notes and Formulae

Resistance and Conductance

According to Ohm's law, for any conductor (metallic or electrolytic),

Resistance = Pot. Difference/Current (i.e. R = E/I

or $\text{Ohms}\,(\Omega) = \frac{\text{Volts}}{\text{Amperes}}$

Conductance (C) = 1/R.

The units are ohm^{-1} or mho or Siemens (S).

Conductivity and Resistivity

If 'l' is the distance between the electrodes, and 'a' is the area of cross-section of the electrode,

$R = \rho \frac{l}{a}$ where ρ is called Specific resistance or Resistivity. Specific conductance or conductivity (K) = $1/\rho$.

Cell Constant

$$\frac{1}{C} = \frac{1}{K}\frac{l}{a} \quad or \quad K = C \times \frac{l}{a}$$

$\frac{1}{a}$ is called cell constant. Its unit is cm^{-1}.

$$\text{As } K = C \times \frac{l}{a}$$

Equivalent Conductance

Equivalent conductance = Sp. conductance x Vol- of sol. in cc containing l g eq. of the electrolyte

$$i.e.\ \Delta_{eq} = K \text{ x } V$$

If C is the normality of the solution i.e. C g eq of the electrolyte are present in 1000 cc of the solution,

$V = \frac{1000}{\text{C}}$. Hence $\Delta_{eq} = K \text{ x } \frac{1000}{\text{Normality}}$

Units of $\Delta_{eq} = K \text{ x } V = \text{ohm}^{-1}\,\text{cm}^{-1}\,(\text{cm}^3\ \text{g eq}^{-1})$

$= \text{ohm}^{-1}\,\text{cm}^2\ \text{g eq}^{-1}$.

Molar Conductance

Molar conductance = Sp. conductance x Vol. of sol. in cc containing l mole of the electrolyte.

$i.e.\ \Delta_m = K \text{ x } V \text{ or } \Delta_m = K \text{ x } \frac{1000}{\text{Molarity}}$

Solubility

For a sparingly soluble salt like AgCl, $BaSO_4$, $PbSO_4$ etc. Solubility in mole L-1 (S) = $\frac{\text{K x 1000}}{\Delta_m^0}$

Units of $\Delta_m = \text{K x V} = \text{ohm}^{-1}\,\text{cm}^{-1}\,(\text{cm}^3\,\text{mol}^{-1})$

$= \text{ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$.

Debye-Huckel Onsager Equation

According to Debye-Huckel Onsager equation

$$\Delta_m^c = \Delta_m^o - b\sqrt{C}$$

Kohlrausch Law

According to Kohlrausch law, for any electrolyte,

$A_x B_y$

$$\Delta_m^o = \lambda_c^0 + \lambda_a^0 \quad and \quad \Delta_m^o = x\lambda_a^0 + y\lambda_a^0, where\ \lambda_c^0$$

$and\ \lambda_a^0$

are the ionic conductivities at infinite dilution for the cation and the anion respectively.

Nernst Equation

According to Nernst equation,

$$\text{E}_{cell}^0 = \frac{\text{RT}}{n\text{F}}\text{In K} = \frac{2.303\,\text{RT}}{n\text{F}}\log\text{K} = \frac{0.0591}{n}\log\text{K}$$

at 298 K. (K = Equilibrium constant of the cell reaction).

$$-\Delta G^0 = nF\ \text{E}_{cell}^0$$

$$\Delta G^0 = RT\,\text{In K} = -2.303\ RT\log K.$$

Thermodynamic Efficiency of a Fuel Cell

$$(\eta) = \frac{\Delta\text{G}}{\Delta\text{H}} = \frac{n\text{FE}}{\Delta\text{H}}$$

Previous Years' Questions

NEET

1. The molar cnductivity of a 0.5 mol/dm^3 solution of $AgNO_3$ with electrolytic conductivity of 5.76×10^{-3} S cm^{-1} at 298 K is **[July 2016]**

(a) 28.8 S cm^2/mol

(b) 2.88 cm^2/mol

(c) 11.52 S cm^2/mol

(d) 0.086 S cm^2/mol

2. The coagulation values in millimoles per litre of the electrolytes used for the coagulation of As_2S_3 are given below:

I. (NaCl) = 52, II. ($BaCl_2$) = 0.69

III. ($MgSO_4$) = 0.22

The correct order of their coagulating power is **[July 2016]**

(a) III > I > II (b) I > II > III

(c) II > I > III (d) III > II > I

3. During the electrolysis of molten sodium chloride, the time required to produce 0.10 mol of chlorine gas using a current of 3 amperes is **[July 2016]**

(a) 330 minutes (b) 55 minutes

(c) 110 minutes (d) 220 minutes

4. If the E^0_{cell} for a given reaction has a negative value, which of the following gives the correct relationships for the values of ΔG^0 and K_{eq}? **[July 2016]**

(a) $\Delta G^0 < 0; K_{eq} < 1$

(b) $\Delta G^0 > 0; K_{eq} < 1$

(c) $\Delta G^0 > 0; K_{eq} > 1$

(d) $\Delta G^0 < 0; K_{eq} > 1$

5. The number of electrons delivered at the cathode during electrolysis by a current of 1 ampere in 60 seconds is (charge on electron = 1.60×10^{-19} C) **[July 2016]**

(a) 7.48×10^{23} (b) 6×10^{23}

(c) 6×10^{20} (d) 3.75×10^{20}

6. Zinc can be coated on iron to produce galvanized iron but the reverse is not possible. It is because **[July 2016]**

(a) Zinc has higher negative electrode potential than iron

(b) Zinc is lighter than iron

(c) Zinc has lower melting point than iron

(d) Zinc has lower negative electrode potential than iron

7. The pressure of H_2 required to make the potential of H_2 electrode zero in pure water at 298K is ? **[May 2016]**

(a) 10^{-14} atm (b) 10^{-12} atm

(c) 10^{-10} atm (d) 10^{-1} atm

8. At 25^{0}C molar conductance of 0.1 molar aqueous solution of ammonium hydroxide is 9.54 ohm^{-1}cm^2 mol^{-1} and at infinite dilution its molar conductance is 238 Ω^{-1}cm^2. The degree of ionisation of ammonium hydroxide at the same concentration and temperature is **[2013]**

(a) 2.080% (b) 20.800%

(c) 4.008% (d) 40.800%

9. A button cell used in watches function as following: **[2013]**

$$Zn_{(s)} + Ag_2O_{(s)} + H_2O_{(l)} \rightleftharpoons 2Ag_{(s)} + Zn^{2+}_{(aq)} + 2OH$$

If half cell potentials are

$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)} : E^0 = -0.76V$

$Ag_2O_{(s)} + H_2O_{(l)} + 2e^- \rightarrow 2Ag_{(s)} + 2OH_{(aq)}$

$E^0 = -0.34V$

The cell potential will be

(a) 0.84 V

(b) 1.34V

(c) 1.10 V

(d) 0.42 V

AIPMT

10. A device that converts energy of combustion of fuels like hydrogen and Methane, directly in to electrical energy is known as **[2015]**

(a) dynamo

(b) Ni-Cd cell

(c) fuel cell

(d) electrolytic cell

11. When 0.1 mol MnO_4^{2-} is oxidised, the quantity of electricity required to completely oxidise MnO_4^{2-} to MnO_4^- is **[2014]**

(a) 96500 C

(b) 2 x 96500C

(c) 9650 C

(d) 96.50 C

12. The weight of silver (at.wt. = 108) displaced by a quantity of electricity which displaces 5600 mL of O_2 at STP will be **[2014]**

(a) 5.4 g

(b) 10.8g

(c) 54.0 g

(d) 108.0 g

13. Standard reduction potentials of the half reactions are given below ; **[2012]**

$F_{2(g)} + 2e^- \rightarrow 2F^-_{(aq)}; E^0 = +2.85 V$

$Cl_{2(g)} + 2e^- \rightarrow 2Cl^-_{(aq)}; E^0 = +1.36 V$

$Br_{2(l)} + 2e^- \rightarrow 2Br_{(aq)}; E^0 = +1.06 V$

$I_{2(s)} + 2e^- \rightarrow 2I^-_{(aq)}; E^0 = +0.53V$

The strongest oxidising and reducing agent respectively are

(a) F_2 and I^-

(b) Br_2 and Cl^-

(c) Cl_2 and Br^-

(d) Cl_2 and I_2

14. The Gibb's energy for the decomposition of Al_2O_3 at 500⁰C is as follows **[2012]**

$\frac{2}{3}Al_2O_3 \rightarrow \frac{4}{3}Al + O_2$

$\Delta G = +960 kJ\ mol^{-1}$

The potential difference needed for the electrolytic reduction of aluminium oxide (Al_2O_3) at 500⁰C is at least

(a) 4.5 V

(b) 3.0V

(c) 2.5 V

(d) 5.0V

15. Standard electrode potential for Sn^{4+}/Sn^{2+} couple is + 0.15 V and that for the Cr^{3+}/Cr couple is -0.74 V. These two couples in their standard state are connected to make a cell. The cell potential will be **[2011]**

(a) + 0.89

(b) + 0.18 V

(c) + 8.73

(d) + 9.08 V

16. Standard electrode potential of three metals X,Y, Z are -1.2 V, + 0.5V, and -3.0 V respectively. The reducing power of these metal will be **[2011]**

(a) Y > Z>X

(b) Y > X> Z

(c) Z> X> Y

(d) X>Y >Z

17. For the reduction of silver ions with copper metal, the standard cell potential was found to be +0.46V at 25⁰C. The value of standard Gibbs energy, ΔG^0 will be (F= 96500 Cmol⁻¹) **[2010]**

(a) -89.0kJ

(b) -89,0J

(c) -44.5kJ

(d) -98.0kJ

18. Consider the following relations for emf of an electrochemical cell. **[2010]**

(i) EMF of cell = (oxidation potential of anode) -reduction potential of cathode)

(ii) EMF of cell= (oxidation potential of anode)+ Reduction potential of cathode)

(iii) EMF of cell= (Reduction potential of anode) + (Reduction potential of cathode)

(iv) EMF of cell = (oxidation potential of anode) - (oxidation potential of cathode)

(a) (iii) and (i) (b) (i) and (ii)

(c) (iii) and (iv) (d) (ii) and (iv)

19. Al_2O_3 is reduced by electrolysis at low potentials and high currents. If 4.5×10^4 A of current is passed through molten Al_2O_3 for 6 hours. What mass of aluminium is produced? **[2009]**

(Assume 100% current efficiency, at mass of $Al = 27 g\ mol^{-1}$)

(a) 9.0×10^3g (b) 8.1×10^4 g

(c) 2.4×10^5g (d) 1.3×10^4g

Answer key

1. (c)	2. (d)	3. (c)	4. (b)	5. (d)	6. (a)	7. (a)
8. (c)	9. (c)	10. (c)	11. (c)	12. (d)	13. (a)	14. (c)
15. (a)	16. (c)	17. (a)	18. (d)	19. (b)		

Detailed Solutions

1. **(c).** $\lambda_M^0 = \frac{K \times 1000}{M} = \frac{5.76 \times 10^{-3} \times 1000}{0.5}$

$= 11.52\ S\ cm^2\ mol^{-1}$.

2. **(d).** Coagulation power $\alpha \frac{1}{Coagulation\ value}$

Higher the coagulation power, lower is coagulation values in millimoles per litre.

$MgSO_4 > BaCl_2 > NaCl$.

3. **(c).** At Cathode : $2H_2O \xrightarrow{2e^-} H_2 + 2OH^-$

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

$$\frac{W}{E} = \frac{It}{96500}$$

$$0.1 \times 2 = \frac{3 \times t(sec)}{96500}$$

t = 6433 sec

t = 107.2 min

$\simeq$ 110 min

4. **(b).** $E^0_{cell} < 0$, so it is a non spontaneous process

$\Delta G^0 = nFE^0$ = +ve, so $\Delta G^0 > 0$

$\Delta G^0 = -2.303\ RT \log K$

So, $K < 1$

5. **(d).** $\frac{W}{E} = \frac{1 \times 60}{96500}$

$= \frac{6}{9650}$ = no. of mole e^-

no. of $e^- = \frac{6}{9650} \times 6.02 \times 10^{23}$

$= 3.75 \times 10^{20}$

6. (a). $E^o_{Zn^{+2}/Zn} = -0.76$ V

$E^0_{Fe^{+2}/Fe} = -0.44$ V

Zn has higher negative SRP (Standard reduction potential) so it works as anode and protect iron to make iron as cathode.

7. **(a).** $2H_{(aq)} + 2e^- \rightarrow H_{2(g)}$

$$E = E^0 - \frac{0.0591}{2} \log \frac{P_{H_2}}{[H^+]^2}$$

$$0 = 0 - 0.0295\log \frac{P_{H_2}}{(10-7)^2}$$

$$\frac{P_{H_2}}{(10^{-7})^2} = 1$$

$P_{H_2} = 10^{-14}$ atm

8. **(c).** Given molar conductance at 0.1 M concentration,

$\lambda_C = 9.5\Omega^{-1}\, cm^2 mol^{-1}$

molar conductance at infinite dilution,

$\lambda_\infty = 238\Omega^{-1}\, cm^2 mol^{-1}$

We know that,

degree of ionisation, $\alpha = \frac{\lambda_c}{\lambda_\infty} \times 100$

$$= \frac{9.54}{234} \times 100 = 4.008\%$$

9. **(c).** $E^0_{cell} = E^0_{op} + E^0_{RP} = 0.76 + 0.34 = 1.10$ V

10. **(c).** Fuel cell

11. **(c).** The oxidation reaction is

$$\overset{+6}{M}nO_4^{2-} \rightarrow \overset{+7}{M}nO_4^{-} + e^-$$

0.1 mol 0.1 mol

Q=0.1 x F = 0.1 x 96500 C = 9650 C

12. **(d).** According to Faraday's second law,

$$\frac{W_{Ag}}{E_{Ag}} = \frac{W_{O_2}}{E_{O_2}} \text{ or } \frac{W_{Ag}}{108} = \frac{\frac{5600}{22400} \times 32}{8}$$

or $\frac{W_{Ag}}{108} = \frac{8}{8} \Rightarrow W_{Ag} = 108g$

13. **(a).** Higher the value of reduction potential higher will be the oxidising power whereas the lower the value of reduction potential higher will be the reducing power.

14. **(c).** $\Delta G^0 = -nFE^0$

F = 96500, $\Delta G^0 = + 960 \times 10^3$ J/mol

$$\frac{2}{3} Al_2\ O_3 \rightarrow \frac{4}{3} Al + O_2$$

Total number of Al atoms in Al_2O_3

$$= \frac{2}{3} \times 2 = \frac{4}{3}$$

$Al^{3+} + 3e^- \rightarrow Al$

As $3e^-$ change occurs for each Al atom

Total n = $\frac{4}{3} \times 3 = 4$

$$E^0 = -\frac{\Delta G^0}{nF} = -\frac{960 \times 1000}{4 \times 96500} = E^0 = -2.48 = -2.5V$$

15. **(a).** $E^0_{Sn^{4+}/Sn^{2+}} = +0.15V$

$E^0_{Cr^{3+}/Cr} = -0.74V$

$E^o_{cell} = E^0_{cathode\ (Rp)} - E^0_{anode\ (Rp)}$

$= 0.15 - (-0.74)$

$= +0.89$ V.

16. **(c).** As the electrode potential drops, reducing power increases.

So, Z (-3.0 V) > X (- 1.2V) > Y (+0.5 V)

17. **(a).** The cell reaction can be written as

$Cu + 2Ag^+ \rightarrow Cu^{2+} + 2Ag$

We know $\Delta G^0 = -nFE^0$ cell

$= -2 \times 96500 \times 0.46$

$= -887880$ J

$= -88.780$ kJ $= -89$ KJ

18. **(d).** EMF of a cell = Reduction potential of cathode- reduction Potential of anode

= Reduction potential of cathode+ Oxidation potential of anode

= oxidation potential of anode -oxidation potential of cathode.

19. **(b).** Al_2O_3 ionises as,

$Al_2O_3 \rightleftharpoons Al^{3+} + AlO_3^{3-}$

At cathode

$Al^{3+} + 3e^- \rightarrow Al$

$3F \rightarrow 27$ g

Mass of aluminium deposited by 3F of electricity = 27 g

Mass of aluminium deposited by $4.0 \times 10^4 \times 6 \times 3600$ C of electricity=

$$= \frac{27\times4.0\times10^4\times6\times3600}{3F} \text{ g}$$

$$= \frac{27\times4.0\times10^4\times6\times3600}{3\times96500} \text{ g}$$

$$= 8.1 \times 10^4 \text{ g}$$

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