Electrochemistry

3
Chapter

① TYPE OF CELLS

- **Electrochemical cell :** Device used to convert chemical energy of a redox reaction into electrical energy. It is also known as galvanic cell.
- **Electrolytic cell :** Device which uses electricity to bring about a non-spontaneous redox reaction.

② DANIELL CELL

- Cell reaction : $Zn(s) + Cu^{2+}(aq.) \longrightarrow Zn^{2+}(aq.) + Cu(s)$
- When external opposite potential is applied to the cell in standard state
  (a) $E_{ext} = 1.1$ V, no flow of electrons.
  (b) $E_{ext} > 1.1$ V, electrons flow from Cu rod to Zn rod.
  (c) $E_{ext} < 1.1$ V, electrons flow from Zn rod to Cu rod.

③ CELL POTENTIAL

- **Electrode potential :** It is the potential difference developed between the electrode and the electrolyte. When the concentration of all the species involved is unity it is known as **standard electrode potential**.
- **Cell potential :** The difference between the electrode potentials (reduction potentials) of the cathode and anode.
- **EMF of cell :** The cell potential when no current is drawn through the cell.
- $E_{cell} = E_{right} - E_{left}$
- $E^\circ_{cell} = E^\circ_R - E^\circ_L$
- In a galvanic cell :
  (a) Anode has negative potential w.r.t solution.
  (b) Cathode has positive potential w.r.t solution.
- **Standard hydrogen electrode :**
  $\underset{(1M)}{H^+(aq.)} + e^- \longrightarrow \underset{(1\,bar)}{\frac{1}{2}H_2(g)}, \quad E^\circ = 0$ Volt (Assumed)

④ NERNST EQUATION

- For the reaction : $M^{n+} + ne^- \longrightarrow M$

$$E = E^\circ - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$$

$$E = E^\circ - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]}$$

- For the reaction : $aA + bB \xrightarrow{ne^-} cC + dD$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

- For a reaction at equilibrium, $E_{cell} = 0$.
- $E^\circ_{cell} = \frac{2.303\,RT}{nF}\log K_C = \frac{0.0591}{n}\log K_C$

⑤ GIBBS ENERGY

- It is the reversible work done by the galvanic cell.
- $\Delta_r G = -nF\,E_{cell}$
- $\Delta_r G^\circ = -nF\,E^\circ_{cell}$
- $\Delta_r G^\circ = -RT\ln K = -2.303\,RT\log K$

⑦ CONDUCTANCE OF ELECTROLYTIC SOLUTIONS

- Resistance : $R = \frac{\rho\ell}{A}$, unit = ohm
- Resistivity : $\rho = \frac{RA}{\ell}$, unit = ohm-cm
- Conductance : $G = \frac{1}{R} = \kappa\frac{A}{\ell}$, unit = ohm^{-1} or S
- Cell constant : $G^* = \frac{\ell}{A}$, unit = cm^{-1}
- Conductivity : $\kappa = \frac{G\ell}{A}$, unit = $ohm^{-1}cm^{-1}$
- Molar conductivity : $\Lambda_m = \frac{\kappa \times 1000}{M}$, unit = $S\,cm^2\,mol^{-1}$

⑥ ELECTROCHEMICAL SERIES

- A negative E° means that the redox couple is stronger reducing agent than the H^+/H_2 couple.
- A positive E° means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

Increasing Strength of Oxidising Agent (↑)

Oxidised form	Reduced form	E°/V
$F_2(g) + 2e^-$	$\rightarrow 2F^-$	2.87
$Co^{3+} + e^-$	$\rightarrow Co^{2+}$	1.81
$Cl_2(g) + 2e^-$	$\rightarrow 2Cl^-$	1.36
$O_2(g) + 4H^+ + 4e^-$	$\rightarrow 2H_2O$	1.23
$Br_2 + 2e^-$	$\rightarrow 2Br^-$	1.09
$Ag^+ + e^-$	$\rightarrow Ag(s)$	0.80
$Fe^{3+} + e^-$	$\rightarrow Fe^{2+}$	0.77
$O_2(g) + 2H^+ + 2e^-$	$\rightarrow H_2O_2$	0.68
$I_2 + 2e^-$	$\rightarrow 2I^-$	0.54
$Cu^{2+} + 2e^-$	$\rightarrow Cu(s)$	0.34
$2H^+ + 2e^-$	**$\rightarrow H_2(g)$**	**0.00**
$Pb^{2+} + 2e^-$	$\rightarrow Pb(s)$	–0.13
$Sn^{2+} + 2e^-$	$\rightarrow Sn(s)$	–0.14
$Cr^{3+} + 3e^-$	$\rightarrow Cr(s)$	–0.74
$Zn^{2+} + 2e^-$	$\rightarrow Zn(s)$	–0.76
$2H_2O + 2e^-$	$\rightarrow H_2(g) + 2OH^-(aq)$	–0.83
$Na^+ + e^-$	$\rightarrow Na(s)$	–2.71
$Ca^{2+} + 2e^-$	$\rightarrow Ca(s)$	–2.87
$K^+ + e^-$	$\rightarrow K(s)$	–2.93
$Li^+ + e^-$	$\rightarrow Li(s)$	–3.05

⑧ DILUTION EFFECT ON CONDUCTANCE

- Conductivity always decreases with decrease in concentration (means on dilution) both for weak and strong electrolytes.
- For weak electrolytes, molar conductivity increases steeply on dilution.
- For strong electrolytes, molar conductivity increases slowly with dilution.
- For strong electrolyte : $\Lambda_m = \Lambda^\circ_m - A\sqrt{C}$.

(9) KOHLRAUSCH LAW OF INDEPENDENT MIGRATION OF IONS

- Limiting molar conductivity of an electrolyte can be represented as the sum of the individual contributions of the anion and cation of the electrolyte at infinite dilution.
- If an electrolyte on dissociation given v_+ cations and v_- anions then $\Lambda_m^\circ = v_+\lambda_+^\circ + v_-\lambda_-^\circ$
  - λ_m°: $H^+ > Ca^{2+} > Mg^{2+} > K^+ > Na^+$
  - λ_m°: $OH^- > SO_4^{2-} > Br^- > Cl^- > CH_3COO^-$
  - For a weak electrolyte : $\alpha = \Lambda_m/\Lambda_m^\circ$
  - For acetic acid : $K_a = \dfrac{C\alpha^2}{1-\alpha} = \dfrac{C\Lambda_m^2}{\Lambda_m^\circ(\Lambda_m^\circ - \Lambda_m)}$

(10) FARADAY'S LAW OF ELECTROLYSIS

- **First law :** $w = ZQ = ZIt = \dfrac{E}{96500}\times It$
- **Second law :** $\dfrac{w_1}{w_2} = \dfrac{E_1}{E_2}$
- 1F = Charge on 1 mol electron = 96487 C = 96500 C

(11) PRODUCTS OF ELECTROLYSIS

- Molten NaCl : Anode : Cl_2, Cathode : Na
- Aqueous NaCl : Anode : Cl_2, Cathode : H_2
- Dilute H_2SO_4 : Anode : O_2, Cathode : H_2
- Concentrated H_2SO_4 : Anode : $S_2O_8^{2-}$, Cathode : H_2

(12) BATTERIES

- **Primary Batteries :** Which cannot be reused.
  (1) **Dry cell :** (Leclanche cell)
  Anode : $Zn(s) \longrightarrow Zn^{2+} + 2e^-$
  Cathode : $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

Fig. A commercial dry cell consists of a graphite (carbon) cathode in a zinc container; the latter acts as the anode.

  (2) **Mercury cell :** Cell potential (≈ 1.35 V) remains constant during its life
  Anode : $Zn(Hg) + 2OH^- \longrightarrow ZnO(s) + H_2O + 2e^-$
  Cathode : $HgO + H_2O + 2e^- \longrightarrow Hg(\ell) + 2OH^-$

- **Secondary batteries :** Which can be recharged
  (1) **Lead storage battery :**
  $$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} 2PbSO_4(s) + 2H_2O(\ell)$$
  (2) **Nickel cadmium cell :** It has longer life than lead storage cell :
  $Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(\ell)$
- **Fuel cells :** Galvanic cell that converts the energy produced during combustion of fuel directly into electrical energy
  e.g: $H_2 - O_2$ fuel cell
  Anode : $H_2(g) + 2OH^-(aq.) \longrightarrow 2H_2O(\ell) + 2e^-$
  Cathode : $O_2(g) + 2H_2O(\ell) + 4e^- \longrightarrow 4OH^-(aq.)$
  The cell was used in Apollo space programme

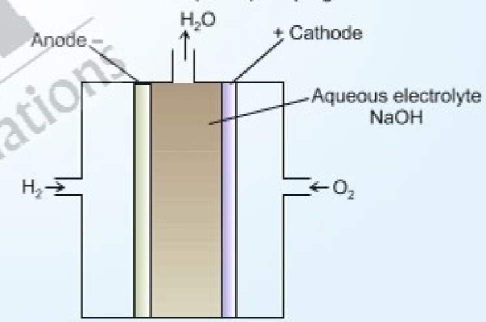
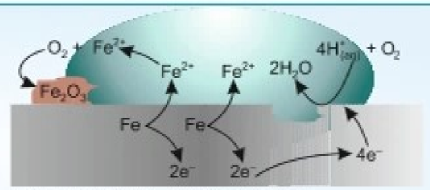


Fig. Fuel cell using H_2 and O_2 produces electricity

(13) CORROSION

- It slowly coats the surfaces of metallic objects with oxides or other salts of metal.
- Corrosion of iron is called rusting. It is an electrochemical phenomenon.
- Rust is $Fe_2O_3 \cdot xH_2O$.
- Prevention of rusting can be done by
  (i) Covering the surface with paint or by chemicals (e.g. bisphenol)
  (ii) Cover the surface by other metals (Sn, Zn etc.)
  (iii) Provide a sacrificial electrode of other metal (Mg, Zn etc.)



Oxidation : $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$
Reduction : $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$
Atmospheric oxidation : $2Fe^{2+}(aq) + 2H_2O(l) + 1/2O_2(g) \rightarrow Fe_2O_3 + 4H^+$
Fig. Corrosion of iron in atmosphere

Sharpen Your Understanding — NCERT Based MCQs

1. If an external opposite potential is applied to Daniell cell (in standard state) the reaction continues to take place till the opposite voltage reaches the value of [NCERT Pg. 66]

(1) 1.1 V (2) 1.8 V

(3) 2.1 V (4) 2.3 V

2. The cell potential is called emf of the cell when [NCERT Pg. 68]

(1) Electrodes are in standard state

(2) One ampere current is drawn through the cell

(3) No current is drawn through the cell

(4) Platinum electrodes are used in the cell

3. For the cell reaction :

$Cu(s) + 2Ag^+(aq.) \longrightarrow Cu^{2+}(aq.) + 2Ag(s)$ [NCERT Pg. 68]

(1) $E_{cell} = E_{Cu^{2+}/Cu} - E_{Ag^+/Ag}$

(2) $E_{cell} = E_{Ag^+/Ag} - E_{Cu^{2+}/Cu}$

(3) $E_{cell} = E_{Ag^+/Ag} + E_{Cu^{2+}/Cu}$

(4) $E_{cell} = 2E_{Ag^+/Ag} + E_{Cu^{2+}/Cu}$

4. The conductivity (κ) of an electrolyte solution depends on [NCERT Pg. 77]

(1) The concentration of electrolyte

(2) Nature of solvent

(3) Temperature

(4) All of these

5. Select the incorrect statement among the following [NCERT Pg. 70, 88, 93]

(1) Electrochemical principles are relevant to the hydrogen economy

(2) Corrosion of metals is an electrochemical phenomenon

(3) Batteries are very useful forms of electrolytic cells

(4) Electrochemical cells are used for determining solubility product

6. Select the correct statements among the following

(a) A negative E° means that the redox couple is a stronger reducing agent than the H^+/H_2 couple

(b) F_2 is strongest oxidising agent among halogens

(c) Among alkali metals lithium is the most powerful reducing agent in aqueous solution

(d) The potential of individual half-cell can not be measured

[NCERT Pg. 68, 70, 71]

(1) a and c only

(2) b and d only

(3) b and c only

(4) a, b, c and d

7. For the electrode reaction

$M^{n+}(aq.) + ne^- \longrightarrow M(s)$,

the Nernst equation is given by [NCERT Pg. 70]

(1) $E(M^{n+}/M) = E^\circ(M^{n+}/M) - \frac{RT}{nF}\log\frac{[M]}{[M^{n+}]}$

(2) $E(M^{n+}/M) = E^\circ(M^{n+}/M) - \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$

(3) $E(M^{n+}/M) = E^\circ(M^{n+}/M) + \frac{RT}{nF}\ln\frac{[M]}{[M^{n+}]}$

(4) $E(M^{n+}/M) = E^\circ(M^{n+}/M) + \frac{RT}{nF}\log\frac{[M]}{[M^{n+}]}$

8. Incorrect relation among the following is [NCERT Pg. 74]

(1) $\Delta_rG = -2.303\ RT \log K$

(2) $E^\circ_{cell} = \frac{2.303\ RT}{nF}\log K_c$

(3) $\Delta_rG^\circ = -RT \ln K$

(4) $\Delta_rG = -nFE_{cell}$

9. The oxidation potential of hydrogen electrode which is in contact with a solution having pH = 10 is [NCERT Pg. 75]

(1) 0.591 V (2) 0.295 V

(3) 1.182 V (4) 0.886 V

10. The emf of cell

$Ni(s)|Ni^{2+}(0.16\ M)||Ag^{+}(0.002\ M)|Ag(s)$,

is ($E^{\circ}_{cell} = 1.05$ V) [NCERT Pg. 75]

(1) –0.91 V (2) +0.46 V

(3) +0.91 V (4) –0.75 V

11. The equilibrium constant of the given reaction at 298 K will be

$2Fe^{3+}(aq.) + 2I^{-}(aq.) \longrightarrow 2Fe^{2+}(aq.) + I_2(s)$,

$E^{\circ}_{cell} = 0.237$ V [NCERT Pg.75]

(1) $10^{12.25}$ (2) $10^{8.02}$

(3) $10^{6.8}$ (4) $10^{9.76}$

12. Which among the following options have highest conductivity? [NCERT Pg. 78]

(1) Pure water (2) 0.1M HCl

(3) 0.01M HAc (4) 0.01M NaCl

13. Among the following incorrect statement is [NCERT Pg. 81, 83]

(1) For strong electrolytes, Λ_m increases slowly with dilution

(2) For strong electrolytes, conductivity decreases with decrease in concentration

(3) For weak electrolytes, Λ_m increases steeply with dilution especially near lower concentration

(4) For weak electrolytes, conductivity increases with decrease in concentration

14. In the equation : $\Lambda_m = \Lambda^{\circ}_m - A\sqrt{C}$, the value of A will be same for [NCERT Pg. 81]

(1) NaCl and KCl

(2) NaCl and $CaCl_2$

(3) $CaCl_2$ and $MgSO_4$

(4) KCl and $MgSO_4$

15. If the Λ°_m of 0.025 M formic acid is 46.1 S cm² mol⁻¹ then the K_a for formic acid will be nearly (given : $\lambda^{\circ}(H^+) = 349.6$ S cm² mol⁻¹ and $\lambda^{\circ}(HCOO^-) = 54.6$ S cm² mol⁻¹) [NCERT Pg. 85]

(1) 2.5×10^{-5}

(2) 2.8×10^{-4}

(3) 3.6×10^{-4}

(4) 5.9×10^{-6}

16. If the Λ°_m for KCl, HCl and CH_3COOK are x, y and z S cm² mol⁻¹ respectively then Λ°_m for CH_3COOH will be [NCERT Pg. 84]

(1) y + z – x

(2) y + x – z

(3) x + y + z

(4) z + x – y

17. One faraday is equal to [NCERT Pg. 86]

(1) 96778 C

(2) 96487 C

(3) 96685 C

(4) 96587 C

18. The mass of Ni deposited at cathode by passing 5 A current for 20 min through $Ni(NO_3)_2$ solution using Pt-electrodes will be (Atomic mass of Ni = 58.7) [NCERT Pg. 94]

(1) 1.56 g

(2) 2.46 g

(3) 1.23 g

(4) 1.82 g

19. Select the correct statement for lead storage battery [NCERT Pg. 89]

(1) It consists a grid of lead packed with PbO_2 as anode

(2) A 50% solution of sulphuric acid is used as an electrolyte

(3) On charging the battery $PbSO_4(s)$ on anode is converted into Pb

(4) On charging the battery concentration of H_2SO_4 decreases

20. A steady current of 1.5 amperes was passed through two electrolytic cells A and B containing $CuSO_4$ and $AgNO_3$ respectively and connected in series. If 1.45 g of Ag is deposited at the cathode of cell B than the mass of copper deposited in cell A will be [NCERT Pg. 94]

(1) 0.43 g

(2) 0.36 g

(3) 0.51 g

(4) 0.59 g

Thinking in Context

1. The reversible work done by a galvanic cell is equal to decrease in its ________. [NCERT Pg. 74]

2. E_{cell} is an ________ parameter. [NCERT Pg. 74]

3. The SI unit of resistivity is ________ [NCERT Pg. 75]

4. Nowadays a number of ceramic materials and mixed oxides show super conductivity at temperatures as high as ________. [NCERT Pg. 76]

5. The conductivity of electrolytic solution ________ with the increase of temperature. [NCERT Pg. 77]

6. The cell constant is usually determined by measuring the resistance of the cell generally containing a solution of ________ whose conductivity is already known. [NCERT Pg. 78]

7. In a galvanic cell, anode has a ________ potential with respect to the solution. [NCERT Pg. 67]

8. The slope of plot Λ_m vs $C^{1/2}$ for strong electrolytes is equal to _______. [NCERT Pg. 81]

9. Prevention of corrosion can be done by covering the metal surface by chemicals _______. [NCERT Pg. 91]

10. Among OH^-, Cl^-, Na^+ and K^+ ions, the limiting molar. Conductivity in water at 298 K is maximum for _______. [NCERT Pg. 83]

11. Standard hydrogen electrode is assigned a ________ potential at all temperatures. [NCERT Pg. 68]

12. The cell potential of mercury cell is approximately _______. [NCERT Pg. 89]

13. The number of Faraday needed to reduce 1 mol of $Cr_2O_7^{2-}$ into Cr^{3+} is _______. [NCERT Pg. 88]

14. During the electrolysis of aqueous NaCl, on account of _______ of oxygen, oxidation of Cl^- is preferred. [NCERT Pg. 87]

15. During the electrolysis of high concentrated H_2SO_4, formation of _______ is preferred at anode. [NCERT Pg. 88]

16. The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical _______. [NCERT Pg. 85]

17. At any concentration C, the degree of dissociation of a weak electrolyte is approximated to the ratio of its molar conductivity (Λ_m) to the its _______. [NCERT Pg. 84]

18. Fuel cells using the reaction of hydrogen with oxygen to form water used for providing electrical power in the ________ space programme. [NCERT Pg. 90]

19. The molar conductivity (in S cm^2 mol^{-1}) of 0.2 M solution of KCl at 298 K having conductivity 0.0248 S cm^{-1} will be _______. [NCERT Pg. 93]

20. On electrolysis of aqueous solution of $AgNO_3$ with silver electrodes, concentration of Ag^+ _______ in the solution. [NCERT Pg. 94]

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