JEE MAIN · PAPER 1 · CHEMISTRY

07 Redox Reactions & Electrochemistry

Formula & concept sheet

Electron transfer, from oxidation numbers and balancing redox equations to titrations, then the electrochemical cell: electrode potentials, the Nernst equation, Gibbs energy and equilibrium, conductance, electrolysis with Faraday's laws, batteries and corrosion. Each idea is explained first, then the formulas, shortcuts and traps.

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READ ALONGSIDE NCERT XI · Redox Reactions · NCERT XII · Electrochemistry

HOW TO USE THIS SHEET

1. **Skim** — Read the Key ideas, then the formula cards.
2. **Memorise** — Learn the formulas and check every Trap box.
3. **Test** — Do the worked examples, then this chapter's PYQs.
4. **Revise** — Use the last-minute checklist before the exam.

Formula memorise · **Key idea** why it works · **Trap** marks lost here · **PYQ** how it is asked

Practise this chapter with real past-paper questions on Prep Vault. Written for revision, not as a first read.

CHAPTER 07

Redox Reactions & Electrochemistry

NCERT XI · Redox Reactions | NCERT XII · Electrochemistry

Covers: oxidation number, redox and disproportionation · balancing and n-factor, redox titrations · electrochemical series · galvanic cell, E° and Nernst equation · ΔG, K · concentration cells · conductance, Kohlrausch's law · electrolysis and Faraday's laws · batteries, fuel cells, corrosion.

1 Oxidation number and types of redox reactions

- **Oxidation** is loss of electrons (rise in oxidation number); **reduction** is gain (fall). They always occur together. The **reducing agent** is oxidised, the **oxidising agent** is reduced.
- The **oxidation number** is the charge an atom would have if every shared pair went entirely to the more electronegative atom. The numbers of a species add up to its charge. It is a bookkeeping device, not a real charge, and it can be fractional (an average).

RULES FOR OXIDATION NUMBERS

ATOM OR GROUP	NUMBER
element in any form (Na, O_2, P_4, S_8)	0
monatomic ion	its charge
H	$+1$ (in metal hydrides NaH: -1)
O	-2 (peroxide H_2O_2: -1; superoxide KO_2: $-\frac{1}{2}$; OF_2: $+2$)
alkali metals; alkaline earth; Al	$+1$; $+2$; $+3$
halogens in compounds	-1 (but positive with more electronegative atoms: Cl in ClO_3^- is $+5$); fluorine is always -1

AVERAGES AND TRICKY CASES

SPECIES	OXIDATION NUMBER	WHY
Fe_3O_4	Fe $+\frac{8}{3}$	$3x + 4(-2) = 0$ (mixed $FeO \cdot Fe_2O_3$: $+2, +3, +3$)
$S_4O_6^{2-}$	S $+2.5$	$4x - 12 = -2$; two S are 0, two are $+5$
$S_2O_3^{2-}$	S $+2$ (average)	$2x - 6 = -2$; one S is $+6$, one -2
CrO_5 (peroxide)	Cr $+6$	four O at -1 (two peroxide groups) and one at -2
H_2SO_5 (Caro's acid)	S $+6$	one peroxide $O-O$ group, -1 each
$Cr_2O_7^{2-}$, MnO_4^-, CrO_2Cl_2	Cr $+6$, Mn $+7$, Cr $+6$	sum rule

REMEMBER

OIL RIG: Oxidation Is Loss, Reduction Is Gain (of electrons). The oxidising agent gains electrons and is itself reduced; $KMnO_4$, $K_2Cr_2O_7$, Cl_2, H_2O_2 (with reductants), O_3 oxidise; Zn, Fe^{2+}, I^-, H_2S, SO_2 (with strong oxidants), $C_2O_4^{2-}$ reduce.

SANITY CHECK

The total rise in oxidation number of the oxidised atoms must equal the total fall of the reduced atoms: this is the quickest way to balance, and the electron count per formula unit is the n-factor.

KINDS OF REDOX REACTION

TYPE	EXAMPLE
combination	$2\,Mg + O_2 \longrightarrow 2\,MgO$
decomposition	$2\,HgO \longrightarrow 2\,Hg + O_2$
displacement	$Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$; $Cl_2 + 2\,KBr \longrightarrow 2\,KCl + Br_2$
disproportionation: one species both oxidised and reduced	$2\,Cu^{+} \longrightarrow Cu^{2+} + Cu$; $3\,MnO_4^{2-} + 4\,H^{+} \longrightarrow 2\,MnO_4^{-} + MnO_2 + 2\,H_2O$; $Cl_2 + 2\,OH^{-} \longrightarrow Cl^{-} + OCl^{-} + H_2O$ (cold); $3\,Cl_2 + 6\,OH^{-} \longrightarrow 5\,Cl^{-} + ClO_3^{-} + 3\,H_2O$ (hot); $P_4 + 3\,OH^{-} + 3\,H_2O \longrightarrow PH_3 + 3\,H_2PO_2^{-}$
comproportionation (reverse)	$2\,H_2S + SO_2 \longrightarrow 3\,S + 2\,H_2O$ (two oxidation states meet at one)

KEY IDEA

A species can disproportionate only if the element is in an **intermediate** oxidation state (it has a higher and a lower one available). ClO_4^{-} and MnO_4^{-} (highest) and Cl^{-} (lowest) cannot. Fluorine never takes a positive state, so F_2 does not disproportionate in that sense.

QUICK CHECK

Oxidation numbers of S in H_2S, SO_2, SO_4^{2-}, S_8, $Na_2S_2O_3$?

Answer: $-2,\ +4,\ +6,\ 0$; thiosulphate average $+2$.

2 Balancing redox equations and redox titrations

ION-ELECTRON (HALF-REACTION) METHOD

1. Split into oxidation and reduction half-reactions (ions only; leave spectator ions out).
2. Balance atoms other than O and H; then O with H_2O; then H with H^{+} (in acid).
3. In basic solution add OH^{-} equal to the H^{+} on both sides, and cancel the H_2O formed.
4. Balance the charge with electrons, multiply the halves to equalise the electrons, add, and check atoms and charge.

KEY HALF-REACTIONS (ATOMS AND CHARGE CHECKED)

SPECIES	HALF-REACTION	N-FACTOR
MnO_4^{-} in acid	$MnO_4^{-} + 8\,H^{+} + 5\,e^{-} \longrightarrow Mn^{2+} + 4\,H_2O$	5
MnO_4^{-} neutral or weakly basic	$MnO_4^{-} + 2\,H_2O + 3\,e^{-} \longrightarrow MnO_2 + 4\,OH^{-}$	3
MnO_4^{-} strongly basic	$MnO_4^{-} + e^{-} \longrightarrow MnO_4^{2-}$	1
$Cr_2O_7^{2-}$ in acid	$Cr_2O_7^{2-} + 14\,H^{+} + 6\,e^{-} \longrightarrow 2\,Cr^{3+} + 7\,H_2O$	6
$C_2O_4^{2-}$ (oxalate)	$C_2O_4^{2-} \longrightarrow 2\,CO_2 + 2\,e^{-}$	2
Fe^{2+}	$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$	1
$S_2O_3^{2-}$ with iodine	$2\,S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2\,e^{-}$	1 (per $S_2O_3^{2-}$)
I_2	$I_2 + 2\,e^{-} \longrightarrow 2\,I^{-}$	2

OVERALL REACTIONS

$$2\,MnO_4^{-} + 5\,C_2O_4^{2-} + 16\,H^{+} \longrightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O$$

8 mol H^{+} per mol MnO_4^{-}; also $MnO_4^{-} + 5\,Fe^{2+} + 8\,H^{+} \longrightarrow Mn^{2+} + 5\,Fe^{3+} + 4\,H_2O$

IODOMETRY

$$I_2 + 2\,S_2O_3^{2-} \longrightarrow 2\,I^{-} + S_4O_6^{2-}$$

thiosulphate titrates the iodine liberated by an oxidant; starch end point (blue to colourless)

EQUIVALENTS

$$\text{eq} = n \times n_f = N \times V$$

n_f = electrons lost or gained per formula unit; $N = M \times n_f$

EQUIVALENCE POINT

$$N_1V_1 = N_2V_2$$

equivalents of oxidant = equivalents of reductant; or mole ratio from the balanced equation

EQUIVALENT MASS

$$E = \frac{M}{n_f}$$

$KMnO_4$: $158/5 = 31.6$ (acid); $K_2Cr_2O_7$: $294/6 = 49$

TRAP

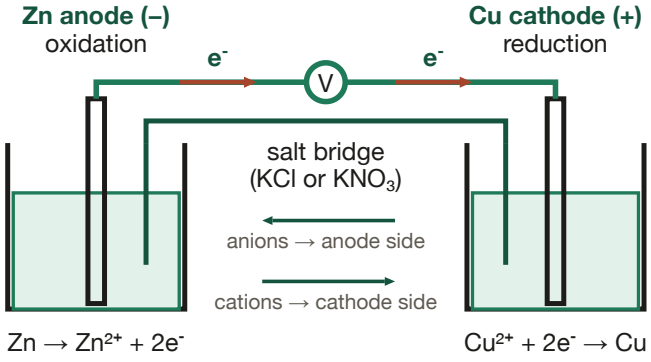
The n-factor of $KMnO_4$ depends on the medium ($5, 3, 1$); of $K_2Cr_2O_7$ is 6 (acid). ${S_2O_3}^{2-} \rightarrow {S_4O_6}^{2-}$ has $n_f = 1$ per thiosulphate, but sulphur oxidised by strong oxidants to ${SO_4}^{2-}$ has $n_f = 8$. Titrate $KMnO_4$ in H_2SO_4, never in HCl (it oxidises chloride).

QUICK CHECK

25 mL of Fe^{2+} needs 20 mL of 0.02 M $KMnO_4$ in acid. Molarity of Fe^{2+}?

Answer: ${MnO_4}^-$ takes 5 Fe^{2+}: $M = \dfrac{5 \times 0.02 \times 20}{25} = 0.08$ M.

3 The electrochemical cell and electrode potential



Zn | Zn²⁺ ‖ Cu²⁺ | Cu E° = +1.10 V

electrons flow from anode to cathode through the wire; conventional current flows the opposite way

GALVANIC CELL A device in which a spontaneous redox reaction produces electrical work. The oxidation (at the **anode**, negative) and reduction (at the **cathode**, positive) are in separate half cells joined by a wire and a **salt bridge** (KCl or KNO_3 in agar), which keeps each solution neutral and completes the circuit by letting ions move.

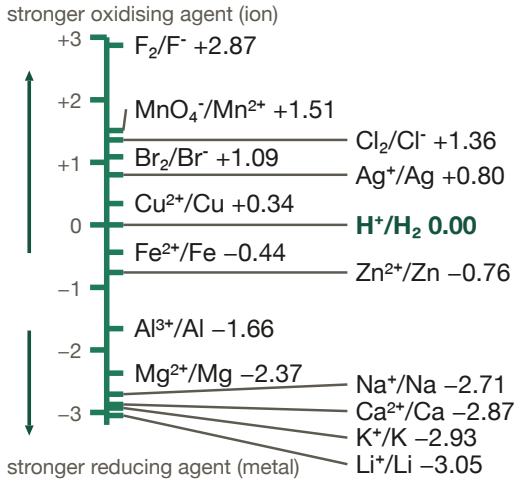
READING A CELL

- Notation: anode | anode ion ‖ cathode ion | cathode; ‖ is the salt bridge.
- Electrons flow in the wire from anode to cathode; anions move towards the anode, cations towards the cathode.
- Daniell cell: $Zn \longrightarrow Zn^{2+} + 2\,e^-$ (anode), $Cu^{2+} + 2\,e^- \longrightarrow Cu$ (cathode); $E^\circ = 1.10$ V.

CELL POTENTIAL

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

both as **reduction** potentials; positive E°_{cell} means spontaneous; E° is intensive: do not multiply it by stoichiometric factors



a species reduces the oxidised form of any couple above it

USING THE SERIES

- A larger (more positive) E° means a stronger **oxidising** agent (F_2 strongest); a lower one, a stronger **reducing** agent (Li in water).
- A metal displaces from solution the ions of any metal with a higher E° (higher up the scale drawn here): Zn (-0.76) displaces Cu ($+0.34$).
- Metals below H_2 (negative E°) dissolve in dilute acids with H_2; Cu, Ag, Au do not.
- Also (V, NCERT values, approximate): Ni^{2+}/Ni -0.25, Pb^{2+}/Pb -0.13, I_2/I^- $+0.54$, Fe^{3+}/Fe^{2+} $+0.77$, $O_2, H^+/H_2O$ $+1.23$, ${Cr_2O_7}^{2-}/Cr^{3+}$ $+1.33$; Mg is -2.36 in NCERT (-2.37 elsewhere).

WHY IT WORKS

The standard hydrogen electrode (Pt, $\mathrm{H_2}$ at 1 bar, 1 M $\mathrm{H^+}$) is the zero of the scale. A half cell with a more negative potential pushes electrons out harder, so it becomes the anode against any half cell with a higher potential.

QUICK CHECK

E° for $\mathrm{Mg} \mid \mathrm{Mg^{2+}} \,||\, \mathrm{Ag^+} \mid \mathrm{Ag}$ and the cell reaction?

Answer: $0.80 - (-2.36) = 3.16$ V; $\mathrm{Mg} + 2\,\mathrm{Ag^+} \longrightarrow \mathrm{Mg^{2+}} + 2\,\mathrm{Ag}$.

4 Nernst equation, Gibbs energy and equilibrium

A cell does not stay at E°: concentrations change as it runs. The Nernst equation gives the potential at any composition, and links it to the Gibbs energy and to the equilibrium constant. At equilibrium ($Q = K$) the cell is flat: $E = 0$ and $\Delta G = 0$.

NERNST (CELL)

$$E = E^\circ - \frac{0.0591}{n} \log Q$$

298 K; general: $E = E^\circ - \frac{RT}{nF} \ln Q$, with $2.303RT/F = 0.0591$ V; n from the balanced equation, solids and water $= 1$ in Q

HALF CELL

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

for $\mathrm{M}^{n+} + \mathrm{ne}^- \longrightarrow \mathrm{M}$; the hydrogen electrode: $E = -0.0591\,pH$ at 1 bar

CONCENTRATION CELL

$$E = \frac{0.0591}{n} \log \frac{C_{cathode}}{C_{anode}}$$

same electrode, two concentrations; $E^\circ = 0$; the more dilute half is the anode

GIBBS ENERGY

$$\Delta G = -nFE, \quad \Delta G^\circ = -nFE^\circ$$

$F = 96500$ C mol^{-1}; ΔG in J per mole of reaction as written

EQUILIBRIUM CONSTANT

$$\log K = \frac{nE^\circ}{0.0591}$$

$E^\circ = 0.0591$ V with $n = 1$ gives $K = 10$; $\Delta G^\circ = -RT \ln K = -nFE^\circ$

NON-ADDITIVE E°

$$E^\circ_3 = \frac{n_1 E^\circ_1 + n_2 E^\circ_2}{n_3}$$

add the ΔG° values, not the potentials; $\mathrm{Fe^{3+}/Fe}$ from 0.77 and -0.44: -0.04 V

TRAP

Take n from the **balanced overall reaction** and write Q with the products on top. The potentials of the two half cells are subtracted, never added, and never doubled when the equation is doubled. For $\mathrm{Mg} \mid \mathrm{Mg^{2+}} \,||\, \mathrm{Ag^+} \mid \mathrm{Ag}$: $E = E^\circ - \frac{0.0591}{2} \log \frac{[\mathrm{Mg^{2+}}]}{[\mathrm{Ag^+}]^2}$.

QUICK CHECK

$E^\circ_{cell} = 1.10$ V for $\mathrm{Zn} + \mathrm{Cu^{2+}} \longrightarrow \mathrm{Zn^{2+}} + \mathrm{Cu}$. Find ΔG° and K; and E for $[\mathrm{Zn^{2+}}] = 0.1$, $[\mathrm{Cu^{2+}}] = 0.01$ M.

Answer: $\Delta G^\circ = -2 \times 96500 \times 1.10 = -212$ kJ; $\log K = \frac{2.20}{0.0591} = 37.2$, $K \approx 10^{37}$; $E = 1.10 - 0.02955 \log 10 = 1.07$ V.

5 Conductance of electrolytic solutions

- **Metallic** conduction is by electrons and falls as temperature rises; **electrolytic** conduction is by ions and **rises** with temperature (ions move faster, viscosity falls).
- On **dilution**, conductivity κ falls (fewer ions per unit volume) but molar conductivity Λ_m rises (more dissociation for a weak electrolyte, less ionic drag for a strong one).

CONDUCTANCE, CONDUCTIVITY

$$G = \frac{1}{R}, \quad \kappa = G\,\frac{l}{A} = G\,G^{*}$$

G in S, cell constant $G^{*} = l/A$ in cm^{-1}; κ in S cm^{-1}

MOLAR CONDUCTIVITY

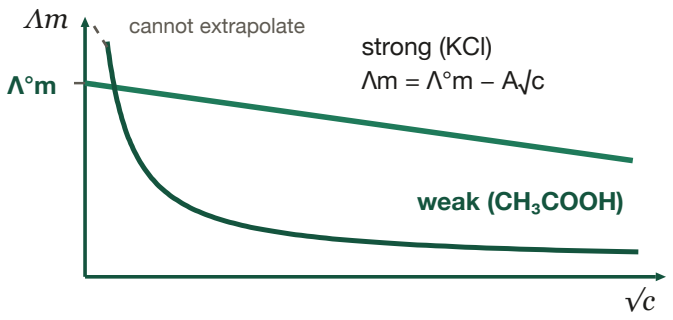
$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

κ in S cm^{-1}, M in mol L^{-1}, Λ_m in S cm^2 mol^{-1}; SI: κ/c with c in mol m^{-3}

KOHLRAUSCH'S LAW

$$\Lambda^{\circ}_m = \nu_+\lambda^{\circ}_+ + \nu_-\lambda^{\circ}_-$$

at infinite dilution each ion contributes independently; e.g. MX with 57 and 73: 130



Kohlrausch: for a weak electrolyte Λ°_m comes from ionic limiting values

TWO KINDS OF CURVE

- **Strong electrolyte** (KCl): a nearly straight line, $\Lambda_m = \Lambda^{\circ}_m - A\sqrt{c}$ (Debye-Hückel-Onsager); extrapolate to $\sqrt{c} = 0$ to read Λ°_m.
- **Weak electrolyte** (acetic acid): very steep rise at low concentration; it cannot be extrapolated, so find Λ°_m from Kohlrausch's law.
- The unusual mobility of H^+ and OH^- in water (proton hopping, Grotthuss mechanism) makes acids and bases the best conductors.

WEAK ELECTROLYTE

$$\alpha = \frac{\Lambda_m}{\Lambda^{\circ}_m}, \quad K_a = \frac{c\alpha^2}{1-\alpha}$$

conductance gives the degree of ionisation and then the acid constant

Λ°_m OF A WEAK ACID

$$\Lambda^{\circ}(\text{CH}_3\text{COOH}) = \Lambda^{\circ}(\text{CH}_3\text{COONa}) + \Lambda^{\circ}(\text{HCl}) - \Lambda^{\circ}(\text{NaCl})$$

$91.0 + 426.2 - 126.5 = 390.7$ S cm^2 mol^{-1} (NCERT values)

WHAT CHANGES ON DILUTION

QUANTITY	STRONG ELECTROLYTE	WEAK ELECTROLYTE
conductivity κ	falls (fewer ions per volume)	falls
molar conductivity Λ_m	rises slowly (less ionic attraction), towards Λ°_m	rises steeply (α increases)
degree of ionisation α	already 1	rises; $\alpha = \Lambda_m/\Lambda^{\circ}_m$
K_a	not applicable	constant (depends on T only)

TRAP

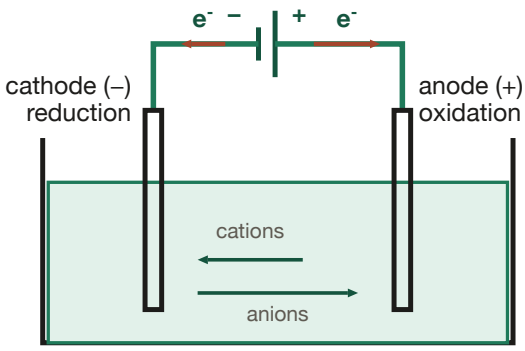
$\Lambda_m = \kappa \times 1000/M$ needs κ in S cm^{-1}; mixing metres and centimetres costs a factor of 100 per length. The cell constant is found with a solution of known κ (0.1 M KCl), $G^{*} = \kappa R$.

QUICK CHECK

A cell of constant 1.29 cm^{-1} reads 100 Ω for 0.1 M KCl. κ and Λ_m?

Answer: $\kappa = \frac{1.29}{100} = 0.0129$ S cm^{-1}; $\Lambda_m = \frac{0.0129 \times 1000}{0.1} = 129$ S cm^2 mol^{-1}.

6 Electrolysis, batteries and corrosion



in an electrolytic cell the cathode is negative and the anode positive: opposite to a galvanic cell

ELECTROLYTIC CELL A cell in which an external source drives a non-spontaneous reaction. The polarity is the reverse of a galvanic cell: the **cathode is negative** (reduction) and the **anode is positive** (oxidation); electrons are pushed from the battery to the cathode. The applied voltage must exceed the cell's own E.

FARADAY'S FIRST LAW

$$m = \frac{M\,I\,t}{n\,F} = Z\,I\,t$$

$Q = It$; Z = electrochemical equivalent; $F = 96500$ C mol^{-1} (one mole of electrons)

FARADAY'S SECOND LAW

$$\frac{m_1}{E_1} = \frac{m_2}{E_2}$$

same charge through cells in series; $E = M/n$ is the equivalent mass

PRODUCTS OF ELECTROLYSIS

ELECTROLYTE (ELECTRODES)	CATHODE	ANODE
molten NaCl	Na	$\mathrm{Cl_2}$
concentrated aqueous NaCl (brine)	$\mathrm{H_2}$ (and NaOH left)	$\mathrm{Cl_2}$ (water would give $\mathrm{O_2}$; chlorine wins by overpotential)
dilute $\mathrm{H_2SO_4}$ (Pt)	$\mathrm{H_2}$	$\mathrm{O_2}$
concentrated $\mathrm{H_2SO_4}$	$\mathrm{H_2}$	$\mathrm{S_2O_8^{2-}}$ (peroxodisulphate)
$\mathrm{CuSO_4}$ (inert electrodes)	Cu	$\mathrm{O_2}$ (solution turns acidic)
$\mathrm{CuSO_4}$ (copper electrodes)	Cu deposits	Cu dissolves (refining)
water, dilute $\mathrm{Na_2SO_4}$	$\mathrm{H_2}$	$\mathrm{O_2}$

CHARGE TO PRODUCT, IN STEPS

- Charge $Q = It$ (coulombs); moles of electrons $= Q/F$.
- Moles of product = moles of electrons $/\,n$ (electrons per formula); mass = moles $\times M$.
- 1 F liberates 11.2 L $\mathrm{H_2}$, 5.6 L $\mathrm{O_2}$, 11.2 L $\mathrm{Cl_2}$ at STP; 1 A for 1 h is 3600 C $= 0.0373$ F.

WHY IT WORKS

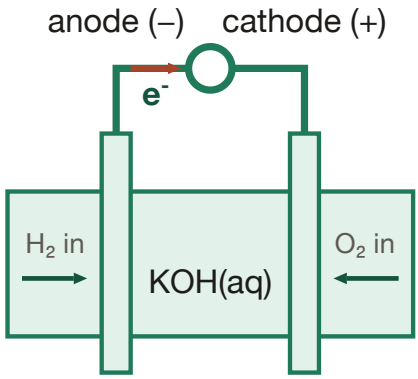
The ion that is easiest to discharge at each electrode wins. In water, $\mathrm{H_2O}$ can also be reduced or oxidised; ions of metals above $\mathrm{H_2}$ on the series (Na, K, Ca, Al) stay in solution and $\mathrm{H_2}$ forms instead. Overpotential explains why $\mathrm{Cl^-}$ beats water at the anode in brine.

BATTERIES AND FUEL CELLS

CELL	ANODE (OXIDATION)	CATHODE (REDUCTION)
Daniell	$\mathrm{Zn \longrightarrow Zn^{2+} + 2\,e^-}$	$\mathrm{Cu^{2+} + 2\,e^- \longrightarrow Cu}$
dry (Leclanché)	$\mathrm{Zn \longrightarrow Zn^{2+} + 2\,e^-}$	$\mathrm{MnO_2}$ with $\mathrm{NH_4^+}$ reduced to $\mathrm{MnO(OH)}$ and $\mathrm{NH_3}$
mercury	$\mathrm{Zn(Hg) + 2\,OH^- \longrightarrow ZnO + H_2O + 2\,e^-}$	$\mathrm{HgO + H_2O + 2\,e^- \longrightarrow Hg + 2\,OH^-}$
lead storage	$\mathrm{Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2\,e^-}$	$\mathrm{PbO_2 + SO_4^{2-} + 4\,H^+ + 2\,e^- \longrightarrow PbSO_4 + 2\,H_2O}$
$\mathrm{H_2}$-$\mathrm{O_2}$ fuel cell	$\mathrm{2\,H_2 + 4\,OH^- \longrightarrow 4\,H_2O + 4\,e^-}$	$\mathrm{O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^-}$

NOTES ON EACH CELL

- **Primary** cells (dry, mercury) cannot be recharged; **secondary** cells (lead storage, Ni-Cd) can, by reversing the reaction with an external current.
- Dry cell: about 1.5 V, falls with use. Mercury cell: 1.35 V and constant, because no ion in the electrolyte changes in the overall reaction ($\mathrm{Zn + HgO \longrightarrow ZnO + Hg}$); watches and hearing aids.
- Lead storage: overall $\mathrm{Pb + PbO_2 + 2\,H_2SO_4 \longrightarrow 2\,PbSO_4 + 2\,H_2O}$; the $\mathrm{H_2SO_4}$ (about 38%) is used up on discharge, so its density falls and shows the state of charge.
- Fuel cell: overall $\mathrm{2\,H_2 + O_2 \longrightarrow 2\,H_2O}$, $E^\circ = 1.23$ V; reactants are fed in continuously, no storage, efficiency about 70%; used on the Apollo missions.



anode:
$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$
cathode:
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
overall $2H_2 + O_2 \rightarrow 2H_2O$; $E^\circ = 1.23$ V

CORROSION OF IRON

- An electrochemical process: anode $\mathrm{Fe \longrightarrow Fe^{2+} + 2\,e^-}$; cathode $\mathrm{O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O}$; then $\mathrm{Fe^{2+}}$ oxidises to rust, $\mathrm{Fe_2O_3 \cdot \mathit{x}\,H_2O}$.
- It needs both water and oxygen, and is quicker in acidic or salty water.
- Prevention: paint, galvanising (zinc coat, which protects even when scratched), sacrificial anodes of Mg or Zn, tin plating (only while intact).

SYLLABUS NOTE

Corrosion and Faraday's laws may fall outside the recalled syllabus list for the current session; they are included because past papers test electrolysis. Secondary cells are rechargeable (lead storage, Ni-Cd); primary cells are not.

QUICK CHECK

Mass of copper deposited by 2 A for 30 min ($M = 63.5$)?

Answer: $Q = 3600$ C; $m = \dfrac{63.5 \times 3600}{2 \times 96500} = 1.18$ g.

7 Worked examples

MOLES OF $\mathrm{H^+}$

Moles of $\mathrm{H^+}$ needed by 1 mol $\mathrm{MnO_4^-}$ to oxidise oxalate to $\mathrm{CO_2}$?

$\mathrm{2\,MnO_4^- + 5\,C_2O_4^{2-} + 16\,H^+ \longrightarrow 2\,Mn^{2+} + 10\,CO_2 + 8\,H_2O}$: $16/2 = 8$

DISPROPORTIONATION

Which are disproportionations: (1) $\mathrm{2\,Cu^+ \longrightarrow Cu^{2+} + Cu}$ (2) $\mathrm{3\,MnO_4^{2-} + 4\,H^+ \longrightarrow 2\,MnO_4^- + MnO_2 + 2\,H_2O}$ (3) $\mathrm{2\,KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2}$?

(1) Cu: $+1 \rightarrow +2, 0$ yes. (2) Mn: $+6 \rightarrow +7, +4$ yes. (3) Mn $+7 \rightarrow +6, +4$ and O is oxidised: Mn is only reduced; not a disproportionation of one element

NERNST

E of $\mathrm{Zn} \mid \mathrm{Zn}^{2+}(0.01) \,||\, \mathrm{Cu}^{2+}(1.0) \mid \mathrm{Cu}$?

$E = 1.10 - \dfrac{0.0591}{2} \log \dfrac{0.01}{1.0} = 1.10 + 0.0591 = 1.159$ V

HYDROGEN ELECTRODE

Potential of a hydrogen electrode at pH 4, $p_{\mathrm{H_2}} = 1$ bar?

$E = -0.0591 \times 4 = -0.236$ V

CONCENTRATION CELL

Cu electrodes in 0.1 M and 0.001 M Cu^{2+}. EMF?

$E = \dfrac{0.0591}{2} \log \dfrac{0.1}{0.001} = 0.0591$ V (the dilute side is the anode)

WEAK ACID

0.001 M acetic acid has $\Lambda_m = 41$ S cm^2 mol^{-1} ($\Lambda_m^\circ = 390.7$). α and K_a?

$\alpha = \dfrac{41}{390.7} = 0.105$; $K_a = \dfrac{c\alpha^2}{1-\alpha} = \dfrac{0.001 \times 0.0110}{0.895} = 1.2 \times 10^{-5}$

FARADAY

Silver deposited by 9650 C through $\mathrm{AgNO_3}$ ($M = 108$)?

$\dfrac{9650}{96500} = 0.1$ mol $\mathrm{e^-}$, 0.1 mol $\mathrm{Ag} = 10.8$ g

SERIES CELLS

The same current deposits 1.08 g of Ag and some Cu (63.5, Cu^{2+}). Mass of Cu?

$\dfrac{m_{Cu}}{31.75} = \dfrac{1.08}{108}$, $m_{Cu} = 0.3175$ g

NON-ADDITIVE E°

$E^\circ(\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}) = 0.77$ and $E^\circ(\mathrm{Fe}^{2+}/\mathrm{Fe}) = -0.44$ V. $E^\circ(\mathrm{Fe}^{3+}/\mathrm{Fe})$?

$\dfrac{1(0.77) + 2(-0.44)}{3} = -0.037$ V

OXIDATION NUMBER

Average oxidation number of Fe in $\mathrm{Fe_3O_4}$ and of S in $\mathrm{S_4O_6^{2-}}$?

Fe: $\dfrac{8}{3}$; S: $\dfrac{-2+12}{4} = +2.5$

8 Last-minute checklist

BEFORE YOU ANSWER

Both potentials as reduction potentials? n from the balanced equation? Is it a galvanic cell (cathode $+$) or electrolytic (cathode $-$)? Units of κ and M?

- Oxidation is loss, reduction gain; $\sum$ oxidation numbers = charge; disproportionation needs an intermediate state; n_f of $\mathrm{KMnO_4}$ is $5, 3, 1$, of $\mathrm{K_2Cr_2O_7}$ 6; $N_1V_1 = N_2V_2$.
- $E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$; positive is spontaneous; $E = E^\circ - \dfrac{0.0591}{n} \log Q$; $\Delta G = -nFE$; $\log K = nE^\circ/0.0591$.
- Concentration cell $E = \dfrac{0.0591}{n} \log(C_c/C_a)$; hydrogen electrode $-0.0591\,pH$; $E_3^\circ = (n_1E_1 + n_2E_2)/n_3$.
- $\kappa = G\,G^*$; $\Lambda_m = 1000\kappa/M$; $\Lambda_m^\circ = \nu_+\lambda_+^\circ + \nu_-\lambda_-^\circ$; $\alpha = \Lambda_m/\Lambda_m^\circ$; κ falls and Λ_m rises on dilution.
- $m = MIt/nF$; 1 F $= 96500$ C; same charge: $m \propto$ equivalent mass; brine gives $\mathrm{H_2}$ and $\mathrm{Cl_2}$; dilute $\mathrm{H_2SO_4}$ gives $\mathrm{H_2}$ and $\mathrm{O_2}$.
- Lead storage: Pb anode, $\mathrm{PbO_2}$ cathode, $\mathrm{PbSO_4}$ both; fuel cell $2\,\mathrm{H_2} + \mathrm{O_2} \longrightarrow 2\,\mathrm{H_2O}$; rust needs $\mathrm{O_2}$ and water.

Now test it. Practise this chapter with past-paper and bank questions on Prep Vault. **Practice this chapter →**