Unit 5 · Electrochemistry

STUDY NOTES

WHAT NEB'S GRADE 12 EXAM ASKS

- **CDC's grid (2078):** Physical Chemistry (Units 1–5 together): 22 of 75 marks; 4 MCQs, 2 short and 1 long question
- **The paper:** 11 MCQs × 1 · 8 short × 5 · 3 long × 8; 3 hours; 1 mark per expected point
- **CDC's model paper:** MCQ: what happens as a lead storage battery discharges (H_2SO_4 used up); long (OR): the Cu–Ag cell from $E°(Cu^{2+}/Cu) = +0.34$ V and $E°(Ag^{+}/Ag) = +0.80$ V: cell notation, E°cell, ΔG°, can $AgNO_3$ be kept in a copper vessel
- **MCQ (1 mark)**
  - electrode potential; standard conditions; SHE = 0 V; calomel as a secondary reference
  - series order; highest E°; which metal displaces Cu; cathode reaction and E° of Zn–Cu
  - E°cell positive → spontaneous; $\Delta G = -nFE$; lead-acid electrolyte; Li-ion in phones; fuel cell gives water; sacrificial metal
- **Short (5 marks, in parts)**
  - define standard electrode potential; describe the SHE and how it gives E° of zinc
  - better reducing agent from E° (Na, Au); can Au^{3+} oxidize Na; why gold is found free
  - corrosion in salt water; Al or Zn as a sacrificial anode and its half-reaction
  - a cell from two half-cells (Ni–Cr, Zn–Fe, Mg–Ni): anode, cathode, notation, reaction, E°cell, ΔG°, effect of concentration
  - no voltage from a cell: reasons; the salt bridge; activity series from displacement data (P–T)
- **Long (8 marks)**: a galvanic cell in full: notation, E°cell, ΔG°, spontaneity, a storage question ($AgNO_3$ in Cu, $ZnSO_4$ in Al); fuel cell reactions and ΔG°

Key terms

Electrochemistry: relation between electrical energy and chemical (redox) reactions.

Electrolytic cell: outside current drives a **non-spontaneous** reaction; electrical → chemical.

Galvanic (voltaic) cell: **spontaneous** redox reaction gives a current; chemical → electrical; two half-cells.

Electrical double layer: charge on the metal + opposite ions held beside it in the solution.

Electrode potential: potential difference between a metal and its ions' solution at their surface; can't be measured alone.

Standard electrode potential E°: electrode potential at 1 mol/L, 298 K, 1 atm, against the SHE (0 V); written as a **reduction** potential.

Reference electrode: one of known potential to measure others against: SHE (primary), calomel (secondary).

Electrochemical series: electrodes in order of standard reduction potential.

Cell potential (e.m.f.): potential difference between the two electrodes with no current drawn; the driving force.

Salt bridge: inert electrolyte (KCl, KNO_3 in agar) joining the half-cells.

Primary battery: used once (dry cell); **secondary**: rechargeable (lead-acid, Ni–Cd); **fuel cell**: fed with fuel and O_2, never run down.

Formulas

$E°_{cell} = E°(\text{cathode}) - E°(\text{anode})$	both **reduction** potentials **Use:** cell voltage
$E_{cell} = E°_{cell} - \frac{0.0592}{n} \log Q$	25 °C; Q from concentrations, solids left out **Use:** Nernst, away from 1 M
$\Delta G = -nFE_{cell}$	F = 96,485 C/mol; n mol electrons **Use:** free energy
$w_{max} = nFE_{cell} = -\Delta G$	J **Use:** maximum work

- E°cell > 0 ⇔ ΔG° < 0: spontaneous, gives a current; 0: equilibrium (flat); < 0: only if driven
- doubling an equation doubles n and ΔG, not E°
- Daniell: 0.34 − (−0.76) = **1.10 V**; Cu–Ag: 0.80 − 0.34 = **0.46 V**
- Daniell $\Delta G° = -2 \times 96{,}485 \times 1.10 \approx -212$ kJ/mol
- tenfold change in Q: a 2-electron cell changes by only 0.030 V

Electrode potential (5.1)

- Zn in Zn^{2+}: atoms leave as ions faster than ions plate → rod **negative**
- Cu in Cu^{2+}: ions plate faster → rod **positive**, SO_4^{2-} held against it
- $M(s) \rightleftharpoons M^{n+}(aq) + n\,e^-$ at equilibrium

Depends on

1. concentration of ions

2. temperature
3. nature of the metal

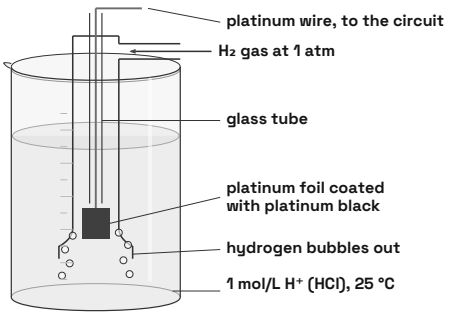
Standard conditions

- 1 mol/L ions
- 298 K (25 °C)
- gas at 1 atm
- **+E°**: reduced more readily than H^+ (Cu^{2+}/Cu +0.34 V)
- **−E°**: oxidized more readily than H_2 (Zn^{2+}/Zn −0.76 V)
- older **oxidation** potentials have the opposite sign (Zn +0.76 V)

Reference electrodes (5.2)

Standard hydrogen electrode (SHE): Pt foil coated with platinum black, in acid with $[H^+] = 1$ mol/L (HCl), pure H_2 at 1 atm bubbled over it, 25 °C; Pt only a surface and contact

$$2\,H^+(aq) + 2\,e^- \rightleftharpoons H_2(g) \qquad E^\circ = 0.00\ V$$



The standard hydrogen electrode.

- Zn vs SHE: reads 0.76 V, electrons leave Zn; Zn the anode: $0.76 = 0 - E(Zn) \rightarrow$ **−0.76 V**
- Cu vs SHE: reads 0.34 V, electrons into Cu; Cu the cathode: $0.34 = E(Cu) - 0 \rightarrow$ **+0.34 V**
- metal above H (negative E°) is the anode against the SHE; below H the cathode

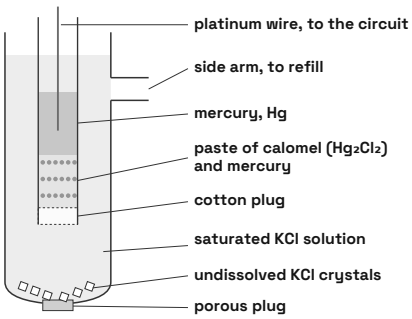
SHE's limits

1. pure H_2 and Pt: expensive
2. gas at exactly 1 atm all the time; Pt black poisoned by S, As, Hg compounds

Calomel electrode (secondary): Pt wire, Hg, paste of Hg + Hg_2Cl_2 (calomel), saturated KCl, porous plug; **SCE +0.241 V** at 298 K

$$Hg_2Cl_2(s) + 2\,e^- \rightleftharpoons 2\,Hg(l) + 2\,Cl^-(aq)$$

- potential fixed by $[Cl^-]$ (saturated KCl)
- reliable, easy to keep, no gas; toxic mercury
- Ag–AgCl (+0.197 V, saturated KCl): inside most pH meters



The saturated calomel electrode.

Electrochemical series (5.3)

Couple	E° (V)	Couple	E° (V)
Li^+/Li	−3.04	Pb^{2+}/Pb	−0.13
K^+/K	−2.93	$2H^+/H_2$	0.00
Ca^{2+}/Ca	−2.87	Sn^{4+}/Sn^{2+}	+0.15
Na^+/Na	−2.71	Cu^{2+}/Cu	+0.34
Mg^{2+}/Mg	−2.37	I_2/I^-	+0.54
Al^{3+}/Al	−1.66	Fe^{3+}/Fe^{2+}	+0.77
Zn^{2+}/Zn	−0.76	Ag^+/Ag	+0.80
Cr^{3+}/Cr	−0.74	Br_2/Br^-	+1.07
Fe^{2+}/Fe	−0.45	O_2/H_2O	+1.23
Cd^{2+}/Cd	−0.40	Cl_2/Cl^-	+1.36
Ni^{2+}/Ni	−0.26	Au^{3+}/Au	+1.50
Sn^{2+}/Sn	−0.14	F_2/F^-	+2.87

Uses

1. **agents**: highest E° strongest oxidizing agent (F_2); lowest strongest reducing agent (Li)
2. **cell voltage**: E°cathode − E°anode
3. **spontaneity**: higher E° must be the cathode, so E°cell > 0
4. **displacement**: a metal above displaces one below: $Zn + CuSO_4 \longrightarrow ZnSO_4 + Cu$
5. **corrosion**: metals at the top corrode most; a lower-E° metal as sacrificial anode
6. **electrolysis products**: cathode, highest E° reduced first (Cu^{2+} before water; water before Na^+); anode, easiest oxidized
7. **H_2 from acids**: only metals with negative E° (above H): $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$; Cu + dil. H_2SO_4: no reaction

- Fe^{3+}/Fe^{2+} (+0.77) with Sn^{4+}/Sn^{2+} (+0.15): Fe^{3+}/Fe^{2+} the cathode, $2\,Fe^{3+} + Sn^{2+} \longrightarrow 2\,Fe^{2+} + Sn^{4+}$, 0.62 V; inert Pt electrodes
- Au (+1.50 V): hardly oxidized, so found free; Au^{3+} oxidizes Na

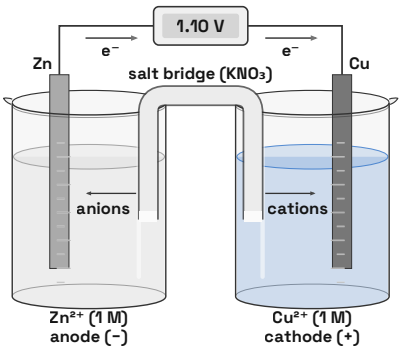
Corrosion: a cell on wet iron

- anode: $Fe \longrightarrow Fe^{2+} + 2\,e^-$
- cathode (edge of the drop, air): $O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^-$
- $Fe(OH)_2 \rightarrow$ rust, $Fe_2O_3 \cdot x\,H_2O$; needs water and air
- salt water conducts ions better → faster
- **sacrificial**: Zn blocks on ship hulls, Mg on pipelines (Al alloys too) corrode instead
- **galvanizing**: zinc coat; still protects where scratched

Galvanic cells (5.4)

Daniell cell (Zn–Cu), Daniell 1836

- anode (−): $Zn(s) \longrightarrow Zn^{2+}(aq) + 2\,e^-$
- cathode (+): $Cu^{2+}(aq) + 2\,e^- \longrightarrow Cu(s)$
- cell: $Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$
- electrons Zn → Cu in the wire; current Cu → Zn; Zn thins, Cu grows, blue fades



The Daniell cell: zinc anode (−), copper cathode (+), salt bridge.

Cell notation

$$\mathrm{Zn(s) \mid Zn^{2+}(aq, 1M) \parallel Cu^{2+}(aq, 1M) \mid Cu(s)}$$

- anode left, cathode right; electrons left → right
- single line: phase boundary; double line: salt bridge; concentrations in brackets
- no metal of its own (ions or gas): Pt at the end; SHE $\mathrm{Pt \mid H_2(g, 1atm) \mid H^+(aq, 1M)}$

Cu–Ag cell: Ag^+/Ag (+0.80) higher → Ag the cathode, Cu the anode

- $\mathrm{Cu \longrightarrow Cu^{2+} + 2\,e^-}$; $\mathrm{Ag^+ + e^- \longrightarrow Ag}$ (× 2)
- $\mathrm{Cu(s) + 2\,Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2\,Ag(s)}$
- $\mathrm{Cu \mid Cu^{2+}(1\,M) \parallel Ag^+(1\,M) \mid Ag}$; 0.46 V; E° not doubled
- so $AgNO_3$ can't be kept in copper: copper displaces silver
- copper: cathode against Zn, anode against Ag

Salt bridge

1. completes the circuit inside (ions move)
2. keeps the solutions from mixing (Cu^{2+} would plate on Zn)
3. keeps each half-cell **neutral**: anions to the Zn beaker, cations to the Cu beaker
4. keeps the liquid junction potential low (K^+, Cl^- or NO_3^- move at the same speed)

- anode always oxidation, cathode reduction; galvanic anode **−**, electrolytic anode **+**

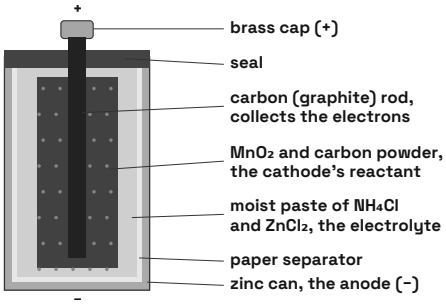
Cell potential and free energy (5.5, 5.6)

- E_{cell} changes with temperature, pressure (gas), concentration
- e.m.f. = E with no current; voltage under load a little less
- Daniell: $Q = [Zn^{2+}]/[Cu^{2+}]$: more Cu^{2+} → E up; more Zn^{2+} → E down; runs down until E = 0 (equilibrium)
- $w_{max} = nFE$ and $-\Delta G = w_{max} \rightarrow \Delta G = -nFE$; standard: $\Delta G^\circ = -nFE^\circ$

Batteries and fuel cells (5.7)

Dry (Leclanché) cell, primary, ~1.5 V: Zn can anode (−); graphite rod in MnO_2 + carbon, cathode (+); NH_4Cl + $ZnCl_2$ paste

- anode: $\mathrm{Zn \longrightarrow Zn^{2+} + 2\,e^-}$
- cathode: $\mathrm{2\,MnO_2 + 2\,NH_4^+ + 2\,e^- \longrightarrow Mn_2O_3 + 2\,NH_3 + H_2O}$
- $\mathrm{2\,MnO_2 + 2\,NH_4Cl + Zn \longrightarrow Mn_2O_3 + Zn(NH_3)_2Cl_2 + H_2O}$
- alkaline cell: KOH electrolyte, lasts longer



A dry cell cut in half.

Lead-acid (secondary), ~2 V a cell, six = 12 V: Pb anode, PbO_2 cathode, dil. H_2SO_4

- anode: $\mathrm{Pb + HSO_4^- \longrightarrow PbSO_4 + H^+ + 2\,e^-}$
- cathode: $\mathrm{PbO_2 + HSO_4^- + 3\,H^+ + 2\,e^- \longrightarrow PbSO_4 + 2\,H_2O}$
- $\mathrm{Pb + PbO_2 + 2\,HSO_4^- + 2\,H^+ \longrightarrow 2\,PbSO_4 + 2\,H_2O}$
- discharge: both plates → $PbSO_4$, **acid used up**, density falls (hydrometer); charging reverses it

Ni–Cd (secondary), ~1.2 V: NiO(OH) +, Cd −, KOH

- anode: $\mathrm{Cd + 2\,OH^- \longrightarrow Cd(OH)_2 + 2\,e^-}$
- cathode: $\mathrm{2\,NiO(OH) + 2\,H_2O + 2\,e^- \longrightarrow 2\,Ni(OH)_2 + 2\,OH^-}$
- $\mathrm{2\,NiO(OH) + Cd + 2\,H_2O \longrightarrow 2\,Ni(OH)_2 + Cd(OH)_2}$; Cd toxic: recycle

Li-ion (phones), ~3.7 V: $\mathrm{LiC_6 + CoO_2 \longrightarrow C_6 + LiCoO_2}$; Li lowest E° (−3.04 V) and light

H_2–O_2 fuel cell (alkaline, porous carbon + catalyst, hot conc. KOH)

- anode: $\mathrm{2\,H_2 + 4\,OH^- \longrightarrow 4\,H_2O + 4\,e^-}$
- cathode: $\mathrm{O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^-}$
- $\mathrm{2\,H_2 + O_2 \longrightarrow 2\,H_2O}$, E° = 1.23 V (0.7–1 V working); only water

COMMON MISTAKES

✗ E°cell = E°cathode + E°anode with reduction potentials
✓ cathode **minus** anode (plus only with the anode's oxidation potential).

✗ every metal is negative against its solution
✓ copper in Cu^{2+} is positive.

✗ doubling the silver half-reaction doubles its E°
✓ E° stays +0.80 V.

✗ the anode is always negative
✓ negative in a galvanic cell, positive in an electrolytic one.

✗ Fe^{3+}/Fe^{2+} half-cell with an iron rod
✓ an inert Pt electrode.

✗ water is reduced at −0.83 V in neutral solution
✓ about −0.41 V (−0.83 V in 1 M alkali).

✗ Apollo's fuel cell gave 27–31 V a cell
✓ 27–31 V for 31 cells, under 1 V each.