Electrochemistry

Galvanic cells, E°cell, the Nernst equation, electrolysis, and the E-ΔG-K triangle.

01 Building a galvanic cell — CORE RULE

Reverse the half-reaction with the more negative standard reduction potential (it becomes the oxidation/anode) so E°cell comes out positive.

02 E°cell — CORE RULE

E°cell = E°(cathode) − E°(anode), both as reduction potentials. Multiplying a half-reaction by a coefficient does NOT change its potential.

03 Cell notation — CORE RULE

anode | anode ion || cathode ion | cathode. Oxidation on the left; no coefficients. Use an inert Pt electrode when neither side is a conducting solid.

04 Nernst equation — CORE RULE

$E = E° - (0.0592/n) \log Q$ at 25 °C (n = electrons transferred, Q = products/reactants). Use it for any non-standard concentration or pressure.

05 pH from cell voltage — CORE RULE

Put the measured E into the Nernst equation, solve for $[H^+]$, then $pH = -\log[H^+]$.

06 Charge & Faraday — CORE RULE

Charge (C) = current(A) × time(s) (convert h/min to s). Moles of e^- = charge / F, with F = 96,485 C/mol e^-.

07 Electrolysis stoichiometry — METHOD

For $M^{n+} + ne^- \rightarrow M$: mol metal = mol e^- / n. Convert that to mass with molar mass to finish a deposition problem.

08 ΔG° = −nFE°cell — CORE RULE

$\Delta G° = -nFE°_{cell}$. $E°_{cell} > 0 \leftrightarrow \Delta G° < 0$ (spontaneous galvanic); $E°_{cell} < 0 \leftrightarrow \Delta G° > 0$ (electrolytic if driven). n = e^- per balanced reaction.

09 K from E°cell — CORE RULE

$\ln K = nFE°_{cell}/(RT)$, or $\log K = nFE°_{cell}/(2.303RT)$. $E°_{cell} > 0 \rightarrow K > 1$. Together with $\Delta G° = -RT \ln K$ this closes the $E°_{cell} \leftrightarrow \Delta G° \leftrightarrow K$ triangle.

10 Concentration cells — CORE RULE

Same chemistry, different [ion], so E° = 0 and $E = -(0.0592/n) \log Q$. Write Q from the balanced overall reaction (M^{n+}: Q = [anode]/[cathode]). At equal concentrations Q = 1, E = 0.

The low-[ion] half-cell is the anode (its concentration rises); the high-[ion] half-cell is the cathode (falls). Electrons flow anode → cathode until concentrations equalize.