

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

$E^\circ_{\text{cell}} = E^\circ(\text{cathode}) - E^\circ(\text{anode})$, 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

$E = E^\circ - (0.0592/n) \log Q$ 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) $\times$ time(s) (convert h/min to s). Moles of e^- = charge / F , with $F = 96,485 \text{ C/mol } e^-$.

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 $\Delta G^\circ = -nFE^\circ_{\text{cell}}$

CORE RULE

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

09 K from E°_{cell}

CORE RULE

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

10 Concentration cells

CORE RULE

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