I. Electrochemical cells:
   a) galvanic or Voltaic cells:
      • spontaneous redox reactions ($\varepsilon^o > 0$; $\Delta G^o < 0$)
      • chemical energy → electrical energy
      • concentration cells (entropy driven)
      • batteries (Pb/PbO$_2$; Zn/NH$_4$Cl(MnO$_2$); Zn/MnO$_2$; Cd/NiO$_2$; Zn/HgO)
      • fuel cells (2H$_2$ + O$_2$ → 2H$_2$O; oxidation of 'organic' compounds)
      • corrosion (passive prevention: paint, coating, galvanization; active: cathodic (Mg, Ti)
   b) electrolytic cell:
      • non-spontaneous redox reactions ($\varepsilon^o < 0$; $\Delta G^o > 0$) – need external work to make it happen
      • electrical energy → chemical energy
      • battery recharging (requires reversible phase changes: Pb/PbO$_2$; Cd/NiO$_2$ alkaline battery)
      • metal separation, isolation and synthesis (Cu/Au; aluminum)
      (compare to separation of metal ions based on their solubility)
      • plating objects (Cr, Pt)

II. Electrolysis:
   • Zn metal in CuSO$_4$ solution →
      A: Zn$(s)$ → Zn$^{2+}$ + 2 e$^-$ $\varepsilon^o = 0.76$ V
      C: Cu$^{2+}$ + 2 e$^-$ → Cu$(s)$ $\varepsilon^o = 0.34$ V $\varepsilon_{cell}^o = 1.1$ V Cu deposit
      $\Delta G^o = -2$ moles 96.5 kC/moles 1.1 J/C = -212.3 kJ formation
      Zn is less noble than Cu
   • Ag metal in CuSO$_4$ solution →
      A: Ag$(s)$ → Ag$^+$ + e$^-$ $\varepsilon^o = -0.80$ V
      C: Cu$^{2+}$ + 2 e$^-$ → Cu$(s)$ $\varepsilon^o = 0.34$ V $\varepsilon_{cell}^o = -0.56$ V no deposit
      $\Delta G^o = -2$ moles 96.5 kC/moles (-0.56 J/C) = 108.1 kJ formation
      Ag is more noble than Cu
      add an additional Ag electrode (cathode) with external potential $U > 0.56$ V → reaction becomes spontaneous → Cu$(s)$ deposit formation
      turn off the external power source → Cu$(s)$ deposit will disappear
   • Ag metal in electrolyte solution →
      A: Ag → Ag$^+$ + e$^-$ with external potential Ag oxidizes on anode
      C: Ag$^+$ + e$^-$ → Ag and Ag$^+$ reduces on cathode electrodes
   • Careful with the external potential!
      - Electrolysis of aqueous solution of CrCl$_3$
        cathode reaction: Cr$^{3+}$ + 3 e$^-$ → Cr $\varepsilon^o = -0.73$ V
        anode reaction: 2 Cl$^-$ → Cl$_2$ + 2 e$^-$ $\varepsilon^o = -1.36$ V
        4 Cr$^{3+}$ + 6 Cl$^-$ → 3 Cl$_2$ + 4 Cr $\varepsilon_{cell}^o = -2.09$ V $U_{ext} > 2.09$ V Cl$_2$ starts to evolve
      - object to be plated with Cr needs to conduct electricity
        1. object has Al → Al$^{3+}$ + 3 e$^-$ $\varepsilon^o = 1.66$ V spontaneous Cr deposition
           external voltage = 0 already work
        2. object has Fe → Fe$^{2+}$ + 2 e$^-$ $\varepsilon^o = 0.44$ V
           external voltage > 0.39 V; $\Delta G^o$ is already negative
           odorless gas evolves, O$_2$
           2 H$_2$O → O$_2$ + 4H$^+$ + 4 e$^-$ $\varepsilon^o = -1.23$ V
• Quantitative treatment of electrolysis
  ♦ external potential in the right range drives the reaction
  ♦ current \([A] = \text{flow of charge per unit time } [\text{Coulomb}]/[\text{second}]
  ♦ quantity of charge flow in Coulomb → Faraday constant → moles of electrons
  ♦ from stoichiometry, molar ratios of formed/consumed products/reactants can be determined

III. Application of electrolysis:
  • water electrolysis
    anode: \(2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4 \text{e}^-\) \(-\varepsilon^\circ = -1.23 \text{ V}\)
    cathode: \(4\text{H}_2\text{O} + 4 \text{e}^- \rightarrow 2 \text{H}_2 + 4 \text{OH}^-\) \(\varepsilon^\circ = -0.83 \text{ V}\)
    \(\varepsilon_{\text{cell}} = -2.06 \text{ V}\)
  ♦ 6 V battery attached to electrodes immersed in pure water, nothing happens! \(6 \text{ V} < 2.06 \text{ V} \) ???
  ♦ pure water has pH = 7.0 \([\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7}\) → far from standard conditions of 1 M
  ♦ overall reaction \(6 \text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2 + 4 \text{H}^+ + 4 \text{OH}^-\)
    \(Q = [\text{H}^+]^4[\text{OH}^-]^4 = K_w^4\)
    \(\varepsilon = \varepsilon^\circ - 0.06/n \log Q = -2.06 \text{ V} - 0.06/4 \log 10^{-56} = -1.22 \text{ V}\)
    \(6 \text{ V} < 1.22 \text{ V} \) ???
  ♦ pure water has very few ions → not a good electrolyte → no salt bridge
  ♦ add a small amount of soluble electrolyte (salt – which cation/anion?) → \(\text{H}_2, \text{O}_2\) generations
    starts instantaneously
  • electrolysis of mixture of ions (\(\text{Na}^+, \text{Al}^{3+}, \text{Fe}^{2+}, \text{Cu}^{2+}, \text{Ag}^+, \text{Au}^{3+}\))
    ♦ need to order ions by reduction potentials → the most positive will occur at the lowest potential first → layered plating from one solution
  • aluminum production
    ♦ Hall-Heroult process: molten \(\text{Al}_2\text{O}_3\) (bauxite)/\(\text{Na}_3\text{AlF}_6\) (cryolite) at 1000 °C
    ♦ Why molten and not aqueous solution?
      \(\text{Al}^{3+} + 3 \text{e}^- \rightarrow \text{Al}\) \(-\varepsilon^\circ = -1.66 \text{ V}\)
      competes with and looses against
      \(2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-\) \(-\varepsilon^\circ = -0.83 \text{ V}\)
      a less negative reduction potential
    ♦ Melting point (\(\text{Al}_2\text{O}_3\)) \~ 2050 °C, but with \(\text{Na}_3\text{AlF}_6\) melting point depression down to 1000 °C
      in addition to formation of \([\text{Al}_2\text{OF}_6]^{2-}\)
    ♦ anode: \([\text{Al}_2\text{OF}_6]^{2-} + 12 \text{F}^- + \text{C} \rightarrow 4 [\text{AlF}_6]^{3-} + \text{CO}_2 + 4 \text{e}^-\)
    ♦ cathode: \([\text{AlF}_6]^{3-} + 3 \text{e}^- \rightarrow \text{Al} + 6 \text{F}^-\) (current 250 000 A)
  • sodium chloride electrolysis – Downs cell, Chlor-Alkali process
    ♦ \(\text{NaCl/CaCl}_2\) molten electrolysis – m.p. depression
    ♦ anode: \(2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2 \text{e}^-\) \(-\varepsilon^\circ = -1.36 \text{ V}\)
      \(\text{Cl}_2\) bubbles through molten salt
    ♦ cathode: \(\text{Na}^+ + \text{e}^- \rightarrow \text{Na}\) \(-\varepsilon^\circ = -2.71 \text{ V}\)
      melted Na is taken from the bottom
    ♦ \(\text{NaCl}\) solution electrolysis with mercury anode/cathode electrodes:
    ♦ anode: \(2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2 \text{e}^-\) \(-\varepsilon^\circ = -1.36 \text{ V}\)
      \(\text{Cl}_2\) bubbles through aqueous solution
    since \(\text{H}_2\) evolution on \(\text{Hg}\) has a very high overpotential (reaction rate and mass transfer rates are comparable – limited solvation of the \(\text{Hg}\) electrode) – no water reduction reaction
    \(\text{Na}^+ + \text{e}^- \rightarrow \text{Na}\) \(-\varepsilon^\circ = -2.71 \text{ V}\)
      Na froms amalgam with \(\text{Hg}\)
  • \(\text{NaHg}\) amalgam is reacted with water to form \(\text{NaOH}\) and \(\text{H}_2\) at the cathode electrode.