
Chapter 2. Section 1. Introduction & examples.

Example 2.1:
Write a suitable diagram of a cell in which the following overall reaction occurs (in aqueous solution):

\[ 2\text{MnO}_4^- + 5\text{Sn}^{2+} + 16\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{Sn}^{4+} + 8\text{H}_2\text{O} \]  
(2.8)

Solution:
The reaction (as written) suggests the permanganate is the oxidant (undergoes reduction) and tin (II) is the reductant (undergoes oxidation). Hence, the Sn^{4+}/Sn^{2+} redox couple should be placed at the left side (oxidation \rightarrow anode).

\[
\text{Pt} | \text{Sn}^{4+} (a_q, a_1), \text{Sn}^{2+} (a_q, a_2) | \text{MnO}_4^- (a_q, a_3), \text{Mn}^{2+} (a_q, a_4), \text{H}^+ (a_q, a_5) | \text{Pt}
\]  
(2.9)

Example 2.2:
Design a cell diagram in which the following overall reaction occurs in aqueous solution:

\[ \text{AgCl(s)} \rightleftharpoons \text{Ag}^{+} (a_q) + \text{Cl}^- (a_q) \]  
(2.10)

Solution:
The reaction can be "decomposed" into two reactions (each one temporarily written as reduction):

\[
\text{Ag}^{+} (a_q) + e^- \rightarrow \text{Ag(s)}
\]  
(2.11)

\[
\text{AgCl(s)} + e^- \rightarrow \text{Ag(s)} + \text{Cl}^- (a_q)
\]  
(2.12)

One can handle the electrochemical reactions in a way analogous to that utilized when one treats thermochemical reactions using the Hess's law. However, one doesn't multiply the potentials when the reaction (stoichiometric coefficients) is multiplied. In the above case, one can reverse the first reaction and add both of them. The outcome is exactly reaction (2.10), as desired. The scheme suggests then, reaction (2.11) to be oxidation (anodic) and reaction (2.12) to be reduction. Therefore, the following scheme should be the solution to the problem:

\[
\text{Ag} | \text{AgCl(s)} | \text{Cl}^- (a_q) || \text{Ag}^{+} (a_q) | \text{Ag}
\]  
(2.13)

Example 2.3:
Calculate the standard cell potential of the Daniell cell, in which reaction (2.2) occurs (scheme (2.6)), if the standard free energy of this reaction is equal to –212 kJ.

Solution:

\[
E_{\text{cell}}^0 = \frac{-\Delta G^0}{nF} = \frac{-212000[J]}{2 \cdot 96500[C]} = 1.10[V]
\]

Example 2.4:
Calculate the standard cell potential of the Daniell cell (scheme (2.6)), in which reaction (2.2) occurs, from the standard potentials of the half-reactions.

Solution:

One can utilize equation (2.15):

\[
E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = 0.34 - (-0.76) = 1.10[V]
\]

Example 2.5:
Calculate the equilibrium constant (solubility product) for reaction (2.10); scheme (2.13), if standard reduction potentials for reactions (2.11) and (2.12) are equal to +0.80 and +0.22 V at 298 K, respectively.
Solution:

Step A. The standard cell (2.13) potential, corresponding to reaction (2.10) is equal to:

\[ E^0 = 0.22 - 0.80 = -0.58 \text{[V]} \]

from equation (2.15).

Step B. We utilize equation (2.21)

\[ K = \exp\left(\frac{nF}{RT}E^0_{\text{cell}}\right) = \exp\left(\frac{96500}{8.314 \cdot 298}(-0.58)\right) = 1.55 \times 10^{-10} \]

which value is quite satisfactory. From the value of \( E^0 = -0.58 \text{ [V]} \) one can come to conclusion that under standard conditions the reaction is not spontaneous (the cell will not be a galvanic one at standard conditions).
Chapter 2. Section 2. Solved problems.

Problem 2.1.

Write the half-reaction occurring at each of the following electrodes and corresponding conventional redox couple notations:

a) \(\text{Pt}|\text{O}_2(g)|\text{H}^+|\text{H}_2\text{O}\);  
b) \(\text{Cd}|\text{Cd}^{2+}|\text{aq}\);  
c) \(\text{I}^-|\text{AgI(s)}||\text{Ag}\);  
d) \(\text{OH}^-|\text{Cd(OH)}_2(s)|\text{Cd}\)

Solution:

a) \(2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-\) 
\(\text{O}_2|\text{H}^+/\text{H}_2\text{O}\)

b) \(\text{Cd}^0 \rightarrow \text{Cd}^{2+} + 2\text{e}^-\)  
\(\text{Cd}^{2+/\text{Cd}}\)

c) \(\text{Ag}^0 + \text{I}^- \rightarrow \text{AgI} + \text{e}^-\) or rather \(\text{AgI} + \text{e}^- \rightarrow \text{Ag}^0 + \text{I}^-\) (the electrode is written as the right one)  
\(\text{AgI}/\text{Ag},\text{I}^-\)

d) \(\text{Cd(OH)}_2 + 2\text{e}^- \rightarrow \text{Cd}^0 + 2\text{OH}^-\) (same rule as c))  
\(\text{Cd(OH)}_2/\text{Cd},\text{OH}^-\)

Problem 2.2.

Write the half-reaction and the electrode notation (both as reduction) for the following systems:

a) barium metal in contact with aqueous solution containing \(\text{Ba}^{2+}\) ions;  
b) platinum wire immersed in alkaline aqueous solution in contact with gaseous oxygen;  
c) platinum foil immersed in aqueous solution containing chloride ions in contact with chlorine gas;  
d) mercury covered with calomel in contact with chloride ions in contact with chlorine gas.

Solution:

a) \(\text{Ba}^{2+} + 2\text{e}^- \rightarrow \text{Ba}^0\);  
\(\text{Ba}^{2+}(aq)|\text{Ba}\)

b) \(\text{O}_2 + 4\text{e}^- + 2\text{H}_2\text{O} \rightarrow 4\text{OH}^-\);  
\(\text{OH}^-|\text{aq}|\text{O}_2(g)|\text{Pt}\)

c) \(\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-\);  
\(\text{Cl}^-(aq)|\text{Cl}_2(g)|\text{graphite}\)

d) \(\text{Hg}_2\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Hg}^0 + 2\text{Cl}^-\);  
\(\text{Cl}^-(aq)|\text{Hg}_2\text{Cl}_2(s)|\text{Hg}\)

Problem 2.3.

Write both half-reactions, the overall cell reaction, and the corresponding cell diagram for the reactions described below:

a) oxidation of iodide ions by ozone in acidic solution;  
b) reduction of hydrogen peroxide by metallic mercury in presence of hydrochloric acid;  
c) \(\text{Sn}^{2+}\) ions in contact with \(\text{MnO}_2\) in acidic solution;  
d) thiosulfate mixed with solution of iodine (the latter in the excess of iodide);  
e) dissociation of silver bromide.

Solution:

a) \(\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{O}_2 + \text{H}_2\text{O}\) 
\(3\text{I}^- \rightarrow \text{I}_3^- + 2\text{e}^-\)  
\(\text{O}_3 + 2\text{H}_2\text{O} + \text{I}_3^- \rightarrow \text{O}_2 + \text{H}_2\text{O} + 3\text{I}^-\)  
\(\text{Pt}|\text{O}_3(g),\text{O}_2(g)|\text{H}^+|\text{aq})||\text{I}^-(aq),\text{I}_3^-(aq)|\text{Pt}\)

b) \(\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O}\)  
\(2\text{Hg}^0 + 2\text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2 + 2\text{e}^-\)  
\(\text{H}_2\text{O}_2 + 2\text{H}_2\text{O} + \text{Hg}_2\text{Cl}_2 \rightarrow 2\text{H}_2\text{O} + \text{Hg}_2\text{Cl}_2\)  
\(\text{Hg}|\text{Hg}_2\text{Cl}_2(s)|\text{Cl}^-(aq)|\text{H}^+(aq),\text{H}_2\text{O}_2(aq)|\text{Pt}\)
Problem 2.4.

Write both half-reactions and the overall reaction for the galvanic cells given by following diagrams:

a) Pt|H₂(g)|H⁺(aq)||H⁺(aq)|O₂(g)|Pt
b) Pt|CO₂(g)|CH₃OH(aq),H⁺(aq)||H⁺(aq)|O₂(g)|Pt
c) Pt|MnO₂(s)||H⁺(aq)|Sn⁺⁺(aq),Sn⁴⁺(aq)||Pt
d) Pt|Cl₂(g)||Cl⁻(aq)||H⁺(aq),MnO₄⁻(aq),Mn²⁺(aq)||Pt

d) I₃⁻ + 2e⁻ → 3I⁻
2S₂O₃²⁻ → S₄O₆²⁻ + 2e⁻
I₃⁻ + 2S₂O₃²⁻ → 3I⁻ + S₄O₆²⁻
Pt|S₂O₃²⁻(aq),S₄O₆²⁻(aq)||I₃⁻(aq),I⁻(aq)||Pt

e) Ag⁺(aq) + e⁻ → Ag(s)
Ag(s) + Br⁻(aq) → AgBr(s) + e⁻
AgBr(s) → Ag⁺(aq) + Br⁻(aq)
Ag|AgBr(s)|Br⁻(aq)||Ag⁺(aq)|Ag

Solution:

a) O₂ + 4e⁻ + 4H⁺ → 2H₂O
2H₂ → 4H⁺ + 4e⁻
2H₂ + O₂ → 2H₂O
b) 3/2O₂ + 6H⁺ + 6e⁻ → 3H₂O
CH₃OH + H₂O → CO₂ + 6H⁺ + 6e⁻
CH₃OH + 3/2O₂ → CO₂ + 2H₂O

Cases a) and b) are so called fuel cells.

c) 2MnO₄⁻(aq) + 8H⁺(aq) + 10e⁻ → 2Mn²⁺(aq) + 4H₂O(l)
10Cl⁻(s) → 5Cl₂(g) + 10e⁻
2MnO₄⁻(aq) + 8H⁺(aq) + 10Cl⁻(aq) → 2Mn²⁺(aq) + 5Cl₂(g) + 4H₂O(l)
d) Ag⁺(aq) + e⁻ → Ag(s)
Ag(s) + I⁻(aq) → AgI(s) + e⁻
AgI(s) → Ag⁺(aq) + I⁻(aq)

Problem 2.5.

Write cathodic and anodic reactions in a lead - acid battery during:

a) discharge,   b) charging.

Solution:

Lead - acid battery is made of 2 metal lead electrodes. One of them is covered with a layer of PbO₂, while the other - with a layer of PbSO₄. Sulfuric acid (ca. 30-40% by mass) constitutes the electrolyte. This is an example of a secondary cell, which may be operated in two directions:

During discharge, the battery behaves like a galvanic cell:

Pb|PbSO₄(s)|H₂SO₄(aq),H⁺(aq)|PbSO₄(s)|PbO₂(s)|Pb
PbO₂(s) + 3H⁺(aq) + H₂SO₄⁺(aq) + 2e⁻ → PbSO₄(s) +2H₂O
cathode
Pb(s) + H₂SO₄⁺(aq) → PbSO₄(s) + H⁺(aq) + 2e⁻
anode
Pb(s) + PbO₂(s) + 2H₂SO₄⁺(aq) + 2H⁺(aq) → 2PbSO₄(s) + 2H₂O
overall
Hence, during the discharge, concentration of sulfuric acid decreases as lead sulfate is being produced on both electrodes. Cathode is the positive terminal (electrons are consumed in the spontaneous reduction process), while anode is the negative one.

During charging, we perform the process of electrolysis (forced) to reverse the overall and both electrode reactions:

\[
\begin{align*}
\text{Pb}(s) + \text{HSO}_4^-(aq) &\rightleftharpoons \text{PbSO}_4(s) + \text{H}^+(aq) + 2e^- & \text{cathode (anode in discharge)} \\
\text{PbO}_2(s) + 3\text{H}^+(aq) + \text{HSO}_4^-(aq) + 2e^- &\rightleftharpoons \text{PbSO}_4(s) + 2\text{H}_2\text{O} & \text{anode (cathode in discharge)} \\
\text{Pb}(s) + \text{PbO}_2(s) + 2\text{HSO}_4^-(aq) + 2\text{H}^+(aq) &\rightleftharpoons 2\text{PbSO}_4(s) + 2\text{H}_2\text{O} & \text{overall}
\end{align*}
\]

Notice, that the direction of arrows is opposite to the discharge process. Concentration of sulfuric acid increases during charging. Negative terminal is attached to the cathode, as we must deliver electrons to force the reduction. It is the best indication that the sign alone does not permit us to determine unambiguously whether an electrode is cathode or anode, while the type of process (reduction or oxidation) does.

**Problem 2.6.**

Calculate the standard cell potential (use tables from Appendix A) and the standard free energy for galvanic cells described by the following overall cell reactions:

a) \( \text{Cu}^{2+} + \text{Zn} \rightarrow \text{Zn}^{2+} + \text{Cu} \) +0.34 \ -0.76
b) \( 3\text{Ce}^{4+} + \text{Bi} \rightarrow 3\text{Ce}^{3+} + \text{Bi}^{3+} \) +1.61 \ +0.20
c) \( 2\text{MnO}_4^- + 10\text{Cl}^- + 8\text{H}^+ \rightarrow 2\text{Mn}^{2+} + 5\text{Cl}_2 + 4\text{H}_2\text{O} \) +1.51 \ +1.36
d) \( \text{MnO}_2 + 4\text{H}^+ + \text{Pb} \rightarrow \text{Mn}^{2+} + \text{Pb}^{2+} + 2\text{H}_2\text{O} \) +1.23 \ -0.13

**Solution:**

a) The cell diagram is (zinc is oxidized, copper(II) reduced):

\[
\begin{array}{c}
\text{Zn}|\text{Zn}^{2+}(aq)||\text{Cu}^{2+}(aq)|\text{Cu}
\end{array}
\]

Standard cell potential (all activities equal to 1 mol/dm³, all gas pressures - 1 atm) is equal to:

\[
E^\circ_\text{cell} = E^\circ_\text{cat} - E^\circ_\text{an} = +0.34 - (-0.76) = 1.10 \text{ [V]}
\]

Standard free energy is equal to:

\[
\Delta G^\circ = -nFE^\circ = -2 \times 9.65 \times 10^4 \times 1.10 = -212.3 \text{ [kJ]}
\]

b) \( \text{Bi}^{3+}(aq)||\text{Ce}^{4+}(aq),\text{Ce}^{3+}(aq)||\text{Pt} \)

\[
E^\circ_\text{cell} = +1.61 - (+0.20) = 1.41 \text{ [V]}
\]

\[
\Delta G^\circ = -3 \times 9.65 \times 10^4 \times 1.41 = -408.2 \text{ [kJ]}
\]

c) \( \text{Pt}||\text{Cl}_2(g)||\text{Cl}^-(aq)||\text{Br}^-(aq),\text{Br}_2(l)||\text{Pt} \)

\[
E^\circ_\text{cell} = +1.51 - (+1.36) = 0.15 \text{ [V]}
\]

\[
\Delta G^\circ = -10.9 \times 9.65 \times 10^4 \times 0.15 = -144.8 \text{ [kJ]}
\]

d) \( \text{Pb}^{2+}(aq)||\text{Mn}^{2+}(aq),\text{H}^+(aq)||\text{MnO}_2(s)||\text{C(graphite)} \)

\[
E^\circ_\text{cell} = +1.23 - (-0.13) = 1.36 \text{ [V]}
\]

\[
\Delta G^\circ = -2.9 \times 10^4 \times 1.36 = -262.5 \text{ [kJ]}
\]

One can notice that all four reactions (as written) are spontaneous under standard conditions, judging by positive standard cell potentials and negative standard free energies.

**Problem 2.7.**

Assuming standard conditions, decide whether the following cells are galvanic cells by checking their standard potentials (standard EMF) and calculating corresponding free energy values. Write the corresponding cell reaction if the cell is galvanic and the reverse reaction if it is not.

a) \( \text{Pt}||\text{Cl}_2(g)||\text{Cl}^-(aq)||\text{Br}^-(aq),\text{Br}_2(l)||\text{Pt} \)
b) \( \text{Pt}||\text{Mn}^{2+}(aq),\text{Mn}^{3+}(aq)||\text{Cr}_2\text{O}_7^{2-}(aq),\text{Cr}^{3+}(aq),\text{H}^+(aq)||\text{Pt} \)
c) \( \text{Pt}||\text{Sn}^{2+}(aq),\text{Sn}^{4+}(aq)||\text{Fe}^{2+}(aq)||\text{Fe} \)
d) \( \text{Ag}||\text{AgI}(s)||\text{I}^-(aq)||\text{Cu}^{2+}(aq),\text{I}^-(aq)||\text{CuI}(s)||\text{C(graphite)} \)

**Solution:**
a) Pt|Cl₂(g)|Cl⁻(aq)||Br⁻(aq),Br₂(l)|Pt
E₀CELL = +1.09 – (+1.36) = –0.27 [V]
ΔG₀ = –2.965×10⁴(–0.27) = 52.10 [kJ]
Hence, the cell is not galvanic and should be rewritten in the opposite direction to become one. The spontaneous overall reaction in the reversed cell would be: Cl₂(g) + Br⁻(aq) → Br₂(l) + Cl⁻(aq). It simply means that gaseous chlorine is a stronger oxidizer than liquid bromine. This reaction is utilized in the industrial process of producing elemental bromine from the brine.

b) Pt|Mn³⁺(aq),Mn²⁺(aq)||Cr₂O₇²⁻(aq),Cr³⁺(aq),H⁺(aq)|Pt
E₀CELL = +1.33 – (+1.51) = –0.18 [V]
ΔG₀ = –6.965×10⁴(–0.18) = 104.2 [kJ]
Again, the cell is not galvanic and the cell reaction is not spontaneous. The thermodynamically possible one would be: 6Mn³⁺ + 2Cr³⁺ + 7H₂O → Cr₂O₇²⁻ + 6Mn²⁺ + 14H⁺, i.e., Mn³⁺ is a stronger oxidizer than Cr₂O₇²⁻.

c) Pt|Sn⁴⁺(aq),Sn²⁺(aq)||Fe²⁺(aq)|Fe
E₀CELL = –0.44 – (+0.15) = –0.59 [V]
ΔG₀ = –2.965×10⁴(–0.59) = 113.9 [kJ]
The same conclusion. The thermodynamically allowed reaction goes: Sn⁴⁺ + Fe → Sn²⁺ + Fe²⁺.

d) Ag|AgI(s)||I⁻(aq),I⁻(aq)|Cu²⁺(aq),I⁻(aq)|CuI(s)|C(graphite)
E₀CELL = +0.86 – (–0.15) = 1.01 [V]
ΔG₀ = –9.65×10⁴(1.01) = –97.5 [kJ]
Reaction in this (hypothetical) cell is spontaneous, the cell itself would be galvanic. Copper(II) ions are capable to oxidize silver in presence of iodide: Cu²⁺ + Ag + 2I⁻(aq) → AgI + Cul.

Problem 2.8.

Arrange chemical species in each of the rows a) through d) in the order of decreasing strength as oxidizing agents (standard conditions):

a) Ce⁴⁺, Ti⁺, Be²⁺, Sn⁴⁺
b) Ag⁺, Fe³⁺, S₂O₃²⁻, U³⁺
c) Cr₂O₇²⁻, MnO₂, H₂O₂, IO₃⁻ (all in acidic solutions)
d) V³⁺, Ti⁴⁺, Bi³⁺, Pu⁴⁺

Solution:
Oxidizing agents undergo reduction. If more than one form at lower oxidation state of the element exists and it is not clear which is in question, let's assume the reduction occurs to the directly lower form (example: if Hg²⁺ is in question, assume the redox couple is Hg²⁺/Hg²⁺ and not Hg²⁺/Hg).

a) Ce⁴⁺, Sn⁴⁺, Ti⁺, Be²⁺
+1.61 +0.15 –0.34 –1.85 (reduction potentials in V)
b) Ag⁺, Fe³⁺, S₂O₃²⁻, U³⁺
+0.80 +0.77 +0.08 –1.79
c) H₂O₂, Cr₂O₇²⁻, MnO₂, IO₃⁻ (all in acidic solutions)
+1.78 +1.33 +1.23 +1.20
d) Pu⁴⁺, Bi³⁺, Ti⁴⁺, V³⁺
+0.97 +0.20 0.00 –0.26
Problem 2.9.

Arrange chemical species in each of the rows a) through d) in the order of increasing strength as oxidizing agents (standard conditions):

a) \( \text{Ag}^{2+}, \text{Cr}^{3+}, \text{Br}_2, \text{Sn}^{2+} \)

b) \( \text{In}^{3+}, \text{Fe}^{2+}, \text{Sr}^{2+}, \text{Ga}^+ \)

c) \( \text{NO}_3^-/\text{NO}, \text{NO}_3^-/\text{NO}_2^-, \text{NO}_3^-/\text{NO}_2^-, \text{HBrO}, \text{H}^+/\text{Br}_2^- \) (full redox couples specified)

d) \( \text{F}_2, \text{O}_2, \text{O}_3, \text{Cl}_2 \) (in acidic solutions if pH plays any role)

Solution:

Do the same assumptions as in the previous problem.

a) \( \text{Cr}^{3+}, \text{Sn}^{2+}, \text{Br}_2, \text{Ag}^{2+} \) (reduction potentials in V):

\[ E_0 \text{cell} = +0.34 - (-0.41) = 0.75 \text{ [V]} \]

\[ K = \exp \left( \frac{2 \cdot 0.75 \cdot 38.93}{8.314 \cdot 298.15} \right) = \exp \left( 58.39 \right) = 2.29 \times 10^{25} \]

b) \( \text{In}^{3+}, \text{Ga}^+, \text{Sr}^{2+}, \text{Fe}^{2+} \):

\[ E_0 \text{cell} = -0.49 - (-1.63) = 1.14 \text{ [V]} \]

\[ K = \exp \left( 2 \cdot 1.14 \cdot 38.93 \right) = \exp \left( 87.98 \right) = 1.62 \times 10^{38} \]

c) \( \text{NO}_3^-/\text{NO}, \text{NO}_3^-/\text{NO}_2^-, \text{NO}_3^-/\text{NO}_2^-, \text{HBrO}, \text{H}^+/\text{Br}_2^- \):

\[ E_0 \text{cell} = +1.81 - (0.68) = 1.13 \text{ [V]} \]

\[ K = \exp \left( 2 \cdot 1.13 \cdot 38.93 \right) = \exp \left( 87.98 \right) = 1.62 \times 10^{38} \]

Problem 2.10.

Write the expression for the equilibrium constant and calculate its value (at 298 K) for the following reactions:

a) \( \text{Cu}^{2+} + 2\text{Cr}^{2+} = \text{Cu}^0 + 2\text{Cr}^{3+} \)

b) \( 2\text{In}^{3+} + \text{Ti}^0 = 2\text{In}^{2+} + \text{Ti}^{2+} \)

c) \( 2\text{Co}^{3+} + \text{H}_2\text{O}_2 = 2\text{Co}^{2+} + \text{O}_2 + 2\text{H}^+ \)

d) \( \text{Cl}_2 + \text{Sn}^{2+} = 2\text{Cl}^- + \text{Sn}^{4+} \)

Solution:

a) \( \text{Cu}^{2+} + 2\text{Cr}^{2+} = \text{Cu}^0 + 2\text{Cr}^{3+} \)

\[ K = \frac{[\text{Cr}^{3+}]^2}{[\text{Cr}^{2+}]^2[\text{Cu}^{2+}]} \]

\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}^0 \text{ cathode, } +0.34 \text{ [V]} \]
\[ 2\text{Cr}^{2+} \rightarrow 2\text{Cr}^{3+} + 2e^- \text{ anode, } -0.41 \text{ [V]} \]

\[ E_0 \text{cell} = +0.34 - (-0.41) = 0.75 \text{ [V]} \]

\[ K = \exp (nF \cdot E_{\text{cell}}/RT) = \exp (n \cdot 9.65 \times 10^4 \cdot (8.314 \cdot 298.15)) = \exp (n \cdot -0.75 \cdot 38.93) = \exp (58.39) = 2.29 \times 10^{25} \]

b) \( 2\text{In}^{3+} + \text{Ti}^0 = 2\text{In}^{2+} + \text{Ti}^{2+} \)

\[ K = \frac{[\text{In}^{2+}]^2}{[\text{In}^{3+}]^2} \]

\[ 2\text{In}^{3+} + 2e^- \rightarrow 2\text{In}^{2+} \text{ cathode, } -0.49 \text{ [V]} \]
\[ \text{Ti} \rightarrow \text{Ti}^{2+} + 2e^- \text{ anode, } -1.63 \text{ [V]} \]

\[ E_0 \text{cell} = -0.49 - (-1.63) = 1.14 \text{ [V]} \]

\[ K = \exp (2 \cdot 1.14 \cdot 38.93) = \exp (88.76) = 3.53 \times 10^{38} \]

c) \( 2\text{Co}^{3+} + \text{H}_2\text{O}_2 = 2\text{Co}^{2+} + \text{O}_2 + 2\text{H}^+ \)

\[ K = \frac{[\text{Co}^{2+}]^2[\text{H}^+]^2}{[\text{Co}^{3+}]^2[\text{H}_2\text{O}_2]} \]

\[ 2\text{Co}^{3+} + 2e^- \rightarrow 2\text{Co}^{2+} \text{ cathode, } +1.81 \text{ [V]} \]
\[ \text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2e^- \text{ anode, } +0.68 \text{ [V]} \]

\[ E_0 \text{cell} = +1.81 - (+0.68) = 1.13 \text{ [V]} \]

\[ K = \exp (2 \cdot 1.13 \cdot 38.93) = \exp (87.98) = 1.62 \times 10^{38} \]
d) \[ \text{Cl}_2 + \text{Sn}^{2+} = 2\text{Cl}^- + \text{Sn}^{4+} \]

\[ K = \frac{[\text{Cl}^-]^2[\text{Sn}^{4+}]}{[\text{Sn}^{2+}] \cdot p_{\text{Cl}_2} / p_s} \]

\[
\begin{array}{l}
\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^- \quad \text{cathode, +1.36 [V]} \\
\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2e^- \quad \text{anode, +0.15 [V]} \\
E^\circ_{\text{cell}} = +1.36 - (+0.15) = 1.21 \text{ [V]} \\
K = \exp(2 \cdot 1.21 \cdot 38.93) = \exp(94.21) = 8.22 \times 10^{40}
\end{array}
\]

**Problem 2.11.**

Calculate values of the equilibrium constants of the reactions occurring in the following cells:

a) \[ \text{Au} | \text{Au}^{3+}(aq), \text{SO}_4^{2-}(aq) | \text{Pt} \]

b) \[ \text{Zn} | \text{Zn}^{2+}(aq) | \text{Cl}^-(aq), \text{Hg}_2\text{Cl}_2(s), \text{Hg} \]

c) \[ \text{Pt} | \text{Ti}^{4+}(aq), \text{Ti}^{3+}(aq) | \text{Sn}^{4+}(aq), \text{Sn}^{2+}(aq) | \text{Pt} \]

d) \[ \text{Ag} | \text{Ag}(s) | \text{I}^-(aq), \text{I}^+(aq) | \text{Ag} \]

**Solution:**

a) \[ \text{Au} | \text{Au}^{3+}(aq), \text{SO}_4^{2-}(aq) | \text{Pt} \]

\[
\begin{array}{l}
3\text{SO}_4^{2-} + 6e^- \rightarrow 6\text{SO}_4^{2-} \quad \text{cathode, +2.05 [V]} \\
2\text{Au} \rightarrow 2\text{Au}^{3+} + 6e^- \quad \text{anode, +1.40 [V]} \\
E^\circ_{\text{cell}} = +2.05 - (+1.40) = 0.65 \text{ [V]} \\
K = \exp(6 \cdot 0.65 \cdot 38.93) = \exp(151.8) = 8.66 \times 10^{65}
\end{array}
\]

b) \[ \text{Zn} | \text{Zn}^{2+}(aq) | \text{Cl}^-(aq), \text{Hg}_2\text{Cl}_2(s), \text{Hg} \]

\[
\begin{array}{l}
\text{Hg}_2\text{Cl}_2 + 2e^- \rightarrow 2\text{Hg}^0 + 2\text{Cl}^- \quad \text{cathode, +0.27 [V]} \\
\text{Zn}^0 \rightarrow \text{Zn}^{2+} + 2e^- \quad \text{anode, -0.76 [V]} \\
E^\circ_{\text{cell}} = +0.27 - (-0.76) = 1.03 \text{ [V]} \\
K = \exp(2.103 \cdot 38.93) = \exp(80.20) = 6.74 \times 10^{34}
\end{array}
\]

c) \[ \text{Pt} | \text{Ti}^{4+}(aq), \text{Ti}^{3+}(aq) | \text{Sn}^{4+}(aq), \text{Sn}^{2+}(aq) | \text{Pt} \]

\[
\begin{array}{l}
\text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+} \quad \text{cathode, +0.15 [V]} \\
2\text{Ti}^{3+} \rightarrow 2\text{Ti}^{4+} + 2e^- \quad \text{anode, +0.00 [V]} \\
E^\circ_{\text{cell}} = +0.15 - (+0.00) = 0.15 \text{ [V]} \\
K = \exp(2 \cdot 0.15 \cdot 38.93) = \exp(11.68) = 1.18 \times 10^{5}
\end{array}
\]

d) \[ \text{Ag} | \text{Ag}(s) | \text{I}^-(aq), \text{I}^+(aq) | \text{Ag} \]

\[
\begin{array}{l}
\text{Ag}^+ + e^- \rightarrow \text{Ag}^0 \quad \text{cathode, +0.80 [V]} \\
\text{Ag}^0 + \text{I}^- \rightarrow \text{AgI} + 2e^- \quad \text{anode, -0.15 [V]} \\
E^\circ_{\text{cell}} = +0.80 - (-0.15) = 0.95 \text{ [V]} \\
K = \exp(0.95 \cdot 38.93) = \exp(36.98) = 1.15 \times 10^{16}
\end{array}
\]

In the last case, the value found is that of the solubility product of silver(I) iodide.

**Problem 2.12.**

Calculate the reaction quotient in the following cells at 298.15 K:

a) \[ \text{Au} | \text{Au}^{3+}(aq), \text{SO}_4^{2-}(aq) | \text{Pt} \quad E_{\text{cell}} = 0.30 \text{ [V]} \]

b) \[ \text{Zn} | \text{Zn}^{2+}(aq) | \text{Cl}^-(aq), \text{Hg}_2\text{Cl}_2(s), \text{Hg} \quad E_{\text{cell}} = 0.30 \text{ [V]} \]

c) \[ \text{Pt} | \text{Ti}^{4+}(aq), \text{Ti}^{3+}(aq) | \text{Sn}^{4+}(aq), \text{Sn}^{2+}(aq) | \text{Pt} \quad E_{\text{cell}} = 0.30 \text{ [V]} \]

d) \[ \text{Ag} | \text{Ag}(s) | \text{I}^-(aq), \text{I}^+(aq) | \text{Ag} \quad E_{\text{cell}} = 0.95 \text{ [V]} \]
Solution:

a) \( \text{Au}[\text{Au}^{3+}(aq)||\text{S}_2\text{O}_8^{2-}(aq), \text{SO}_4^{2-}(aq)]\text{Pt} \)
\[ E^\circ_{\text{cell}} = +2.05 - (+1.40) = 0.65 \text{ [V]} \]
\[ Q = \exp((E^0_{\text{cell}} - E_{\text{cell}})nF/(RT)) = \exp(0.35 - 3.68) = 3.20 \times 10^{35} \]

b) \( \text{Zn}[\text{Zn}^{2+}(aq)||\text{Cl}^-(aq), \text{Hg}_2\text{Cl}_2(s)]\text{Hg} \)
\[ E^\circ_{\text{cell}} = +0.27 - (-0.76) = 1.03 \text{ [V]} \]
\[ Q = \exp(0.73 - 3.89) = 4.83 \times 10^{24} \]

c) \( \text{Pt}[\text{Ti}^{4+}(aq), \text{Ti}^{3+}(aq)||\text{Sn}^{4+}(aq), \text{Sn}^{2+}(aq)]\text{Pt} \)
\[ E^\circ_{\text{cell}} = +0.15 - (+0.00) = 0.15 \text{ [V]} \]
\[ Q = \exp(-0.15 - 3.89) = 8.47 \times 10^{-6} \]

d) \( \text{Ag}[\text{Ag}(s)||\text{Ag}^+(aq)\text{Ag} \)
\[ E^\circ_{\text{cell}} = +0.80 - (-0.15) = 0.95 \text{ [V]} \]
\[ Q = \exp(0.00 - 3.89) = 1 \]

Problem 2.13.

Calculate the EMF of the following cells: (M stands for mole/dm³)

a) \( \text{Pt}[\text{Ti}^{4+}(aq;0.10M), \text{Ti}^{3+}(aq;0.0050M)||\text{Sn}^{4+}(aq;0.080M), \text{Sn}^{2+}(aq;0.0040M)]\text{Pt} \)
\[ \text{Sn}^{4+} + 2\text{Ti}^{3+} \rightarrow 2\text{Ti}^{4+} + \text{Sn}^{2+} \]
\[ E^0_{\text{cell}} = +0.15 - (+0.00) = 0.15 \text{ [V]} \]
\[ \text{EMF} = E^0_{\text{cell}} - 0.0592/n \times \log Q = 0.15 - 0.0592/2 \times \log (0.102 \times 0.004/0.005^2/0.08) = 0.111 \text{ V} \]

b) \( \text{Zn}[\text{Zn}^{2+}(aq;0.150M)||\text{Cl}^-(aq;0.150M), \text{Hg}_2\text{Cl}_2(s)]\text{Hg} \)
\[ \text{Hg}_2\text{Cl}_2 + \text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{Cl}^- + 2\text{Hg} \]
\[ E^0_{\text{cell}} = +0.27 - (-0.76) = 1.03 \text{ [V]} \]
\[ \text{EMF} = 1.03 - 0.0592/2 \times \log (0.150^3) = 1.103 \text{ V} \]

c) \( \text{Pt}[\text{Cr}_2\text{O}_7^{2-}(aq;0.0020M), \text{Cr}^{3+}(aq;0.040M), \text{H}^+(pH=2)||\text{Mn}^{3+}(aq;0.030M), \text{Mn}^{2+}(aq;0.10M)]\text{Pt} \)
\[ 6\text{Mn}^{3+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \rightarrow 6\text{Mn}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \]
\[ E^0_{\text{cell}} = +1.51 - (+1.33) = 0.18 \text{ [V]} \]
\[ \text{EMF} = 0.18 - 0.0592/6 \times \log (0.10^3 \times 0.002 \times 0.0114^4/0.036) = 0.414 \text{ V} \]

d) \( \text{Pt}[\text{H}_2(g;500\text{Torr})||\text{H}^+(aq;pH=1)||\text{H}^+(aq;pH=1)||\text{O}_2(g;400\text{Torr})\text{Pt} \)
\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \text{ anode} \]
\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O} \text{ cathode} \]
\[ \text{EMF} = E_{\text{cath}} - E_{\text{anode}} = E^0_{\text{cath}} - 0.0592/4 \times \log \left(\frac{1/(p_{\text{O}_2}/p_{\text{H}_2})^{0.5}}{1/(p_{\text{H}_2}/p_{\text{O}_2})^{0.5}}\right) \]
\[ = 1.17 \times 0.0592/4 \times \log \left(\frac{1/(400/760 \times 0.1)}{1/(760/400 \times 0.1)}\right) \]
\[ = 1.167 + 0.054 = 1.221 \text{ [V]} \]

Problem 2.14.

Determine the missing parameter in the following cells: (\( E_{\text{cell}} \) is just another notation for the EMF).

a) \( \text{Pt}[\text{H}_2(g;500\text{Torr})||\text{H}^+(aq;pH=?)||\text{Cl}^-(aq;1.0M)||\text{AgCl}(s)]\text{Ag} \)
\[ E_{\text{cell}} = 0.292 \text{ V} \]

b) \( \text{Pt}[\text{Pu}^{3+}(aq;0.0010M)||\text{S}_2\text{O}_8^{2-}(aq;0.20M), \text{SO}_4^{2-}(aq;0.10M)]\text{Ag} \)
\[ E_{\text{cell}} = 1.16 \text{ V} \]

c) \( \text{Ti}[\text{Ti}^{4+}(aq;0.40M)||\text{Pt}^4+(aq;?)\text{Pt} \)
\[ E_{\text{cell}} = 1.475 \text{ V} \]

d) \( \text{U}[\text{U}^{5+}(aq;?)||\text{OH}^-(aq;pH=11)||\text{O}_2(g;76 \text{ Torr})\text{Pt} \)
\[ E_{\text{cell}} = 2.432 \text{ V} \]
Solution:

Generally, \( E_{\text{cell}} = E_0^{\text{cell}} - 0.0592/n \times \log Q \), and \( Q = 10^{\left( (E_0^{\text{cell}} - E_{\text{cell}}) \times n/0.0592 \right)} \) (\(^n\) sign means raising to the power).

a) \( \text{H}_2 + 2\text{AgCl} \rightarrow 2\text{H}^+ + 2\text{Cl}^- + 2\text{Ag} \)

\( E_{\text{cell}} = 0.292 \text{ V} \)

\( E_0^{\text{cell}} = 0.22 - 0.00 = 0.22 \text{ V} \)

\[ Q = 10^{((0.22 - 0.292) \times 2/0.0592)} = 3.7 \times 10^{-3} \]

\[ \left[ \text{H}^+ \right] = \left( Q \times \frac{\text{pH}_2/\text{ps}}{[\text{Cl}^-]^2} \right)^{1/2} = \left( 3.7 \times 10^{-3} \times 500/760/1^2 \right)^{1/2} = 4.94 \times 10^{-3} \]

\[ \text{pH} = -\log 4.94 \times 10^{-3} = 1.3 \]

b) \( 2\text{Pu}^{3+} + \text{S}_2\text{O}_8^{2–} \rightarrow 2\text{SO}_4^{2–} + 2\text{Pu}^{4+} \)

\( E_{\text{cell}} = 1.16 \text{ V} \)

\( E_0^{\text{cell}} = 2.05 - 0.97 = 1.08 \text{ V} \)

\[ Q = 10^{((1.08 - 1.16) \times 2/0.0592)} = 2.0 \times 10^{-3} \]

\[ \left[ \text{Pu}^{4+} \right] = \left( \left[ \text{Pu}^{4+} \right]^2 \times [\text{SO}_4^{2–}]^2 / (\left[ \text{Pu}^{3+} \right]^2 \times [\text{S}_2\text{O}_8^{2–}]^2) \right)^{1/2} = (0.0011^2 \times 0.12 / (2.0 \times 10^{-3} \times 0.2))^{1/2} = 0.005 \text{ M} \]

Problem 2.15.

What is the value of [\( \text{Ti}^{2+} / \text{Ti}^{3+} \)] ratio in the cell:

\( \text{Pt}\mid\text{Ti}^{3+} (\text{aq}), \text{Ti}^{2+} (\text{aq}) \mid \text{H}_2 (\text{g; } 500 \text{ Torr}) \mid \text{H}^+ (\text{aq; } \text{pH} = 1) \mid \text{Pt} \)

if its EMF is 0.3444 [V] ?

Solution:

Overall reaction is: \( 2\text{H}^+ + 2\text{Ti}^{2+} \rightarrow \text{H}_2 + 2\text{Ti}^{3+} \). Unknown ratio: \( [\text{Ti}^{2+}] / [\text{Ti}^{3+}] = X \)

\[ E_{\text{cell}} = E_0^{\text{cell}} - 0.0592/n \times \log Q = (E_0^{\text{cath}} - E_0^{\text{an}}) - 0.0592/2 \times \log ((\text{ps}_{\text{H}_2}/\text{ps}) \times [\text{Ti}^{3+}]^2 / ([\text{H}^+]^2 \times [\text{Ti}^{2+}]^2)) = (0.00 - (-0.37)) - 0.0592/2 \times \log ((\text{ps}_{\text{H}_2}/\text{ps}) \times [\text{H}^+]^2 / X^2) = 0.37 - 0.0592/2 \times \log (500/760/0.01/X^2) = 0.3444 \text{ V} \]

Therefore:

\[ X = \sqrt[2]{\frac{500}{760 \times 0.01} \times 10^{2(0.37-0.3444)/0.0592}} = 2.997 \approx 3 \]

Problem 2.16.

a) What is the volume of gas (at STP) produced during 150 minutes of electrolysis of water at 2 A ?

b) During electrolysis of aqueous solution of sodium chloride sodium is produced on mercury cathode (hydrogen does not evolve due to its high overpotential on mercury) and chlorine gas on an anode. Assuming 100% current efficiency on both electrodes, calculate the amount of chlorine (at STP) produced on the anode while 1 t of sodium is reduced on the cathode. (\( M_{\text{Na}} = 23 \text{ g/mol} \))

Solution:

a) Cathode: \( 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2 \); anode: \( 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \)

Total gas amount is 3 moles (\( 3 \times 22.4 \text{ dm}^3 \)) while the charge equal to 4 F is consumed.

\( V = 3 \times 22.4 \times 150 \times 60 / (4 \times 96500) = 3.13 \text{ dm}^3 \).

b) Cathode: \( 2\text{Na}^+ + 2\text{e}^- \rightarrow 2\text{Na} \); anode: \( 2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^- \)

Reduction of 2 moles of metallic sodium is accompanied by evolution of 22.4 dm\(^3\) of gaseous chlorine. Hence:

\( \text{V} = 10^6 \ [\text{g Na}] / 23 [\text{g Na/mol Na}] / 2 [\text{mol Na/mol Cl}_2] \times 22.4 [\text{dm}^3/\text{mol Cl}_2] = 486956.5 \text{ dm}^3 = 487 \text{ m}^3 \).
Problem 2.17.

a) What is the thickness of a nickel layer electrodeposited with current density of 80 mA/cm² from a solution containing Ni²⁺ during 200 seconds of deposition? Density of nickel d = 8.9 g/cm³; molar mass MNi = 58.7 g/mol.

b) What is the thickness of a gold layer electrodeposited with current density of 100 mA/cm² from Au[CN]₂⁻ solution during 12 seconds of deposition? Density of gold d = 19.3 g/cm³, molar mass MAu = 197 g/mol.

c) In a silver coulometer mass of the cathode increased by 38.2 mg. How big electric charge was passed through the circuit? (molar mass MAg = 107.9 g/mol.

Solution:

a) Cathodic reduction: \( \text{Ni}^{2+} + 2e^- \rightarrow \text{Ni} \).

Mass of nickel deposited \( m = \frac{7}{F} \cdot \frac{58.7 \cdot 0.08 \cdot 200}{96500} = 4.866 \times 10^{-3} \text{ g/cm}^2 \).

Layer thickness = \( 4.866 \times 10^{-3} \text{ g/cm}^2 : 8.9 \text{ g/cm}^3 = 5.47 \times 10^{-4} \text{ cm} = 5.47 \mu\text{m} \).

b) Cathodic reduction: \( \text{Au[CN]}_2^- + 2\text{H}^+ + e^- \rightarrow \text{Au} + 2\text{HCN} \).

Mass of gold deposited \( m = \frac{197}{F} \cdot 0.100 \cdot 12/96500 = 2.45 \times 10^{-3} \text{ g/cm}^2 \).

Layer thickness = \( 2.45 \times 10^{-3} \text{ g/cm}^2 : 19.3 \text{ g/cm}^3 = 1.27 \times 10^{-4} \text{ cm} = 1.27 \mu\text{m} \).

c) In a silver coulometer cathodic reduction: \( \text{Ag}^+ + e^- \rightarrow \text{Ag} \) occurs from a solution of AgNO₃.

Mass of silver deposited \( m = \frac{38.2 \cdot 96500}{107.9} = 34164 \text{ mC} \) (mass was substituted in mg, hence, millicoulombs).

Electrochemical cells.

Conventional cell notation.

Electrodes (half-cells). Anode and cathode.

Electrode reaction. Overall cell reaction.

Problem II.I.

Problem II.II.

Electrode potential. Electromotive force (EMF).

Standard potential.

Nernst equation. Dependence of electrode potential on the electrolyte composition.
Exercise 17.41:
To calculate the reaction quotient, according to equation (2.26) we need:
- properly balanced overall redox reaction to get number of electrons exchanged,
- a value of the standard cell potential,
- temperature (we must assume 298K, as the standard potentials in the tables are given at this temperature).

Solution:
Part a)
Step A. It's rather simple to write the overall reaction corresponding to the scheme given:

Cathode (reduction): \( \text{Pb}^{4+} + 2e^- \rightarrow \text{Pb}^{2+} \quad \mathcal{E}^0 = +1.67 \text{ [V]} \)

Anode (oxidation): \( \text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2e^- \quad \mathcal{E}^0 = +0.15 \text{ [V]} \) (standard reduction potential)

One can get the overall reaction by simple addition of the 2 half-reactions (hence \( n=2 \)):
\[ \text{Pb}^{4+} + \text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + \text{Pb}^{2+} \]

Step B. Using equation (2.15) one can get the value of the standard cell potential,:
\[ \mathcal{E}^0 = 1.67-0.15 = 1.52 \text{ [V]} \]

Step C. Final calculation of the \( Q \) value from equation (2.26): (poprawić w tym obliczeniu poniżej)
\[ Q = \exp \left( \frac{nF}{RT} (\mathcal{E}^0_{\text{cell}} - \mathcal{E}_{\text{cell}}) \right) = \exp \left( \frac{2 \cdot 96500}{8.314 \cdot 298} (0.87 - 1.33) \right) = 2.74 \times 10^{-16} \]

A very small value of the reaction quotient leads us to conclude that the actual composition of the system favors the reactants to a significant degree. (sprawdź wniosek!!)

Part b)
Step A. It's rather complicated to write the overall reaction corresponding to the diagram given. Let's have a look. There are no problems at the cathodic side:

Cathode (reduction): \( \text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \quad \mathcal{E}^0 = +1.33 \text{ [V]} \)

At the anodic side, from the scheme given, one cannot identify the redox couple easily. Only \( \text{O}_2 \) and \( \text{H}^+ \) are mentioned. If the latter is an Ox, then \( \text{H}_2 \) would be a corresponding Red (and it is not indicated). If the former is an Ox, then its Red counterpart is not given, either. Actually, the missing counterpart, obviously present in the system but missing in the scheme (it's presence is too obvious) is \( \text{H}_2\text{O} \):

Anode (oxidation): \( 2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4e^- \mathcal{E}^0 = +1.23 \text{ [V]} \) (standard reduction potential)

One can get the overall reaction by:

i) multiplying the cathodic reaction by 2,

ii) multiplying the anodic reaction by 3 (hence, after balancing, \( n=12 \)),

iii) simple addition of the multiplied half-reactions:
\[ 2\text{Cr}_2\text{O}_7^{2-} + 28 \text{H}^+ + 12e^- \rightarrow 4\text{Cr}^{3+} + 14\text{H}_2\text{O} \]
\[ 6\text{H}_2\text{O} \rightarrow 3\text{O}_2 + 12\text{H}^+ + 12e^- \]
\[ 2\text{Cr}_2\text{O}_7^{2-} + 16\text{H}^+ \rightarrow 4\text{Cr}^{3+} + 3\text{O}_2 + 8\text{H}_2\text{O} \]

Step B. Using equation (2.15) one can get the value of the standard cell potential:
\[ \mathcal{E}^0 = 1.33-1.23 = 0.10 \text{ [V]} \]

Step C. We can notice that the given value of \( \mathcal{E} \) is equal to that of \( \mathcal{E}^0 \). It simply means that the actual conditions are, most probably, standard conditions. Hence, the value of the reaction quotient, \( Q \), will be equal to 1 (by definition at standard conditions). The same can be found by virtue of equation (2.26). Final calculation:
\[ Q = \exp\left( \frac{nF}{RT} (E_{\text{cell}}^0 - E_{\text{cell}}) \right) = \exp\left( \frac{12.96500}{8.314 \cdot 298} (0.10 - 0.10) \right) = 1 \]

A very large value of the equilibrium constant leads us to conclude that at equilibrium composition of the system, the products are favored to a significant degree:

\[ K = \exp\left( \frac{nF}{RT} E_{\text{cell}}^0 \right) = \exp\left( \frac{12.96500}{8.314 \cdot 298} (0.10) \right) = 2.0 \times 10^{20} \]

**Exercise 17.35:**

To write the expression for the equilibrium constant, we must deduce, from the cell notation, a properly balanced overall redox reaction.

**Solution:**

**Part a)**

Step A. The scheme suggests the following half-cells reactions:

Cathode (reduction): \( \text{AgCl(s)} + e^- \rightarrow \text{Ag(s)} + \text{Cl}^- (aq) \)

Anode (oxidation): \( \text{H}_2(g) \rightarrow 2\text{H}^+(aq) + 2e^- \)

One can get the overall reaction by:

i) multiplying the cathodic reaction by 2,

ii) addition of the two half-reactions:

\( 2\text{AgCl(s)} + 2e^- \rightarrow 2\text{Ag(s)} + 2\text{Cl}^- (aq) \)

\( \text{H}_2(g) \rightarrow 2\text{H}^+(aq) + 2e^- \)

\( 2\text{AgCl(s)} + \text{H}_2(g) \rightarrow 2\text{Ag(s)} + 2\text{H}^+(aq) + 2\text{Cl}^- (aq) \)

Step B. Writing the expression for the equilibrium constant:

\[ K = \frac{[\text{H}^+]^2 [\text{Cl}^-]^2}{p_{\text{H}_2}} \]

**Part b)**

Step A. The scheme suggests the following half-cells reactions:

Cathode (reduction): \( \text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightarrow \text{NO(g)} + 2\text{H}_2\text{O} \)

Anode (oxidation): \( \text{Fe}^{2+}(aq) \rightarrow \text{Fe}^{3+}(aq) + e^- \)

One can get the overall reaction by:

i) multiplying the anodic reaction by 3,

ii) addition of the two half-reactions:

\( 3\text{NO}_3^-(aq) + 4\text{H}^+(aq) + 3e^- \rightarrow \text{NO(g)} + 3\text{Fe}^{3+}(aq) + 2\text{H}_2\text{O} \)

Step B. Writing the expression for the equilibrium constant:

\[ K = \frac{P_{\text{NO}_3}[\text{Fe}^{3+}]^3}{[\text{Fe}^{2+}]^3 [\text{H}^+]^4 [\text{NO}_3^-]} \]
**Exercise 17.56:**

**Solution:** One should notice that the charge in question is equal to the Faraday constant, \( F \). To calculate the desired amounts of electrolysis products, one must write the suitable half-reaction:

Part a) Metallic silver is produced in the cathodic reduction process:

\[
\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)
\]

Hence, 1 mole of electrons (1 \( F \)) is required to produce 1 mole of silver metal. This is equivalent to 107.9 g.

Part b) Gaseous chlorine is produced in the anodic oxidation process:

\[
2\text{Cl}^-(aq) \rightarrow \text{Cl}_2(g) + 2e^-
\]

Hence, 2 moles of electrons (2 \( F \)) are required to produce 1 mole of chlorine gas. This is equivalent to 22.4 dm³ at STP. If 1\( F \) is passed, one will get half of this amount, i.e., 11.2 dm³ at STP.

Part c) Metallic copper is produced in the cathodic reduction process:

\[
\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)
\]

Hence, 2 moles of electrons (2 \( F \)) are required to produce 1 mole of silver metal. If 1\( F \) is passed, one will get half of this amount, i.e., 63.54/2 g = 31.77 g.

**Exercise 17.57**

**Answers:**

a) 7.87 seconds,
b) 1.295 milligram.

**Exercise 17.43**

**Solution:** To solve the problem, usually one can utilize suitably modified equation (2.26), i.e., an appropriate expression for the reaction quotient should be introduced:

Part a) First, we must calculate potentials of both half-cells from equation (2.30):

That of the right half-cell is equal to zero, as the right half cell is simply an SHE, and that of the left:

\[
E = E^0 - \frac{0.0592}{n} \log \frac{[\text{Red}]}{[\text{Ox}]} = -0.0592 \cdot \log \frac{p_{H_2}^{1/2}}{[H^+]} = +0.0592 \cdot \log(0.0010) = -0.1776 \text{[V]}
\]

Second, we must calculate the cell EMF, according to equation (2.15):

\[
E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 0 - (-0.1776) = 0.1776 \text{[V]}
\]

Final conclusion will be that while on the right side reduction would take place and at the left one - oxidation of hydrogen (concentration of acid would gradually rise in the left compartment). This is an example of a **concentration cell**.

Part b) First, we must calculate the standard cell potential from equation (2.15):

\[
E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = E_{\text{Ni(II)/Ni(0)}}^0 - E_{\text{Zn(II)/Zn(0)}}^0 = -0.23 - (-0.76) = 0.53 \text{[V]}
\]

Second, we can find the unknown cell potential (EMF) from equation (2.26):

\[
E = E^0_{\text{cell}} - \frac{RT}{nF} \ln(Q) = 0.53 - \frac{0.0592}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]} = 0.53 - 0.0296 \cdot \log \frac{0.10}{0.0010} = 0.4708 \text{[V]}
\]

Part c) We can solve it exactly the same way as part b). Standard cell potential:

\[
E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = E_{\text{H+/H2}}^0 - E_{\text{Cl2/Cl-}}^0 = 0 - (1.36) = -1.36 \text{[V]}
\]

The overall reaction is:

\[
2\text{Cl}^- + 2\text{H}^+ \rightarrow \text{Cl}_2 + \text{H}_2
\]
And the unknown cell potential:

$$E_{\text{cell}} = -1.36 - 0.0592 \log \frac{P_{\text{Cl}_2} P_{\text{H}_2}}{[\text{Cl}^-]^2 [\text{H}^+]^2} = -1.36 - 0.0296 \log \frac{100 \times 450}{760 \times 760}$$

$$= -1.36 - 0.0296 \times \log \frac{450}{76^2 \times 10^{-4}} = -1.36 - 0.0296 \times 2.892 = -1.446 [V]$$

It seems that the reaction cannot go the way the cell diagram is written, but rather in the opposite direction.

**Exercise 17.44:**

**Answers:**

a) 0.482 Volt,

b) 0.0046 Volt (The reaction, for all practical purposes is at equilibrium. Well, almost.),

c) 0.6068 Volt.

**Exercise 17.45:**

**Solution:** To solve the problem, usually one can utilize suitably modified equation (2.26), i.e., an appropriate expression for the reaction quotient should be introduced:

Our unknown is: $X = [\text{Fe}^{2+}] / [\text{Fe}^{3+}]$. Standard cell potential:

$$E_{\text{cell}}^0 = E_{\text{cathode}}^0 - E_{\text{anode}}^0 = E_{\text{Hg}^{2+}/\text{Hg}(0)}^0 - E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 = 0.79 - 0.77 = -0.02 [V]$$

The overall reaction is:

$$2\text{Fe}^{2+} + \text{Hg}^{2+} \rightarrow 2\text{Fe}^{3+} + 2\text{Hg} \quad n=2$$

And the actual cell potential can be expressed by modified equation (2.26):

$$E_{\text{cell}} = E_{\text{cell}}^0 + 0.0592 \log X$$

as $[\text{Hg}^{2+}] = 1.0$, then:

$$X = 10^{\frac{E_{\text{cell}} - E_{\text{cell}}^0}{0.0592}} = 10^{0.676} = 4.74$$

**Exercise 17.47:**

**Solution:** We use the same method as in the previous problem, although with concentrations of individual ions as the unknowns:

**Answers:**

a) $pH = 1.01$,

b) 0.10 mol/dm$^3$. 