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# CHEMISTRY II

Verónica San Miguel Arnanz

Teresa Pérez Prior

Berna Serrano Prieto

Department of Materials Science and Engineering and Chemical Engineering

# SOLUTIONS OF ELECTROCHEMISTRY I EXERCISES

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**Exercise 1.** Iron (II) is oxidized by dichromate ion in acidic solution to yield $Fe^{3+}$ and $Cr^{3+}$. Write the balanced ionic equation.

**SOLUTION**

Oxidation: $Fe^{2+} \rightarrow Fe^{3+} + 1e^{-}$

Reduction: $Cr_2O_7^{2-} + 14\ H^{+} + 6\ e^{-} \rightarrow 2\ Cr^{3+} + 7\ H_2O$

Overall Reaction: $6\ Fe^{2+} + Cr_2O_7^{2-} + 14\ H^{+} \rightarrow 6\ Fe^{3+} + 2\ Cr^{3+} + 7\ H_2O$

**Exercise 2.** In the oxidation of $CN^{-}$ by permanganate ion in basic medium, the following products are generated: $CNO^{-}$ and $MnO_2$. Write the balanced ionic equation.

**SOLUTION**

Oxidation: $CN^{-} + 2\ OH^{-} \rightarrow CNO^{-} + 2\ e^{-} + H_2O$

Reduction: $MnO_4^{-} + 2\ H_2O + 3\ e^{-} \rightarrow MnO_2 + 4\ OH^{-}$

Overall Reaction: $3\ CN^{-} + 2\ MnO_4^{-} + H_2O \rightarrow 3\ CNO^{-} + 2\ MnO_2 + 2\ OH^{-}$

**Exercise 3.** A galvanic cell consists of a Mg electrode in a 1 M $Mg(NO_3)_2$ solution and a Ag electrode in a 1 M $AgNO_3$ solution. Calculate the standard cell potential of this cell at 25 ºC.
Data: $E°\ (Mg^{2+}/Mg) = -2.37$ V; $E°\ (Ag^{+}/Ag) = +0.80$ V.

**SOLUTION**

Oxidation (Anode): $Mg \rightarrow Mg^{2+} + 2e^{-}$ $E^0 = +2.37$ V

Reduction (Cathode): $Ag^{+} + e^{-} \rightarrow Ag$ $E^0 = +0.80$ V

Overall Reaction: $Mg + 2\ Ag^{+} \rightarrow Mg^{2+} + 2\ Ag$ $\underline{E^0 = +3.17\ V}$

**Exercise 4.** Given the following cell diagram: $Pt|Fe^{2+}, Fe^{3+}||Ag^{+}|Ag$

a) Write the overall reaction in the cell. Indicate the oxidizing and reducing species.
b) Calculate the equilibrium constant at 25 °C if the standard potential of the cell at this temperature is 0.028 V.

Data: $E^0\ (Fe^{3+}/Fe^{2+}) = +0.77$ V; $E^0\ (Ag^{+}/Ag) = +0.80$ V; $R = 8.314\ J\ K^{-1}\ mol^{-1}$; $F = 96500\ C\ mol^{-1}$.

**SOLUTION**

a) Oxidation (Anode): $Fe^{2+} \rightarrow Fe^{3+} + 1\ e^{-}$ $E^0 = -0.77$ V

Reduction (Cathode): $Ag^{+} + e^{-} \rightarrow Ag$ $E^0 = +0.80$ V

Overall Reaction: $Fe^{2+} + Ag^{+} \rightarrow Fe^{3+} + 2\ Ag$ $\underline{E^0 = +0.03\ V}$

Reducing agent: $Fe^{2+}$

Oxidizing agent: $Ag^+$

b) $K = e^{nFE°/RT}$; <u>$K = 2.97$</u>

**Exercise 5.** A cell built with an electrode of solid $MnO_2$ introduced in a solution of $Mn^{2+}$ (0.05 M) connected to another electrode of solid Zn in a solution of $Zn^{2+}$ (0.01 M) generates a potential of 1.947 V at 25 °C and pH = 4.

a) Write the half-reactions that take place at the anode and at the cathode and balance the global redox process. Identify the reducing and the oxidazing agents.
b) Reason qualitatively how the cell potential varies if pH increases.

Data: $E^0$ ($Zn^{2+}/Zn$) = – 0.76 V; $E^0$ ($MnO_2/Mn^{2+}$) = + 1.23 V.

**SOLUTION**

a) Oxidation (Anode): $Zn \rightarrow Zn^{2+} + 2\ e^-$ $E^0 = +\ 0.76$ V

Reduction (Cathode): $MnO_2 + 4\ H^+ + 2\ e^- \rightarrow Mn^{2+} + 2\ H_2O$ $E^0 = +\ 1.23$ V

Overall Reaction: $Zn + MnO_2 + 4\ H^+ \rightarrow Zn^{2+} + Mn^{2+} + 2\ H_2O$ $E^0 = +\ 1.99$ V

Reducing agent: Zn

Oxidizing agent: $MnO_2$

b) The Nernst equation: $E = E^0 - (RT/nF) \ln [Mn^{2+}] [Zn^{2+}] / [H^+]^4$

If pH increases, $[H^+]$ decreases and E decreases.

**Exercise 6.** Calculate the potential of the following cell at 25 °C:

$$Mg\ (s) \mid Mg^{2+}(0.24\ M) \mid\mid Mg^{2+}(0.53\ M) \mid Mg\ (s)$$

Data: $E^0$ ($Mg^{2+}/Mg$) = – 2.37 V.

**SOLUTION**

Concentration cell.

The Nernst equation: $E = E^0 - (RT/nF) \ln [Mg^{2+}]_{diluted}/[Mg^{2+}]_{concentrated}$

$E = 0 - [(0.082\ atm\ L\ K^{-1}\ mol^{-1} \times 298\ K) / (2 \times 96500\ C\ mol^{-1})] \ln [0.24\ M] / [0.53\ M] =$ <u>0.010 V.</u>

**Exercise 7.** Given the following cell diagram in acidic medium and at 25 °C:

$$MnO_2(s) \mid Mn^{2+}(aq) \mid\mid Ce^{4+}(aq), Ce^{3+}(aq)$$

a) Write the oxidation and reduction half-reactions and the adjusted overall redox equation.
b) If the electrochemical cell works under standard conditions, would it be spontaneous? Would it be working as a galvanic cell or an electrolytic cell? Justify your answers.

If $[Ce^{3+}] = 10^{-2}$ M, $[Ce^{4+}] = 10^{-1}$ M, and $[Mn^{2+}] = 10^{-1}$ M:

c) Calculate the pH at which the electrochemical cell is able to generate a potential of +0.65 V.

d) Calculate the concentration of a HF solution necessary to reach the pH obtained in d).

Data: $E^0(MnO_2/Mn^{2+}) = +1.23$ V; $E^0(Ce^{4+}/Ce^{3+}) = +1.61$ V; $K_a$ (HF) = $6.6 \times 10^{-4}$, R = 8.314 J $K^{-1}$ $mol^{-1}$; F = 96500 C $mol^{-1}$.

**SOLUTION**

a) Oxidation (Anode): $Mn^{2+} + 2\ H_2O \rightarrow MnO_2 + 4\ H^+ + 2\ e^-$ $\quad E^0 = -1.23$ V

Reduction (Cathode): $Ce^{4+} + 1\ e^- \rightarrow Ce^{3+}$ $\quad E^0 = +1.61$ V

Overall Reaction: $Mn^{2+} + 2\ H_2O + 2\ Ce^{4+} \rightarrow MnO_2 + 4\ H^+ + 2\ Ce^{3+}$ $\quad E^0 = +0.38$ V

b) Under standard conditions, the potential $E^0 = +0.38$ V, so $\Delta G^0 = -nFE^0 < 0$ and the process is spontaneous. This cell works as a galvanic cell.

c) The Nernst equation: $E = E^0 - (RT/nF) \ln [H^+]^4 [Ce^{3+}]^2 / [Mn^{2+}] [Ce^{4+}]^2$

0.65 V = 0.38 V – [(0.082 atm L $K^{-1}$ $mol^{-1}$ × 298 K) / (2× 96500 C $mol^{-1}$)] ln $[H^+]^4 \times [0.01\ M]^2 / [0.1\ M] \times [0.1\ M]^2$

$[H^+] = 9.12 \times 10^{-3}$ M; pH = 2.04.

d) $K_a = [F^-][H^+] / [HF]$; $6.6 \times 10^{-4} = x^2 / ([HF]_0 - x)$ where $x = 9.12 \times 10^{-3}$ M

The initial concentration of hydrofluoric acid will be: $\underline{[HF]_0 = 0.14\ M}$.