
OpenCourseWare (2023)

CHEMISTRY II

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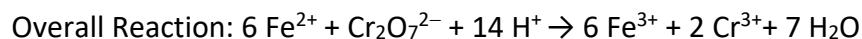
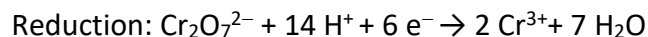
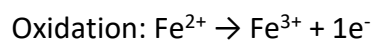
Department of Materials Science and Engineering and Chemical Engineering

SOLUTIONS OF ELECTROCHEMISTRY I EXERCISES



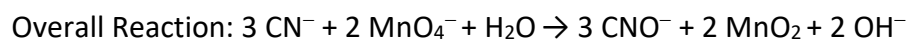
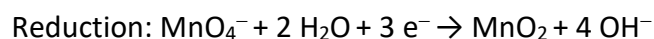
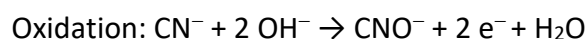
Exercise 1. Iron (II) is oxidized by dichromate ion in acidic solution to yield Fe^{3+} and Cr^{3+} . Write the balanced ionic equation.

SOLUTION



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.

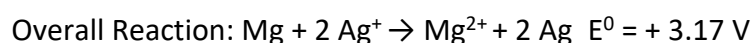
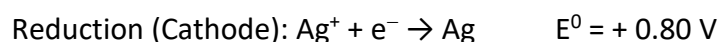
SOLUTION



Exercise 3. A galvanic cell consists of a Mg electrode in a 1 M $\text{Mg}(\text{NO}_3)_2$ solution and a Ag electrode in a 1 M AgNO_3 solution. Calculate the standard cell potential of this cell at 25 °C.

Data: $E^\circ (\text{Mg}^{2+}/\text{Mg}) = -2.37\text{ V}$; $E^\circ (\text{Ag}^+/\text{Ag}) = +0.80\text{ V}$.

SOLUTION

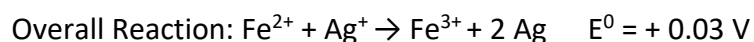
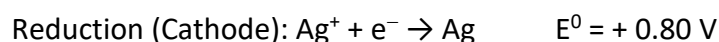


Exercise 4. Given the following cell diagram: $\text{Pt}|\text{Fe}^{2+}, \text{Fe}^{3+}||\text{Ag}^+|\text{Ag}$

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

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

SOLUTION



Reducing agent: Fe^{2+}

Oxidizing agent: Ag^+

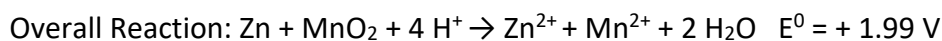
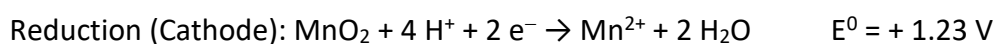
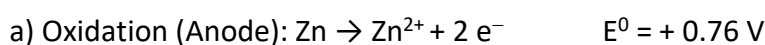
b) $K = e^{nFE^\circ/RT}$; $K = 2.97$

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.

- 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 oxidizing agents.
- Reason qualitatively how the cell potential varies if pH increases.

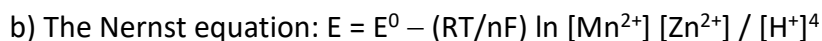
Data: $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$; $E^\circ(\text{MnO}_2/\text{Mn}^{2+}) = +1.23 \text{ V}$.

SOLUTION



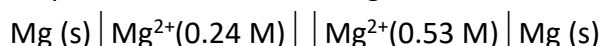
Reducing agent: Zn

Oxidizing agent: MnO_2



If pH increases, $[\text{H}^+]$ decreases and E decreases.

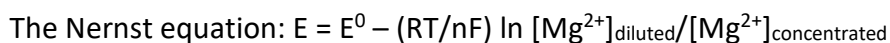
Exercise 6. Calculate the potential of the following cell at 25 °C:



Data: $E^\circ(\text{Mg}^{2+}/\text{Mg}) = -2.37 \text{ V}$.

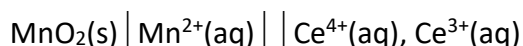
SOLUTION

Concentration cell.



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

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



- Write the oxidation and reduction half-reactions and the adjusted overall redox equation.
- 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 $[\text{Ce}^{3+}] = 10^{-2} \text{ M}$, $[\text{Ce}^{4+}] = 10^{-1} \text{ M}$, and $[\text{Mn}^{2+}] = 10^{-1} \text{ M}$:

- 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: $E^0(\text{MnO}_2/\text{Mn}^{2+}) = +1.23 \text{ V}$; $E^0(\text{Ce}^{4+}/\text{Ce}^{3+}) = +1.61 \text{ V}$; $K_a(\text{HF}) = 6.6 \times 10^{-4}$, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$; $F = 96500 \text{ C mol}^{-1}$.

SOLUTION

a) Oxidation (Anode): $\text{Mn}^{2+} + 2 \text{H}_2\text{O} \rightarrow \text{MnO}_2 + 4 \text{H}^+ + 2 \text{e}^-$ $E^0 = -1.23 \text{ V}$

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

Overall Reaction: $\text{Mn}^{2+} + 2 \text{H}_2\text{O} + 2 \text{Ce}^{4+} \rightarrow \text{MnO}_2 + 4 \text{H}^+ + 2 \text{Ce}^{3+}$ $E^0 = +0.38 \text{ V}$

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

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

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

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

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

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