CHEM 20B Week 9

Aidan Jan

March 11, 2024

Electrochemistry

General Rules to Balance Oxidation-Reduction Equation:

1. Write the two unbalanced half-reactions.
2. Balance both half-reactions for all atoms except O and H.
3. Balance each half-reaction for O by adding H_2O, and then balance for H by adding H^+.
4. Balance each half-reaction for charge by adding elecrons to the side with greater positive charge.
5. Multiply each half-reaction by a factor to make the electron count the same in both half-reactions.
6. Add the two balanced reactions together and cancel species that appear on both sides of the equation.
   - Stop here for acidic solutions
7. For a basic solution, "neutralize" the excess H^+ by adding OH^- and cancel any water (if possible).

Example: Balancing Reaction of MnO_4^- and Br^- in Basic Solution

1. Write the two unbalanced half-reactions

$$\begin{aligned} Br^- &\rightarrow BrO_3^- \\ MnO_4^- &\rightarrow MnO_2 \end{aligned}$$

2. Balance both half-reactions for all atoms except O and H.

$$\begin{aligned} Br^- &\rightarrow BrO_3^- \\ MnO_4^- &\rightarrow MnO_2 \end{aligned}$$

3. Balance each half-reaction for O by adding H_2O, and then balance for H by adding H^+.

$$\begin{aligned} Br^- + 3H_2O &\rightarrow BrO_3^- + 6H^+ \\ 4H^+ + MnO_4^- &\rightarrow MnO_2 + 2H_2O \end{aligned}$$

4. Balance each half-reaction for charge by adding electrons to the side with greater positive charge.

$$\begin{aligned} Br^- + 3H_2O &\rightarrow BrO_3^- + 6H^+ + 6e^- \\ 4H^+ + MnO_4^- + 3e^- &\rightarrow MnO_2 + 2H_2O \end{aligned}$$

5. Multiply each half-reaction by a factor to make the electron count the same in both half-reactions.

$$\begin{aligned} Br^- + 3H_2O &\rightarrow BrO_3^- + 6H^+ + 6e^- \\ 8H^+ + 2MnO_4^- + 6e^- &\rightarrow 2MnO_2 + 4H_2O \end{aligned}$$

6. Add the two balanced reactions together and cancel species that appear on both sides of the equation.

$$Br^- + 3H_2O + 8H^+ + 2MnO_4^- + 6e^- \rightarrow BrO_3^- + 6H^+ + 6e^- + 2MnO_2 + 4H_2O$$
$$2H^+ + 2MnO_4^- + Br^- \rightarrow BrO_3^- + 2MnO_2 + H_2O$$

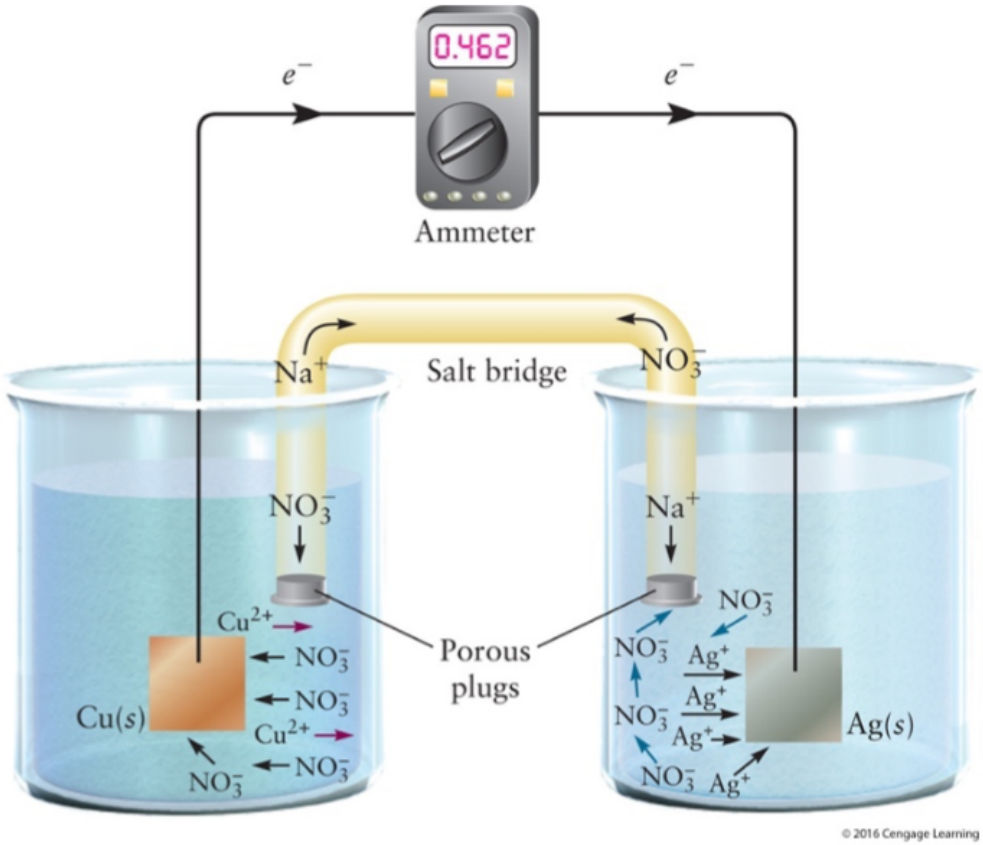
7. Since the reaction occurs in a basic solution, "neutralize" the excess H^+ by adding OH^- and cancel any water (if possible).

$$2H^+ + 2OH^- + 2MnO_4^- + Br^- \rightarrow BrO_3^- + 2MnO_2 + H_2O + 2OH^-$$
$$2MnO_4^- + Br^- + H_2O \rightarrow BrO_3^- + 2MnO_2 + 2OH^-$$

Electrochemical cells

An **electrochemical cell** is a device in which an electric current is either produced by a spontaneous chemical reaction or used to bring about a nonspontaneous reaction.

- **Galvanic cell:** electrochemical cell in which a spontaneous chemical reaction is used to generate an electric current.
- For example, batteries
  - If we simply mix two species that undergo a redox reaction, energy is released as heat, but no electricity is generated. However, if we separate the reactants and provide a pathway for the electrons to travel, the electrons can do work, generating an electric current.
- A galvanic cell consists of **two electrodes:**
  - **Anode:** the electrode at which oxidation (Loss of electrons) occurs.
  - **Cathode:** the electrode at which reduction (gain of electrons) occurs.
  - Electrons flow from the anode to cathode.



Voltage

- Electrostatic Potential: Φ (V)
- Electrostatic Potential Energy: E_p (J)
- The SI unit for potential in the volt:

$$1V = 1J \cdot C^{-1}$$

$$\Delta E_p = q\Delta\Phi$$

Faraday's Laws

- The mass of a given substance that is produced or consumed in an electrochemical reaction is proportional to the quantity of electric charge passed.
- The magnitude of the charge on a single electron:

$$|-e| = e = 1.60 \times 10^{-19} C$$

- The magnitude of the charge of one mole of electrons:

$$Q = (6.022 \times 10^{23})(1.60 \times 10^{-19} C) = 96485.34 C$$

$$Q = e \cdot N$$

- Faraday constant: Denoted as F, the magnitude of the charge per mole of electrons:

$$F = 96,485.34\, C \cdot mol^{-1}$$

- Electric Current: is the amount of charge that flows through a circuit per second, measured in the SI unit, the ampere (A):

$$1\, C = (1\, A)(1\, s)$$

- *The amount of charge that has passed when a current of 1 amperes has flowed for t seconds is*

$$Q = I \cdot t$$

- The number of moles of electrons n transferred:

$$n = \frac{I \cdot t}{96485.34}$$

Cell Potentials and the Gibbs Free Energy

Change in the potential energy associated with the transfer of N electrons:

$$\Delta E_p = -N \cdot e \Delta \Phi$$

$$Q = N \cdot e$$

$$\Delta E_p = -Q \Delta \Phi = -nF \Delta \Phi$$

$$\Delta E_p = -Q \Delta E_{cell} = -nF \Delta E_{cell}$$

Where ΔE_{cell} is the cell potential difference measured in volts.
Note: E in electrochemistry represents *potential*, not *energy*.
ΔE_p is the change in potential energy of the electrons. It is defined as the electrical work, w_{elec} is measured in Joules.

$$w_{elec} = \Delta E_p = -Q \Delta E_{cell} = -nF \Delta E_{cell}$$

In summary, **work is equal to the change in potential**.

There are two types of cells:

1. Electrolytic cells
    - **Work done on the system by external power supply:** electrons move from regions of more positive potentials to regions of more negative potential (increasing their potential energy)
2. Galvanic cells

- **Work done by the system:** electrons move from regions of more negative potentials to regions of more positive potential (decreasing their potential energy)

$$\Delta E_{cell} = E_{cathode} - E_{anode}$$

At constant pressure and temperature, the following is true:

$$w_{elec,rev} = \Delta G = -nF\Delta E_{cell}$$

Standard States and Standard Cell Potentials

$$\Delta G^\circ = -nF\Delta E^\circ_{cell}$$

n is the number of moles of electrons transferred in the reduction-oxidation reaction.

Concentration Effects and the Nernst Equation

The Nernst equation allows us to calculate the electric potential of a cell in non-standard conditions

$$\Delta G = \Delta G^\circ + RT \ln Q$$

When combined with the Faraday relation:

$$\Delta G = -nF\Delta E_{cell}$$

$$\Delta G^\circ = -nF\Delta E^\circ_{cell}$$

we get:

$$\Delta E_{cell} = -\frac{\Delta G}{nF} = \frac{\Delta G^\circ + RT \ln Q}{nF} = -\frac{\Delta G^\circ}{nF} - \frac{RT}{nF} \ln Q$$

i.e.,

$$\Delta E_{cell} = \Delta E^\circ_{cell} - \frac{RT}{nF} \ln Q$$