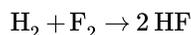


7.1: Electrochemical Cells

Electrochemistry is the study of chemical processes that cause electrons to move. This movement of electrons is called electricity, which can be generated by movements of electrons from one element to another in a reaction known as an oxidation-reduction ("redox") reaction. A redox reaction is a reaction that involves a change in oxidation state of one or more elements. When a substance loses an electron, its oxidation state increases; thus, it is oxidized. When a substance gains an electron, its oxidation state decreases, thus being reduced. For example, for the redox reaction

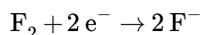


can be rewritten as follows:

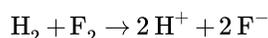
- Oxidation reaction



- Reduction reaction:



- Overall Reaction



Oxidation is the loss of electrons, whereas reduction refers to the acquisition of electrons, as illustrated in the respective reactions above. The species being oxidized is also known as the reducing agent or reductant, and the species being reduced is called the oxidizing agent or oxidant. In this case, H_2 is being oxidized (and is the reducing agent), while F_2 is being reduced (and is the oxidizing agent). The following acronym is useful in remembering this concept:

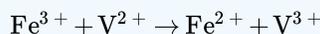
"OIL RIG"

"OIL RIG" is a useful mnemonic for remembering the definitions of oxidation and reduction.

Oxidation Is Losing electrons; Reduction Is Gaining electrons

Example 7.1.1: Iron-Vanadium Couple

Given the redox reaction

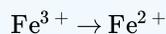


which species is oxidized? Which is reduced? Identify the reducing agent and the oxidizing agent.

Solution

Fe^{3+} is *reduced* into Fe^{2+} and V^{2+} is *oxidized* into V^{3+} . This is because the oxidized species loses electrons, and the reduced species gains electrons.

Iron gains an electron



and vanadium loses an electron



Thus, Fe^{3+} is the oxidizing agent and V^{2+} is the reducing agent.

Oxidation States

Rules for Assigning Oxidation States

- Free elements have an oxidation state of 0. (e.g., He, N₂, O₂ has an oxidation state of 0)
- The oxidation state of one ion must equal the net charge. (e.g., F⁻ oxidation state is -1, K⁺ oxidation state is +1)
- The sum of the oxidation state has to equal the total net charge for a compound. (e.g., MnO₄⁻ has a net charge of -1 with Mn(+7)O₄(-8)= -1)
- The alkali metals ([Group I elements](#)) have an oxidation state of +1. (e.g., Li₂O, Li= +1)
- The alkaline earth metals ([Group II elements](#)) always have an oxidation state of +2. (e.g., CaO, Ca=+2)
- Oxygen has an oxidation state of -2 in a compound
- Fluorine has an oxidation state of -1 in a compound
- Hydrogen has an oxidation state of +1 in a compound.
- Transition metals and other metals may have more than one common ionic charge. (e.g., Chromium's common ionic charges are Cr⁺² and Cr⁺³)

? Exercise 7.1.1

What is the oxidation state of magnesium in MgF₂?

Answer

Using rule 5 and 7.

MgF₂ total charge=0 Total Charge=(+2)+(-1*2)=0

? Exercise 7.1.2

What is the oxidation state of hydrogen in H₂O?

Answer

Using rule 6 and 8

H₂O total charge=0 Total Charge=(+1*2)+(-2)=0

Balancing Redox Reactions

Method 1: Oxidation Number Method

- Step 1: Assign oxidation numbers to each atom.
- Step 2: Determine the net change in charge to determine the ratio of atoms
- Step 3: Use the ratio to eliminate the net charge change
- Step 4: Use the ratio as coefficients for the elements
- Step 5: Add H⁺ (under acidic conditions), OH⁻ (under basic conditions), and H₂O to balance charges.

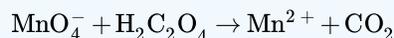
Method 2: Half-Reaction Method

- Step 1: Determine oxidation numbers for each atom
- Step 2: Use oxidation numbers to determine what is oxidized and what is reduced.
- Step 3: Write a half-reaction for reduction
- Step 4: Write a half-reaction for oxidation
- Step 5: Balance all elements except H and O
 - if have acid redox reaction: Balance the O using H₂O, balance the H using protons
 - if have base redox reaction: Balance O using OH⁻
- Step 6: Add up the charge on each side
- Step 7: Balance the charges by adding electrons
- Step 8: Multiply the half-reactions by factors that cancel out electrons

- Step 9: Add the two half-reactions back together to eliminate out intermediates

✓ Example 7.1.2: Manganese

Balance the following reaction in an acidic aqueous Solution

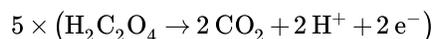


Solution

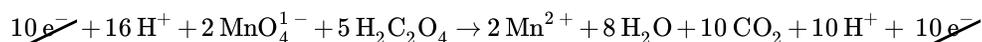
- Reduction half-reaction:



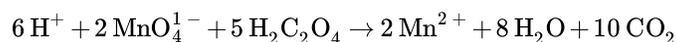
- Oxidation half-reaction:



Combining and canceling gives the following:



Answer



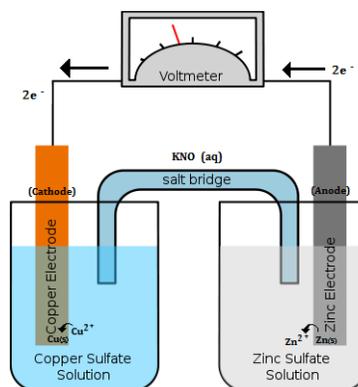
Voltaic (Galvanic) Cells

In 1793, Alessandro Volta discovered that electricity could be produced by placing different metals on the opposite sides of a wet paper or cloth. He made his first battery by placing Ag and Zn on the opposite sides of a moistened cloth with salt or weak acid Solution. Therefore, these batteries acquired the name voltaic cells. Voltaic (galvanic) cells are electrochemical cells that contain a **spontaneous reaction**, and always have a positive voltage. The electrical energy released during the reaction can be used to do work. A voltaic cell consists of two compartments called half-cells. The half-cell where oxidation occurs is called the **anode**. The other half-cell, where reduction occurs, is called the **cathode**. The electrons in voltaic cells flow from the negative electrode to the positive electrode—from anode to cathode (see figure below). (Note: the electrodes are the sites of the oxidation and reduction reactions). The following acronym is useful in keeping this information straight:

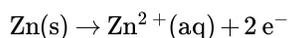
Red Cat and An Ox

Reduction Cathode and Anode Oxidation

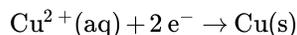
For an oxidation-reduction reaction to occur, the two substances in each respective half-cell are connected by a closed circuit such that electrons can flow from the reducing agent to the oxidizing agent. A salt bridge is also required to maintain electrical neutrality and allow the reaction to continue.



The figure above shows that Zn(s) is continuously oxidized, producing aqueous Zn^{2+} :



Conversely, in the cathode, Cu^{2+} is reduced and continuously deposits onto the copper bar:



As a result, the Solution containing $\text{Zn}(\text{s})$ becomes more positively charged as the Solution containing $\text{Cu}(\text{s})$ becomes more negatively charged. For the voltaic cell to work, the Solutions in the two half-cells must remain electrically neutral. Therefore, a salt bridge containing KNO_3 is added to keep the Solutions neutral by adding NO_3^{-} , an anion, into the anode Solution and K^{+} , a cation, into the cathode Solution. As oxidation and reduction proceed, ions from the salt bridge migrate to prevent charge buildup in the cell compartments.

The **cell diagram** (or **cell notation**) is a shorthand notation to represent the redox reactions of an electrical cell. For the cell described, the cell diagram is as follows:



- A double vertical line (||) is used to separate the anode half reaction from the cathode half reaction. This represents the salt bridge.
 - The anode (where oxidation occurs) is placed on the left side of the (||).
 - The cathode (where reduction occurs) is placed on the right side of the (||).
- A single vertical line (|) is used to separate different states of matter on the same side, and a comma is used to separate like states of matter on the same side. For example:

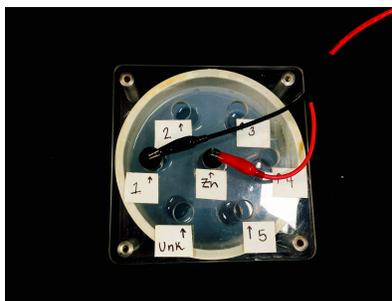
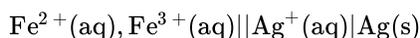
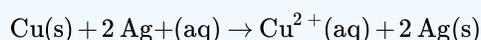


Figure 7.1.2: A voltaic cell works by the different reactivity of metal ions, and not require external battery source. Image taken at Hope College as part of their General Chemistry Lab curriculum.

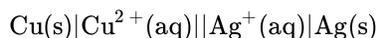
The figure above shows a set of electrochemical half-cells that can be used to measure various voltages within galvanic cells. The cells shown are made of agar saturated with KCl Solution so as to act as a salt bridge. The zinc electrode in the middle can be used as a reference while the various concentrations of copper (labeled 1, 2, 3, 4 and 5) can be tested to form a calibration curve. The potential of the unknown can be used to determine the concentration of an unknown copper Solution. This application of the Nernst equation allows for rapid data collection without the need for a complicated salt bridge apparatus.

✓ Example 7.1.3: Copper-silver Reaction

Write the cell diagram for this reaction:



Solution

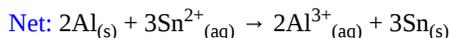
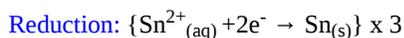


✓ Example 7.1.4: Aluminum-Tin Reaction

Write cell reactions for this cell diagram:



Answer



Cell Potentials

The oxidation of $Zn_{(s)}$ into Zn^{2+} and the reduction of Cu^{2+} to $Cu_{(s)}$ occur spontaneously. In other words, the redox reaction between Zn and Cu^{2+} is spontaneous. This is due to the difference in potential energy between the two substances. The difference in potential energy between the anode and cathode dictates the direction of electronic movement. Electrons move from areas of higher potential energy to areas of lower potential energy. In this case, the anode has a higher potential energy; electrons therefore move from anode to cathode. The potential difference between the two electrodes is measured in units of volts. One volt (V) is the potential difference necessary to generate a charge of 1 coulomb (C) from 1 joule (J) of energy.

For a voltaic cell, this potential difference is called the **cell potential (or EMF for electromotive force, although it is not really a force)**, which is denoted E_{cell} . For a spontaneous reaction, E_{cell} is positive and ΔG (Gibbs free energy, used to determine if a reaction occurs spontaneously) is negative. Thus, when ΔG is negative the reaction is spontaneous. Merging electrochemistry with thermodynamics gives this formula:

$$\Delta G = -nFE_{cell}$$

Cell potential is different for each voltaic cell; its value depends upon the concentrations of specific reactants and products as well as temperature of the reaction. For **standard cell potential**, temperature of the reaction is assumed to be 25° Celsius, the concentration of the reactants and products is 1 M, and reaction occurs at 1 atm pressure. The standard cell potential is denoted E°_{cell} , and can be written as oxidation potential + reduction potential. For voltaic cells:

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{Anode} \quad (7.1.1)$$

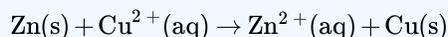
Warning

To use Equation 7.1.1, the cell potentials must be in reduction form.

Since standard potentials are given in the form of standard reduction potential for each half-reaction, to calculate the standard cell potential E°_{cell} , the substance is being oxidized must be identified; then the standard reduction potential of the oxidation reaction is subtracted from the standard reduction potential of the reducing reaction.

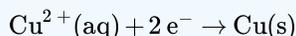
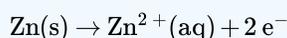
Example 7.1.5

What is the cell potential for the following reaction?



Solution

$Zn_{(s)}$ is being oxidized, and $Cu_{(s)}$ is being reduced. The potentials for the two half reaction are given in the reduction form:



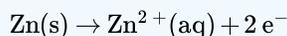
The cell potentials indicate which reaction takes place at the anode and which at the cathode. The cathode has a more positive potential energy, and thus:

- $Cu_{(s)}$ is the *cathode*
- $Zn_{(s)}$ is the *anode*.

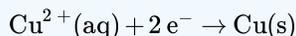
To calculate E°_{cell} , subtract the E° of the oxidized half reaction from the E°_{cell} of the reduction half reaction, we use Equation 7.1.1):

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

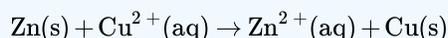
Oxidation half reaction: $E^{\circ} = -0.763\text{V}$



- Reduction half reaction: $E^{\circ} = +0.342\text{V}$



Net reaction:

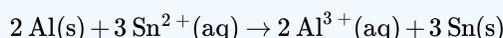


Therefore:

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = 0.340\text{V} - (-0.763\text{V}) = +1.103\text{V}$$

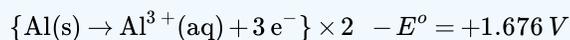
✓ Exercise 7.1.6

Calculate E_{cell}° for the following redox reaction under standard conditions:

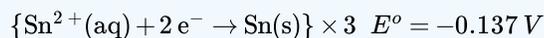


Answer

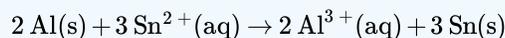
Oxidation:



Reduction:



Net reaction:

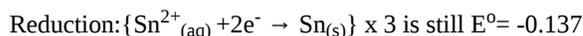
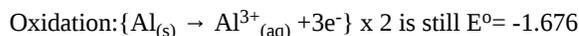


Then using Equation 7.1.1

$$E_{\text{cell}}^{\circ} = -0.137\text{V} - (-1.676\text{V}) \\ = +1.539\text{V}$$

Voltage is an Intensive Property

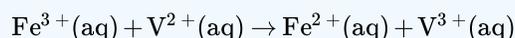
Standard reduction potential is an intensive property, meaning that changing the stoichiometric coefficient in a half reaction does not affect the value of the standard potential. For example,



If the stoichiometric coefficient is multiplied by 2, the standard potential does not change:

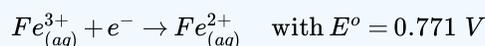
✓ Example 7.1.7: Iron/Vanadium Chemistry

Calculate the cell potential in the following redox reaction under standard conditions:



Solution

Consult the table of standard reduction potentials (Table P1) for each half reaction:





The cell potential is

$$E_{cell}^{\circ} = E_{cathode}^{\circ} - E_{anode}^{\circ} = 0.771 \text{ V} - (-0.255 \text{ V}) = 1.026 \text{ V}$$

Glossary

- Anode: Electrode in an electrochemical cell on which the oxidation reaction occurs.
- Cathode: Electrode in an electrochemical cell on which the reduction reaction occurs
- Electrochemistry: A field of chemistry that focuses on the interchange between electrical and chemical energy
- Electricity: Flow of electrons over a wire that is affected by the presence and flow of electric charge.
- Electrolysis: The decomposition of a substance by means of electric current. This method pushes a redox reaction toward the non-spontaneous side.
- Electrolytic cell: Electrochemical cell that is being pushed toward the non-spontaneous direction by electrolysis.
- Electromotive force, EMF (or cell potential): Difference of potential energy of electrons between the two electrodes.
- Oxidation number: Charge on an atom if shared electrons were assigned to the more electronegative atom.
- Oxidation: Lose of electrons, can occur only in combination with reduction. [remember: Oxidation Is Loss, Reduction Is Gain = OIL RIG]
- Reduction: Gain of electrons, can occur only in combination with oxidation. [remember: OIL RIG]
- Redox reaction: Shorthand for reduction-oxidation reaction.
- Voltaic cell or galvanic cell: An electrochemical cell that uses redox reaction to produce electricity spontaneously.

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Contributors and Attributions

- Matthew Bui (UCD), Wen Chung Chou (UCD)
- Justin Shorb (Hope College), Yong Chul Yoon (Hope College)

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