Previous Chapter Table of Contents Next Chapter

Chapter 19: Electrochemistry

Section 19.1: Introduction to Electrochemistry

Electrochemistry is the study of the relationships between electrical energy and chemical reactions. Before proceeding further in this chapter, it is important that you thoroughly review the following topics in Chapter 2.

1) Concepts of oxidation and reduction
2) Calculating oxidation numbers
3) Balancing half-reactions in acidic and basic solutions
4) Balancing redox reactions in acidic and basic solutions

Electrochemistry is mainly the study of two types of electrochemical cells:

Voltaic or Galvanic Cell and Electrolytic Cell

a) Voltaic or Galvanic Cell

In this type of cell, a chemical reaction produces electrical energy. All batteries contain Voltaic cells. The electrical energy from Voltaic cells is used to operate electrical devices such as flashlights, CD players, etc… Hence, during the operation of a Voltaic cell, work (w) is done by the system on the surroundings.

b) Electrolytic Cell

In this type of cell, energy from an external power supply is used to force a chemical reaction. Electroplating and extraction of metals from ores use electrolytic cells. Hence, during the operation of an Electrolytic cell, work (w) is done by the surroundings on the system.

Sections 19.2 - 19.3: Voltaic Cell

Consider the redox reaction occurring in a Voltaic cell:

$$\mathbf{Zn_{(s)} + Cu^{+2}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + Cu_{(s)}}$$

Break the redox reaction into an oxidation half-reaction,

$$Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2\ e^-$$

and a reduction half-reaction,

$$Cu^{+2}{}_{(aq)} + 2\ e^{-} \rightarrow Cu_{(s)}$$

Thus, a Voltaic cell consists of two **compartments**, or two beakers, one where the oxidation half-reaction occurs, and the other where the reduction half-reaction occurs.

Assume that:

the oxidation half-reaction occurs in the left beaker.

the reduction half-reaction occurs in the right beaker.

Thus, the half-reactions are:

$$Zn_{(s)} \rightarrow Zn^{+2}{}_{(aq)} + 2\ e^{-} \qquad Cu^{+2}{}_{(aq)} + 2\ e^{-} \rightarrow Cu_{(s)}$$

In this redox reaction, we have solid Zn and Cu. Both Zn and Cu are metals. Hence, they conduct electricity. Substances made of materials that conduct electricity can be used as **electrodes**. Thus, there are two electrodes in a Voltaic cell. In this example, we use strips of Zn and Cu as electrodes.

$$\underset{\text{Oxidation}}{Zn_{(s)} \rightarrow Zn^{+2}{}_{(aq)} + 2\ e^{-}} \qquad \underset{\text{Reduction}}{Cu^{+2}{}_{(aq)} + 2\ e^{-} \rightarrow Cu_{(s)}}$$

For a chemical reaction to occur, these electrodes are dipped in aqueous solutions containing Zn^{+2} and Cu^{+2} ions. These aqueous solutions are **electrolytes**. Recall, electrolytes are solutions that conduct electricity.

One of the electrodes is called the **cathode**, and the other is called the **anode**.

$$\overset{\text{anode}}{\underset{\text{Oxidation}}{Zn_{(s)} \rightarrow Zn^{+2}{}_{(aq)} + 2\ e^{-}}} \qquad \overset{\text{cathode}}{\underset{\text{Reduction}}{Cu^{+2}{}_{(aq)} + 2\ e^{-} \rightarrow Cu_{(s)}}}$$

The cathode is always the electrode at which the reduction half-reaction occurs. In this example, Cu is the cathode. Recall, reduction is the gain of electrons. This means that a cathode accepts electrons.

The anode is always the electrode at which the oxidation half-reaction occurs. In this example, Zn is the anode. Recall, oxidation is the loss of electrons. This means that an anode gives out electrons.

To allow the transfer of electrons between the two electrodes, the anode and the cathode are connected to each other with a wire. This is called creating a circuit. Thus, electrons always flow from the anode to the cathode.

There is an excess negative charge at the anode, since this is where the oxidation (i.e. loss of electrons) takes place. For this reason, a negative charge is shown at the anode.

There is a deficit of negative charge at the cathode, since this is where reduction (i.e. gain of electrons) occurs. For this reason, a positive charge is shown at the cathode.

The electrons will flow from the anode to the cathode momentarily because the electrical circuit is not complete. Why?

Consider the oxidation half-cell. The oxidation half-cell contains a Zn^{+2} solution. Now, the loss of two e^- at the Zn electrode is accompanied by the ionization of Zn to Zn^{+2}, and the release of this ion into solution. Thus, a net positive charge would develop in solution.

Consider the reduction half-cell. The gain of two e^- at the Cu electrode is accompanied by the migration of a Cu^{+2} ion onto the cathode, and its transformation to Cu metal. Hence, the reduction half-reaction decreases $[Cu^{+2}]$ in solution. Thus, a net negative charge would develop in solution.

Overall, this results in a charge build-up, which stops the flow of electrons. To enable the flow of electrons, we use a **salt bridge** to connect the two half-cells. The salt bridge completes the circuit by allowing the ions to flow between the two half-cells. The salt bridge prevents charge build-up, and allows the continuous flow of electrons from the anode to the cathode.

The salt bridge is an inverted U-tube containing a gel. The gel contains a solution of non-reactive ions (e.g. Na^+ and SO_4^{-2} ions). Note: These non-reactive ions can diffuse into and out of the half-cells via the salt bridge, but the solutions cannot.

In Section 19.3, practice the Interactive Problems.

Sections 19.4 - 19.5: Notation for Voltaic Cells

Consider the redox reaction:

$$\mathbf{Zn_{(s)} + Cu^{+2}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + Cu_{(s)}}$$

The notation used for the description of the components in a Voltaic cell is:

$$Zn_{(s)} \mid Zn^{+2}_{(aq)} \parallel Cu^{+2}_{(aq)} \mid Cu_{(s)}$$

The redox reaction in a Voltaic cell can be divided into two half-reactions. Hence, we can imagine that the Voltaic cell is divided into two half-cells.

1. Oxidation 2. Reduction

Double vertical lines, representing a salt bridge connection, separate oxidation and reduction half-cells. The oxidation half-cell is always to the left of the double vertical lines. The reduction half-cell is always to the right of the double vertical lines. The vertical lines within oxidation and reduction half-cells represent boundaries between different phases. For example, the phase boundary between Zn and Zn^{+2} is represented as:

$$Zn_{(s)} \mid Zn^{+2}_{(aq)}$$

Here, we say Zn is oxidized to Zn^{+2}.

Similarly, the phase boundary between Cu^{+2} and Cu is represented as:

$$Cu^{+2}_{(aq)} \mid Cu_{(s)}$$

Here, we say Cu^{+2} is reduced to Cu.

The electrodes used in this reaction are Zn and Cu. Since these electrodes are substances involved in the redox reaction, they are called **active electrodes**.

Consider the following redox reaction:

$$2\ MnO_4^-{}_{(aq)} + 16\ H^+{}_{(aq)} + 10\ I^-{}_{(aq)} \rightarrow 2\ Mn^{+2}{}_{(aq)} + 5\ I_{2\ (s)} + 8\ H_2O_{(l)}$$

The notation for the corresponding Voltaic cell is:

$$\text{graphite} \mid I^-{}_{(aq)} \mid I_{2\ (s)} \parallel H^+{}_{(aq)}, MnO_4^-{}_{(aq)}, Mn^{+2}{}_{(aq)} \mid \text{graphite}$$

Since we cannot use active electrodes (iodide and manganese ions are not metallic conductors), we use **inactive electrodes** like graphite. In this notation, a comma separates half-cell components that are in the same phase. Double vertical lines, representing a salt bridge connection, separate oxidation and reduction half-cells. The oxidation half-cell is always to the left of the double vertical lines, while the reduction half-cell is always to the right of the double vertical lines.

In Section 19.5, practice the Interactive Problems.

Section 19.6: Potential of a Voltaic Cell

A Voltaic cell converts the free energy change of a chemical reaction into the kinetic energy of electrons moving from the anode to the cathode. For a Voltaic cell to function, the reaction must occur spontaneously. During a spontaneous reaction, electrons flow from the anode to the cathode, producing electrical energy that can do work (w). This electrical energy is proportional to the difference in electrical potential between the anode and the cathode.

The difference in electrical potential between the two electrodes is called the **cell potential**, or the **electromotive force** (**emf**). The cell potential is written as E_{cell}. The SI unit of electrical potential used to express E_{cell} is the Volt (V).

Recall: During a spontaneous redox reaction, the anode is negatively charged and the cathode is positively charged. Hence, the cell operates spontaneously when the difference in electrical potential between the cathode and the anode is positive.

If $E_{cell} > 0$, the redox reaction occurs spontaneously. The electrical work (w) is directly proportional to E_{cell}. Hence, the greater the cell potential, the more work (w) the cell can do. For example, a common alkaline battery has E_{cell} of 1.5 V, and a car battery usually has 6 cells, each with E_{cell} of 2.0 V. Thus, the overall E_{cell} of a car battery is 12.0 V.

If $E_{cell} < 0$, the redox reaction does not occur spontaneously. In this case, an external power supply must be used to force the reaction.

If $E_{cell} = 0$, the cell redox reaction has reached equilibrium. If the cell reaction is at equilibrium, no work (w) can be done by the cell.

Section 19.7: Standard Cell Potentials

The standard cell potential is expressed as E°. The standard cell potential is the potential of a cell in which all species are in their standard state. The standard state for:

a) gases is the pure gas state at 1 atm

b) electrolytes is the solute at 1 M (1 mol/L) concentration

The standard electrode potential is the potential associated with a given half-reaction in either an oxidation or a reduction half-cell. The standard electrode potential is expressed as $E°_{half\text{-}cell}$. By convention, a standard electrode potential, $E°_{half\text{-}cell}$, always refers to the reduction half-cell.

You may have noted that the potential given in the potential table on the DVD for the standard hydrogen electrode is zero.

$$2\,H^+_{(aq)} + 2\,e^- \rightarrow H_{2\,(g)} \qquad E°_{half\text{-}cell} = 0$$

The standard hydrogen electrode is chosen as the standard reference electrode. The potential of the standard reference electrode is defined as zero.

The values of $E°_{\text{half-cell}}$ for reduction half-reactions are always referenced to, or compared to, the standard hydrogen electrode. Hence, the standard electrode potential measures the electrode's relative ability to pull electrons compared to the standard hydrogen electrode.

For the reduction of Cu^{+2} to Cu, $E°_{\text{half-cell}} = + 0.34$ V. Hence, Cu^{+2} has a greater ability to pull electrons that H^{+}. Conversely, for the reduction of Zn^{+2} to Zn, $E°_{\text{half-cell}} = - 0.76$ V. Hence, Zn^{+2} has a lesser ability to pull electrons than H^{+}.

Since the Voltaic cell consists of an anode and a cathode, the standard cell potential, $E°_{\text{cell}}$, is calculated as:

$$E°_{\text{cell}} = E°_{\text{cathode}} - E°_{\text{anode}}$$

$E°_{\text{cathode}}$ is the standard electrode potential for the reduction half-reaction.

$- E°_{\text{anode}}$ is the standard electrode potential for the oxidation half-reaction.

Note: The negative sign is used since $E°_{\text{half-cell}}$ *values always refer to reduction half-reactions.*

Remember:

a) A cell operates spontaneously only if $E°_{\text{cell}}$ is positive.

b) If a cell operates spontaneously, it is a Voltaic or Galvanic cell.

Sections 19.8 - 19.9: Calculating Standard Cell Potentials

Example: Calculate the standard cell potential for:

$$\mathbf{Fe_{(s)} \mid Fe^{+2}_{(aq)} \mid\mid Ag^{+}_{(aq)} \mid Ag_{(s)}}$$

The oxidation half-reaction is:

$$Fe_{(s)} \rightarrow Fe^{+2}_{(aq)} + 2\,e^{-}$$

The reduction half-reaction is:

$$Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)}$$

The overall cell potential, $E°_{\text{cell}} = E°_{\text{cathode}} - E°_{\text{anode}}$

By convention, the standard electrode potentials, $E°_{half\text{-}cell}$, are given for reduction half-reactions.

The oxidation half-reaction for Fe/Fe^{+2}:

$$Fe_{(s)} \rightarrow Fe^{+2}_{(aq)} + 2\,e^{-} \qquad E°_{anode} = -\,0.44\text{ V}$$

The reduction half-reaction for Ag^{+}/Ag:

$$Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)} \qquad E°_{cathode} = +\,0.80\text{ V}$$

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

$$E°_{cell} = (+\,0.80\text{ V}) - (-\,0.44\text{ V})$$

$$E°_{cell} = +\,1.24\text{ V}$$

The two half-reactions are:

$Fe_{(s)} \rightarrow Fe^{+2}_{(aq)} + 2\,e^{-}$	Oxidation	$E°_{anode} = -\,0.44\text{ V}$
$Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)}$	Reduction	$E°_{cathode} = +\,0.80\text{ V}$

In order to write the overall redox reaction, multiply the reduction half-reaction by 2, but NOT the potential value. Thus,

$Fe_{(s)} \rightarrow Fe^{+2}_{(aq)} + 2\,e^{-}$	Oxidation	$E°_{anode} = -\,0.44\text{ V}$
$2 \times (Ag^{+}_{(aq)} + e^{-} \rightarrow Ag_{(s)})$	Reduction	$E°_{cathode} = +\,0.80\text{ V}$

Hence,

$Fe_{(s)} \rightarrow Fe^{+2}_{(aq)} + 2\,e^{-}$	Oxidation	$E°_{anode} = -\,0.44\text{ V}$
$2\,Ag^{+}_{(aq)} + 2\,e^{-} \rightarrow 2\,Ag_{(s)}$	Reduction	$E°_{cathode} = +\,0.80\text{ V}$

$Fe_{(s)} + 2\,Ag^{+}_{(aq)} \rightarrow Fe^{+2}_{(aq)} + 2\,Ag_{(s)}$ is the cell reaction ($E°_{cell} = +\,1.24$ V).

Since $E°_{cell}$ is positive, the cell operates spontaneously.

In Section 19.9, practice the Interactive Problems.

Section 19.10: Oxidizing and Reducing Agents

Consider the redox reaction:

$$Zn_{(s)} + Cu^{+2}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + Cu_{(s)}$$

In this reaction, we note that Zn is oxidized to Zn^{+2} and Cu^{+2} is reduced to Cu. Thus, Zn is the reducing agent and Cu^{+2} is the oxidizing agent. The questions one needs to answer for the redox reaction are:

Why is Zn the reducing agent?

Why is Cu^{+2} the oxidizing agent?

The measurement of standard half-cell potentials, $E°_{half\text{-}cell}$, gives us information about the relative strength of oxidizing and reducing agents.

The standard half-cell potentials for Zn and Cu^{+2} are:

$$Cu^{+2}_{(aq)} + 2\,e^{-} \rightarrow Cu_{(s)} \qquad E°_{half\text{-}cell} = +\,0.34\ V$$

$$Zn^{+2}_{(aq)} + 2\,e^{-} \rightarrow Zn_{(s)} \qquad E°_{half\text{-}cell} = -\,0.76\ V$$

Remember: By convention, standard half-cell potentials refer to half-reactions written as reduction reactions.

Now, look at the values of these standard half-cell potentials. The more positive the $E°_{half\text{-}cell}$ value, the greater the tendency of the reactant to be reduced. (*Note: The species that is reduced is the oxidizing agent.)* Thus, in the example, Cu^{+2} is a stronger oxidizing agent than Zn^{+2}.

Conversely, the more negative the $E°_{half\text{-}cell}$ value, the greater the tendency of the product to be oxidized. (*Note: The species that is oxidized is the reducing agent.)* Thus, in the example, Zn is a greater reducing agent than Cu.

In the Potential Table on the DVD, the reduction half-reactions are arranged in order of decreasing standard half-cell potentials, $E°_{half\text{-}cell}$. All half-cell potentials are given relative to the standard hydrogen electrode whose potential is, by convention, 0 V (i.e. $E°_{H+/H2} = 0$ V). Since these reactions are written as reduction half-reactions, reactants are oxidizing agents and products are reducing agents.

You can see from the $E°_{half\text{-}cell}$ values that F_2 is the strongest oxidizing agent (most positive electrode potential) and Li is the strongest reducing agent (most negative electrode potential). Because Li is the strongest reducing agent, it readily loses an electron to get oxidized to Li^+. Because F_2 is the strongest oxidizing agent, it readily accepts electrons to be reduced to F^-.

Commonly used reducing agents are H_2, alkali metals and alkaline earth metals. Other metals whose cations have a negative $E°_{half\text{-}cell}$ value can also be used as reducing agents.

Examples: Cl_2 is a stronger oxidizing agent than Br_2 because $E°_{half\text{-}cell}$ for Cl_2 is more positive than $E°_{half\text{-}cell}$ for Br_2.

Cd^{+2} is a stronger reducing agent than Ni^{+2} because $E°_{half\text{-}cell}$ for Cd^{+2} is more negative than $E°_{half\text{-}cell}$ for Ni^{+2}.

Section 19.11: Standard Cell Potential and the Equilibrium Constant

In Chapter 18, we learned that: $\Delta G = - R\ T \ln K$. We also learned that a spontaneous reaction occurring at constant temperature and pressure has a negative free energy change, i.e. $\Delta G < 0$. For a spontaneous reaction occurring in the standard state, $\Delta G° < 0$. The more negative the free energy change, the larger the equilibrium constant, K, and the larger the tendency of reactants to form products.

In this chapter, we stated that: For a spontaneous electrochemical reaction, the standard cell potential is positive, i.e. $E°_{cell} > 0$, and electric work (w) is done by the cell ($w < 0$). The larger $E°_{cell}$, the larger the tendencies for the oxidizing agent to gain electrons, and for the reducing agent to lose electrons.

These statements suggest that there are specific relationships between $\Delta G°$, K, w, $E°_{cell}$ and the number of electrons transported. To obtain these relationships, recall another result from Chapter 18.

"The change in free energy, $\Delta G°$, for a spontaneous process occurring at constant T and P is equal to the maximum work, w_{max}, that can be done by the system."

Under standard conditions, we write:

$$\Delta G° = w_{max}$$

The work, w_{max}, is the electrical work produced by the redox cell. Electrical work is defined as the product of the charge transported, q, by the electric potential difference, V, which moves the charge.

$$w_{max} = q \times V$$

In the case of a redox cell transporting "n" moles of electrons from the anode to the cathode:

V, the electric potential difference is $E°_{cell}$, the difference in potential between the anode and the cathode, and,

q is the electric charge associated with “n” moles of electrons.

The S.I. unit of charge is the coulomb, C. The charge of one electron expressed in coulombs is $q_{e^-} = -1.602 \times 10^{-19}$ C.

The <u>absolute value</u> of the charge of one mole of electrons is called the **Faraday constant** and is expressed as *F*.

$$F = \text{Avogadro's Number} \times |q_{e^-}|$$

$$F = (6.02214 \times 10^{23}\ \text{mol}^{-1}) \times |(-1.60218 \times 10^{-19}\ \text{C})|$$

$$F = 96{,}485\ \text{C/mol e}^-$$

Hence, q, the charge of one mole of electrons, is equal to – *F*. For “n” moles of electrons transferred in the balanced redox reaction, the charge, q, is expressed as:

$$q = -n F$$

The maximum electrical work produced by the flow of “n” moles of electrons during the redox reaction is obtained by substituting the above quantities in the expression for w_{max}.

$$w_{max} = -n F E°_{cell}$$

Now, using the relationship between w_{max} and $\Delta G°$, we obtain:

$$\Delta G° = -n F E°_{cell} \qquad \text{Memorize this}$$

Remember, for a cell reaction to run spontaneously, $\Delta G°$ must be negative and $E°_{cell}$ must be positive.

Using this relationship and $\Delta G° = -R\,T \ln K$, the standard potential, $E°_{cell}$, of an electrochemical cell can be related to the equilibrium constant, K of the associated redox reaction.

$$-R\,T \ln K = -n F E°_{cell}$$

$$E^{o}_{cell} = \frac{R\,T}{n F} \ln K$$

R = gas constant = $8.314\ \text{J.mol}^{-1}.\text{K}^{-1}$

However, here we will express R in J/K, since “per mole” is not relevant when R is introduced through ΔG° = - R T ln K. Why can we do that?

When you consider a reaction such as: 2 A + 3 B → 5 C, the quantity ΔG° refers to the reaction as written (for 2 mol A, 3 mol B and 5 mol C), NOT to 1 mol of any particular substance. The ln K has no unit, T is expressed in Kelvin, and ΔG° is expressed in joules, NOT joules per mole.

Hence, when using ΔG° = - R T ln K, always express R in J/K.

R = gas constant = 8.314 J/K

T = 25°C (under standard conditions) = 298 K

$F = 96{,}485 \text{ C/mol e}^-$

$$E^o{}_{\text{cell}} = \frac{8.314 \text{ J.K}^{-1} \times 298 \text{ K}}{\text{n mol e}^- \times 96{,}485 \dfrac{\text{C}}{\text{mol e}^-}} \times \ln K$$

$$\text{coulomb (C)} = \frac{\text{joule (J)}}{\text{volt (V)}}$$

$$E^o{}_{\text{cell}} = \frac{8.314 \text{ J} \times 298}{\text{n} \times 96{,}485 \dfrac{\text{J}}{\text{V}}} \times \ln K$$

$$E^o{}_{\text{cell}} = \frac{0.0257 \text{ V}}{\text{n}} \ln K \quad \text{and} \quad E^o{}_{\text{cell}} = \frac{0.0592 \text{ V}}{\text{n}} \log K$$

Memorize these two relationships between the standard cell potential, $E°_{\text{cell}}$, and the equilibrium constant, K. Note that the different constants (0.0257 and 0.0592) arise from the difference between ln K and log K.

Sections 19.12 - 19.13: Problems on the Standard Cell Potential and the Equilibrium Constant

Example: Given the following redox reaction:

$$\mathbf{Zn_{(s)} + 2\,Ag^{+}{}_{(aq)} \leftrightarrows Zn^{+2}{}_{(aq)} + 2\,Ag_{(s)}}$$

a) Calculate $E°_{\text{cell}}$

Write the reduction half-reactions involving Zn and Ag, and find the corresponding half-cell potentials from the Potential Table on the DVD.

$Zn^{+2}{}_{(aq)} + 2\ e^- \rightarrow Zn_{(s)}$ $\qquad E°_{Zn^{+2}/Zn} = -\ 0.44\ V$

$Ag^+{}_{(aq)} + e^- \rightarrow Ag_{(s)}$ $\qquad E°_{Ag^+/Ag} = 0.80\ V$

In the redox reaction, Zn is oxidized to Zn^{+2}, so the reverse of this half-reaction (oxidation) occurs at the anode. In the redox reaction, Ag^+ is reduced to Ag, so the half-reaction (reduction) occurs at the cathode.

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

$$E°_{cell} = 0.80\ V - (-\ 0.76\ V)$$

$$E°_{cell} = +\ 1.56\ V$$

Since $E°_{cell}$ is positive, the above redox reaction occurs spontaneously.

b) Calculate ΔG° for the redox reaction

$$\Delta G° = -\ n\ F\ E°_{cell}$$

Remember: When balancing the redox reaction, cancel out the electrons. In this reaction, 2 e^- are given at the anode, and 1 e^- is used at the cathode. Hence, multiply the cathode reaction by 2 to obtain the overall reaction. Here,

$n = 2\ mol\ e^-$ $\qquad F = 96{,}485\ C/mol\ e^-$

$$\Delta G^o = -\ 2\ mol\ e^- \times 96{,}485\ \frac{C}{mol\ e^-} \times 1.56\ V$$

$\Delta G^o = -\ 3.01 \times 10^5\ J$ $\qquad$ Recall: $J = C \times V$

$\Delta G^o = -\ 301\ kJ$ $\qquad$ Recall: $1000\ J = 1\ kJ$

c) Calculate the equilibrium constant, K, at 298 K for the above redox reaction.

To calculate K, use the relation:

$$\log K = \frac{n\ E^o{}_{cell}}{0.0592}$$

$$\text{Here, } n = 2 \text{ mol } e^{-} \qquad \text{and} \qquad E^{o}_{cell} = 1.56 \text{ V}$$

$$\log K = \frac{2 \times 1.56}{0.0592}$$

$$\log K = 52.7$$

$$K = 10^{52.7}$$

$$K = 5.01 \times 10^{52}$$

In Section 19.13, practice the Interactive Problems.

Sections 19.14 - 19.15: The Nernst Equation

Up to this point, we have discussed redox reactions in which reactants and products are initially in their standard states. Recall: The concentration of a solute in its standard state is 1.0 M. Because the chemical species involved in the cell redox reaction are initially present at the standard concentration, the cell potential is initially the standard cell potential, $E°_{cell}$. As the redox reaction proceeds, the concentrations of reactants change. Hence, the cell potential will not remain constant during the operation of the Galvanic cell. Let us call E_{cell} the electric potential generated by the cell under non-standard conditions.

The mathematical relationship between E_{cell}, $E°_{cell}$ and the concentrations of reactants and products in the redox reaction under non-standard conditions is derived as follows:

We learned in Chapter 18 that ΔG, the free energy change for a chemical reaction, can be expressed as:

$$\Delta G = \Delta G° + R\ T \ln Q$$

ΔG = free energy change under non-standard conditions

ΔG° = free energy change under standard conditions

Q = reaction quotient

We showed in section 19.11 that:

$$\Delta G° = -\ n\ F\ E°_{cell}$$

$$\text{Similarly,} \qquad \Delta G = -\ n\ F\ E_{cell}$$

Combining the previous equations, we obtain:

$$- n F E_{cell} = - n F E°_{cell} + R T \ln Q$$

$$E_{cell} = E^{o}_{cell} - \frac{R T}{n F} \ln Q$$

This equation is called the **Nernst Equation**.

Recall: For a general reaction of the type,

$$a A_{(aq)} + b B_{(aq)} \leftrightarrows c C_{(aq)} + d D_{(aq)}$$

where A and B are the reactants, C and D are the products, and a, b, c, and d are the respective stoichiometric coefficients,

$$\text{the reaction quotient, } Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Remember that pure liquids or solids have an activity of one, and do not contribute in the calculation of Q or K.

The Nernst Equation is used to calculate the cell potential, E_{cell}, when the cell operates under non-standard conditions. Using R = 8.314 J/K.mol, F = 96,485 C, replacing T by the temperature of interest (in kelvin), and using logarithm base 10, we obtain:

$$\text{At 298 K,} \qquad E_{cell} = E^{o}_{cell} - \frac{0.0592}{n} \log Q$$

Memorize the Nernst equation.

Example: Consider the following redox reaction at 298 K:

$$\mathbf{Zn_{(s)} + Cu^{+2}_{(aq)} \rightarrow Zn^{+2}_{(aq)} + Cu_{(s)}}$$

Calculate the cell potential when $[Cu^{+2}]$ = 0.15 M and $[Zn^{+2}]$ = 0.68 M.

In the reaction, the concentrations of Cu^{+2} and Zn^{+2} are not 1.0 M. Thus, the cell operates under non-standard conditions.

$$E_{cell} = E^{o}_{cell} - \frac{0.0592}{n} \log Q$$

First, calculate the standard cell potential, $E°_{cell}$.

In order to calculate $E°_{cell}$, use the Potential Table on the DVD to locate the half-reactions and corresponding potentials for Cu^{+2}/Cu and Zn^{+2}/Zn.

$$Cu^{+2}{}_{(aq)} + 2\,e^{-} \rightarrow Cu_{(s)} \qquad E°_{Cu^{+2}/Cu} = +\,0.34\text{ V}$$

$$Zn^{+2}{}_{(aq)} + 2\,e^{-} \rightarrow Zn_{(s)} \qquad E°_{Zn^{+2}/Zn} = -\,0.76\text{ V}$$

Examine the overall cell redox reaction. Zn is oxidized at the anode, and Cu^{+2} is reduced at the cathode.

$$E°_{cell} = E°_{cathode} - E°_{anode}$$

$$E°_{cell} = 0.34\text{ V} - (-\,0.76\text{ V})$$

$$E°_{cell} = +\,1.10\text{ V}$$

$$\text{In this reaction, } n = 2 \qquad \text{and} \qquad Q = \frac{[Zn^{+2}]}{[Cu^{+2}]} = \frac{(0.68)}{(0.15)}$$

$$E^{o}{}_{cell} = +1.10\text{ V} \qquad n = 2 \qquad Q = \frac{(0.68)}{(0.15)}$$

$$E_{cell} = E^{o}{}_{cell} - \frac{0.0592}{n}\log Q$$

$$E_{cell} = 1.10\text{ V} - \frac{0.0592}{2}\log\frac{(0.68)}{(0.15)}$$

$$E_{cell} = 1.10\text{ V} - 0.019\text{ V}$$

$$E_{cell} = 1.08\text{ V}$$

Since E_{cell} is positive, the cell operates spontaneously. *Note: When the cell reaches equilibrium, then Q = K, and $E_{cell} = 0$.*

In Section 19.15, practice the Interactive Problems.

Section 19.16: Concentration Cells

Because cell potentials depend on the concentrations of the species being oxidized and reduced, we can construct a cell where both half-cells contain the same components at different concentrations.

Consider the following cell:

$$\mathbf{Cu_{(s)} \mid Cu^{+2}_{(aq)}\ (0.10\ M) \mid\mid Cu^{+2}_{(aq)}\ (1.0\ M) \mid Cu_{(s)}}$$

There are two beakers. Oxidation occurs in the left beaker, while reduction occurs in the right beaker. Since both beakers have the same species, i.e. Cu being oxidized and Cu^{+2} being reduced, strips of Cu can be used for the anode and for the cathode.

Now, look at the cell diagram:

$$Cu_{(s)} \mid Cu^{+2}_{(aq)}\ (0.10\ M) \mid\mid Cu^{+2}_{(aq)}\ (1.0\ M) \mid Cu_{(s)}$$

The oxidation beaker contains a Cu^{+2} solution with a 0.10 M concentration.

The reduction beaker contains a Cu^{+2} solution with a 1.0 M concentration.

An electric wire connects the anode to the cathode so that electrons can flow between the two electrodes. In order to prevent a charge build-up and complete the electrical circuit, a salt bridge is used to connect the solutions of both beakers.

In the oxidation beaker, Cu atoms from the Cu electrode give up two electrons to form Cu^{+2} ions. These Cu^{+2} ions go into the solution. Hence, the concentration of Cu^{+2} in the oxidation beaker increases. As this happens, the Cu anode becomes depleted.

In the reduction beaker, Cu^{+2} ions migrate from the solution to the electrode where they accept two electrons to form neutral Cu atoms. These Cu atoms are deposited on the Cu cathode. The concentration of Cu^{+2} in the oxidation beaker decreases.

The cell operates until the concentrations of Cu^{+2} in the oxidation and reduction cells become equal. A cell in which both half-cells have the same components at different concentrations is called a **concentration cell**. Typically, the potential generated by a concentration cell is small compared to that obtained in a Voltaic cell.

Application of concentration cells:

Membrane potentials in biological cells can be calculated assuming that biological cells are concentration cells. A membrane potential is an electrical potential, E_{cell}, which exists across the membranes of various kinds of cells (e.g. muscle cells and nerve cells).

Section 19.17: Electrolysis

Electrolysis is performed in an **electrolytic cell**. In an electrolytic cell, the electrical energy from an external power supply is used to force a non-spontaneous reaction. Examples of electrolysis include charging a battery, electroplating objects (gold or chrome), and extracting metals from ores. To understand the concept of electrolysis, consider a cell, which has components similar to those found in a Galvanic cell:

$$Cu^{+2}{}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{+2}{}_{(aq)}$$

In this Galvanic cell, electrons produced at the anode by the oxidation of Zn metal to Zn^{+2} are used at the cathode to reduce Cu^{+2} to Cu metal.

$$E°_{cell} = E°_{cathode} – E°_{anode}$$

$$E°_{cell} = E°_{Cu+2/Cu} - E°_{Zn+2/Zn}$$

$$E°_{cell} = + 1.10 \text{ V}$$

The spontaneity of this reaction is confirmed by the positive value of the cell standard potential, $E°_{cell}$.

We will now construct an electrolytic cell using the reverse redox reaction:

$$Cu_{(s)} + Zn^{+2}{}_{(aq)} \rightarrow Cu^{+2}{}_{(aq)} + Zn_{(s)}$$

This redox reaction is NOT SPONTANEOUS, since the reverse reaction

$$Cu^{+2}{}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{+2}{}_{(aq)} \qquad E°_{cell} = + 1.10 \text{ V}$$

is SPONTANEOUS.

This electrolytic cell consists of two separate half-cells, each with its own solution and electrode. Oxidation of Cu metal to Cu^{+2} will occur in one of the half-cells (left-hand side compartment). Reduction of Zn^{+2} to Zn metal will occur in the other half-cell (right-hand side compartment). Hence, strips of Cu and Zn will be used as electrodes in the left and right half-cells, respectively.

The left and right compartments of the electrolysis cell are filled with 1.0 M $CuSO_4$ and 1.0 M $ZnSO_4$ solutions, respectively. Reduction occurs at the cathode (right-hand side), and oxidation occurs at the anode (left-hand side).

In an electrolytic cell, electrical energy is supplied from an external source. Therefore, a power supply is connected to both electrodes. The power supply pushes electrons into the cathode, allowing the reduction of the oxidizing agent at the cathode:

$$Zn^{+2}{}_{(aq)} + 2\ e^- \rightarrow Zn_{(s)}$$

The power supply pulls electrons from the anode. These electrons are generated at the anode by oxidation of the reducing agent:

$$Cu_{(s)} \rightarrow Cu^{+2}{}_{(aq)} + 2\ e^-$$

In summary, the power supply pulls electrons from the anode and pushes them to the cathode, maintaining a continuous stream of electrons flowing between the two electrodes.

Now, the question is: What potential should be applied to the electrolytic cell by the power supply for the reaction to proceed from left to right?

$$Cu_{(s)} + Zn^{+2}{}_{(aq)} \rightarrow Cu^{+2}{}_{(aq)} + Zn_{(s)}$$

Without power supply, the cell would be a Voltaic cell. Hence, electrons would naturally flow from the Zn anode to the Cu cathode, since the above reaction is spontaneous from right to left ($E°_{cell} = +\ 1.10\ V$). However, in the direction given, the reaction is non-spontaneous. Hence, a minimum potential of 1.10 V is needed to carry out electrolysis.

This leads to electroplating of the cathode with zinc metal, and depletion of the copper anode.

In the previous example, we introduced the Electrolytic cell in the context of what we learned about Voltaic or Galvanic cells. Now, we consider more typical electrolytic cells, such as those used in the electrolysis of water. As with most electrolytic reactions, the electrolysis of water is carried out in a cell consisting of two electrodes partially immersed in a common aqueous solution. The two electrodes are connected to a power supply, which forces the non-spontaneous reaction to occur.

Here, use of an external power supply can force the dissociation of water into hydrogen and oxygen gases.

$$2\ H_2O_{(l)} \rightarrow 2\ H_{2\ (g)} + O_{2\ (g)}$$

Inactive Pt electrodes are used for the electrolysis of water. This redox reaction can be decomposed into a reduction reaction at the cathode, and an oxidation reaction at the anode.

Cathode	$4\ H_2O_{(l)} + 4e^- \rightarrow 2\ H_{2\ (g)} + 4\ OH^-{}_{(aq)}$	$E°_{cathode} = -\ 0.83\ V$
Anode	$4\ OH^-{}_{(aq)} \rightarrow O_{2\ (g)} + 4e^- + 2\ H_2O_{(l)}$	$E°_{anode} = +\ 0.40\ V$

The standard cell potential is:

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$E^\circ_{cell} = -\ 0.83 - 0.40$$

$$E^\circ_{cell} = -\ 1.23\ V$$

The cell potential is negative, confirming that the dissociation of water is non-spontaneous. Hence, to produce oxygen and hydrogen gases by the electrolysis of water, a minimum potential of + 1.23 V should be applied to the electrolytic cell.

Another very common electrolytic cell is that used for molten salts. Electrical energy is often used to transform a salt into its pure elements.

For example: Electrolysis of NaCl at high temperatures, where the salt is molten (i.e. in the liquid state), results in the formation of liquid Na and Cl_2. The cell used in the electrolysis of NaCl consists of two electrodes immersed in the molten NaCl salt. Reduction of the sodium ions occurs at the cathode:

$$Na^{+}_{(aq)} + e^{-} \rightarrow Na_{(l)}$$

Oxidation of the chloride ions occurs at the anode:

$$2\ Cl^{-}_{(aq)} \rightarrow Cl_{2\ (g)} + 2\ e^{-}$$

Differences between Voltaic Cells and Electrolytic Cells

Voltaic Cell	Electrolytic Cell
1. Electrons are generated at the anode. Thus, the anode is negative.	1. Electrons are supplied by an external power supply at the cathode. Thus, the cathode is negative.
2. Electrons are consumed at the cathode. Thus, the cathode is positive.	2. Electrons are removed from the anode. Thus, the anode is positive.

A rechargeable battery is the best example of both a Voltaic cell and an Electrolytic cell. When a rechargeable battery is discharging, it functions as a Voltaic cell. When it is charging, it operates like an electrolytic cell.

Sections 19.18 - 19.19: Stoichiometry of Electrolytic Processes

In this section, we describe the relationship between the amount of material produced or consumed during electrolysis and the flow of electric current for a specified period of time.

There are four steps involved in these calculations.

Step 1. Calculate the charge in coulombs:

In order to perform electrolysis, a certain amount of electric current is supplied for a given time. Current is expressed with the S.I. unit of amperes. The symbol for ampere is A.

$$1\ \text{A} = \frac{1\ \text{coulomb of charge (C)}}{\text{second (s)}}$$

To free yourself from the worries of units, always express time in seconds (s). Remember: 1 hr = 60 min = 3600 s and always multiply current in amperes by time in seconds to get charge in coulombs.

$$\text{charge (C)} = \text{current (A)} \times \text{time (s)}$$

Step 2. Convert the charge in coulombs to moles of e^-, using the Faraday's constant. Recall the definition of *F*, the Faraday's Constant.

$$F = \frac{96{,}485\ \text{C}}{\text{mol e}^-}$$

Thus, dividing the electric charge obtained in Step 1 by *F* allows us to transform the charge, in coulombs (C), to the number of moles of electrons that passed through the electrodes.

$$\text{number mol e}^- = \text{charge (C)} \times \frac{\text{mol e}^-}{96{,}485\ \text{C}}$$

Step 3. Convert the moles of electrons to the moles of oxidizing agent.

First, look at the stoichiometry of the reduction half-reaction. Determine how many moles of oxidizing agent are reduced by one mole of electrons.

$$\text{mole ratio} = \frac{\text{mol oxidizing agent}}{\text{mol e}^-}$$

Now, multiply the number of moles of e^- obtained in Step 2 by the mole ratio to get the number of moles of oxidizing agent that have reacted.

$$\text{number mol oxidizing agent} = \text{charge (C)} \times \frac{\text{mol e}^-}{96{,}485\ \text{C}} \times \frac{\text{mol oxidizing agent}}{\text{mol e}^-}$$

Step 4. Convert the moles of oxidizing agent to the mass of oxidizing agent.

Multiply the number of mol oxidizing agent by its molar mass to obtain the mass of oxidizing agent that has been reduced during electrolysis.

mass oxidizing agent (g) = moles oxidizing agent (mol) x molar mass (g/mol)

Example: Calculate the mass of copper deposited when a 10.0 A current is passed through a solution of Cu^{+2} for 20.0 minutes.

Step 1. Calculate the charge in coulombs

$$1\,\text{A} = \frac{1\,\text{C}}{\text{s}}$$

Remember to express time in seconds.

$$\text{charge} = 10.0\,\frac{\text{C}}{\text{s}} \text{ x } 20.0\text{ min x } \frac{60\text{ s}}{\text{min}} = 12{,}000\text{ C} = 1.20 \text{ x } 10^4\text{ C}$$

Step 2. Convert the charge to moles of e$^-$ using Faraday's Constant, *F*

$$1F = \frac{96{,}485\text{ C}}{\text{mol e}^-}$$

$$\text{number mol e}^- = \text{charge (C) x } \frac{\text{mol e}^-}{96{,}485\text{ C}}$$

$$\text{number mol e}^- = 1.20 \text{ x } 10^4\text{ C x } \frac{\text{mol e}^-}{96{,}485\text{ C}} = 0.124\text{ mol e}^-$$

Step 3. Convert moles of e$^-$ to moles of the oxidizing agent

Look at the reduction half-reaction:

$$\text{Cu}^{+2}{}_{(aq)} + 2\text{ e}^- \rightarrow \text{Cu}_{(s)}$$

For every mole of Cu^{+2} reduced, 2 mol e$^-$ are required.

$$\text{mole ratio} = \frac{1\text{mol Cu}^{+2}}{2\text{ mol e}^-}$$

$$\text{number mol Cu}^{+2} = 0.124\text{ mol e}^- \times \frac{1\text{ mol Cu}^{+2}}{2\text{ mol e}^-} = 0.062\text{ mol Cu}^{+2}$$

The stoichiometry of the reduction half-reaction indicates that 0.062 mol Cu is deposited if 0.062 mol Cu^{+2} are reduced.

Step 4. Convert moles of oxidizing agent to mass of oxidizing agent

$$\text{molar mass of Cu} = \frac{63.5\text{ g}}{\text{mol}}$$

$$\text{moles} = \frac{\text{mass}}{\text{molar mass}}$$

$$\text{mass} = \text{moles} \times \text{molar mass}$$

$$\text{mass} = 0.062\text{ mol} \times 63.5\frac{\text{g}}{\text{mol}} = 3.9\text{ g}$$

In Section 19.19, practice the Interactive Problems.

Section 19.20: Applications of Electrolysis

Electrolysis of Mixtures of Ions

Consider an electrolytic cell containing a mixture of ions, such as Ni^{+2}, Fe^{+2} and Ag^{+}. In which order will these metals be electroplated?

Electroplating of metals always takes place at the cathode because

1) Metals are obtained by reduction reactions

2) The cathode is the site of reduction reactions

To determine the order of plating, we look at the half-reaction potentials.

$Ni^{+2}{}_{(aq)} + 2\,e^- \rightarrow Ni_{(s)}$ $E°_{Ni+2/Ni} = -0.28\text{ V}$

$Fe^{+2}{}_{(aq)} + 2\,e^- \rightarrow Fe_{(s)}$ $E°_{Fe+2/Fe} = -0.44\text{ V}$

$Ag^{+}{}_{(aq)} + e^- \rightarrow Ag_{(s)}$ $E°_{Ag+/Ag} = 0.80\text{ V}$

Recall: The more positive the E° value, the higher the tendency for the reaction to proceed in the reduction direction. Therefore, looking at the E° values, we conclude that Ag will be electroplated first, followed by Ni and Fe.

Previous Chapter   Table of Contents   Next Chapter