

17.1: Balancing Oxidation-Reduction Reactions

Learning Objectives

- Define electrochemistry and a number of important associated terms
- Split oxidation-reduction reactions into their oxidation half-reactions and reduction half-reactions
- Produce balanced oxidation-reduction equations for reactions in acidic or basic solution
- Identify oxidizing agents and reducing agents

Electricity refers to a number of phenomena associated with the presence and flow of electric charge. Electricity includes such diverse things as lightning, static electricity, the current generated by a battery as it discharges, and many other influences on our daily lives. The flow or movement of charge is an electric current (Figure 17.1.1). Electrons or ions may carry the charge. The elementary unit of charge is the charge of a proton, which is equal in magnitude to the charge of an electron. The SI unit of charge is the coulomb (C) and the charge of a proton is 1.602×10^{-19} C. The presence of an electric charge generates an electric field. Electric current is the rate of flow of charge.



Figure 17.1.1: Electricity-related phenomena include lightning, accumulation of static electricity, and current produced by a battery. (credit left: modification of work by Thomas Bresson; credit middle: modification of work by Chris Darling; credit right: modification of work by Windell Oskay).

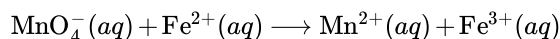
The SI unit for electrical current is the SI base unit called the ampere (A), which is a flow rate of 1 coulomb of charge per second ($1 \text{ A} = 1 \text{ C/s}$). An electric current flows in a path, called an electric circuit. In most chemical systems, it is necessary to maintain a closed path for current to flow. The flow of charge is generated by an electrical potential difference, or potential, between two points in the circuit. Electrical potential is the ability of the electric field to do work on the charge. The SI unit of electrical potential is the volt (V). When 1 coulomb of charge moves through a potential difference of 1 volt, it gains or loses 1 joule (J) of energy. Table 17.1.1 summarizes some of this information about electricity.

Table 17.1.1: Common Electrical Terms

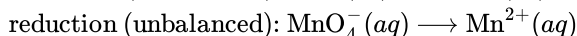
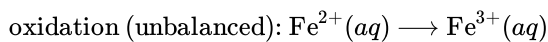
Quantity	Definition	Measure or Unit
Electric charge	Charge on a proton	$1.602 \times 10^{-19} \text{ C}$
Electric current	The movement of charge	ampere = $\text{A} = 1 \text{ C/s}$
Electric potential	The force trying to move the charge	volt = $\text{V} = \text{J/C}$
Electric field	The force acting upon other charges in the vicinity	

Electrochemistry studies oxidation-reduction reactions, which were first discussed in an earlier chapter, where we learned that oxidation was the loss of electrons and reduction was the gain of electrons. The reactions discussed tended to be rather simple, and conservation of mass (atom counting by type) and deriving a correctly balanced chemical equation were relatively simple. In this section, we will concentrate on the half-reaction method for balancing oxidation-reduction reactions. The use of half-reactions is important partly for balancing more complicated reactions and partly because many aspects of electrochemistry are easier to discuss in terms of half-reactions. There are alternate methods of balancing these reactions; however, there are no good alternatives to half-reactions for discussing what is occurring in many systems. The half-reaction method splits oxidation-reduction reactions into their oxidation “half” and reduction “half” to make finding the overall equation easier.

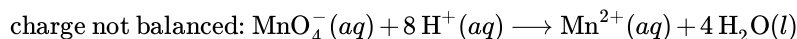
Electrochemical reactions frequently occur in solutions, which could be acidic, basic, or neutral. When balancing oxidation-reduction reactions, the nature of the solution may be important. It helps to see this in an actual problem. Consider the following unbalanced oxidation-reduction reaction in acidic solution:



We can start by collecting the species we have so far into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction. Each of these half-reactions contain the same element in two different oxidation states. The Fe^{2+} has lost an electron to become Fe^{3+} ; therefore, the iron underwent oxidation. The reduction is not as obvious; however, the manganese gained five electrons to change from Mn^{7+} to Mn^{2+} .

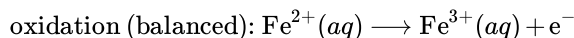


In acidic solution, there are hydrogen ions present, which are often useful in balancing half-reactions. It may be necessary to use the hydrogen ions directly or as a reactant that may react with oxygen to generate water. Hydrogen ions are very important in acidic solutions where the reactants or products contain hydrogen and/or oxygen. In this example, the oxidation half-reaction involves neither hydrogen nor oxygen, so hydrogen ions are not necessary to the balancing. However, the reduction half-reaction does involve oxygen. It is necessary to use hydrogen ions to convert this oxygen to water.



The situation is different in basic solution because the hydrogen ion concentration is lower and the hydroxide ion concentration is higher. After finishing this example, we will examine how basic solutions differ from acidic solutions. A neutral solution may be treated as acidic or basic, though treating it as acidic is usually easier.

The iron atoms in the oxidation half-reaction are balanced (mass balance); however, the charge is unbalanced, since the charges on the ions are not equal. It is necessary to use electrons to balance the charge. The way to balance the charge is by *adding* electrons to one side of the equation. Adding a single electron on the right side gives a balanced oxidation half-reaction:



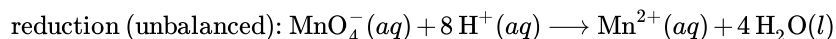
You should check the half-reaction for the number of each atom type and the total charge on each side of the equation. The charges include the actual charges of the ions times the number of ions and the charge on an electron times the number of electrons.

Fe: Does $(1 \times 1) = (1 \times 1)$? Yes.

Charge: Does $[1 \times (+2)] = [1 \times (+3) + 1 \times (-1)]$? Yes.

If the atoms and charges balance, the half-reaction is balanced. In oxidation half-reactions, electrons appear as products (on the right). As discussed in the earlier chapter, since iron underwent oxidation, iron is the reducing agent.

Now return to the reduction half-reaction equation:



The atoms are balanced (mass balance), so it is now necessary to check for charge balance. The total charge on the left of the reaction arrow is $[(-1) \times (1) + (8) \times (+1)]$, or +7, while the total charge on the right side is $[(1) \times (+2) + (4) \times (0)]$, or +2. The difference between +7 and +2 is five; therefore, it is necessary to add five electrons to the left side to achieve charge balance.



You should check this half-reaction for each atom type and for the charge, as well:

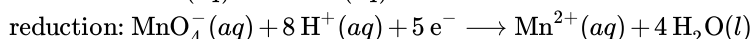
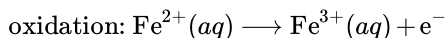
Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.

H: Does $(8 \times 1) = (4 \times 2)$? Yes.

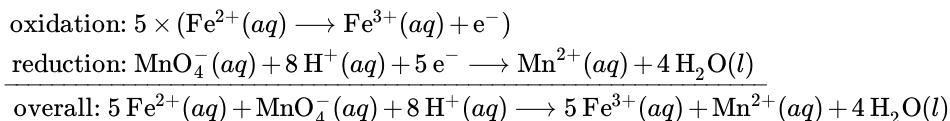
O: Does $(1 \times 4) = (4 \times 1)$? Yes.

Charge: Does $[1 \times (-1) + 8 \times (+1) + 5 \times (-1)] = [1 \times (+2)]$? Yes.

Now that this half-reaction is balanced, it is easy to see it involves reduction because electrons were gained when MnO_4^- was reduced to Mn^{2+} . In all reduction half-reactions, electrons appear as reactants (on the left side). As discussed in the earlier chapter, the species that was reduced, MnO_4^- in this case, is also called the oxidizing agent. We now have two balanced half-reactions.



It is now necessary to combine the two halves to produce a whole reaction. The key to combining the half-reactions is the electrons. The electrons lost during oxidation must go somewhere. These electrons go to cause reduction. The number of electrons transferred from the oxidation half-reaction to the reduction half-reaction must be equal. There can be no missing or excess electrons. In this example, the oxidation half-reaction generates one electron, while the reduction half-reaction requires five. The lowest common multiple of one and five is five; therefore, it is necessary to multiply every term in the oxidation half-reaction by five and every term in the reduction half-reaction by one. (In this case, the multiplication of the reduction half-reaction generates no change; however, this will not always be the case.) The multiplication of the two half-reactions by the appropriate factor followed by addition of the two halves gives



The electrons do not appear in the final answer because the oxidation electrons are the same electrons as the reduction electrons and they “cancel.” Carefully check each side of the overall equation to verify everything was combined correctly:

Fe: Does $(5 \times 1) = (5 \times 1)$? Yes.

Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.

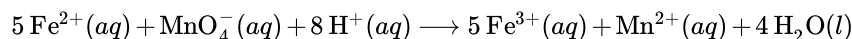
H: Does $(8 \times 1) = (4 \times 2)$? Yes.

O: Does $(1 \times 4) = (4 \times 1)$? Yes.

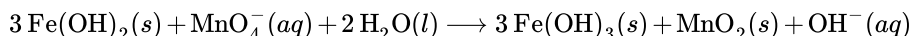
Charge: Does $[5 \times (+2) + 1 \times (-1) + 8 \times (+1)] = [5 \times (+3) + 1 \times (+2)]$? Yes.

Everything checks, so this is the overall equation in acidic solution. If something does not check, the most common error occurs during the multiplication of the individual half-reactions.

Now suppose we wanted the solution to be basic. Recall that basic solutions have excess hydroxide ions. Some of these hydroxide ions will react with hydrogen ions to produce water. The simplest way to generate the balanced overall equation in basic solution is to start with the balanced equation in acidic solution, then “convert” it to the equation for basic solution. However, it is necessary to exercise caution when doing this, as many reactants behave differently under basic conditions and many metal ions will precipitate as the metal hydroxide. We just produced the following reaction, which we want to change to a basic reaction:



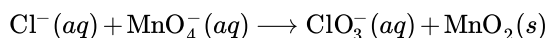
However, under basic conditions, MnO_4^{-} normally reduces to MnO_2 and iron will be present as either $\text{Fe}(\text{OH})_2$ or $\text{Fe}(\text{OH})_3$. For these reasons, under basic conditions, this reaction will be



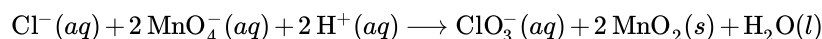
(Under very basic conditions MnO_4^{-} will reduce to MnO_4^{2-} , instead of MnO_2 .)

It is still possible to balance any oxidation-reduction reaction as an acidic reaction and then, when necessary, convert the equation to a basic reaction. This will work if the acidic and basic reactants and products are the same or if the basic reactants and products are used before the conversion from acidic or basic. There are very few examples in which the acidic and basic reactions will involve the same reactants and products. However, balancing a basic reaction as acidic and then converting to basic will work. To convert to a basic reaction, it is necessary to add the same number of hydroxide ions to each side of the equation so that all the hydrogen ions (H^{+}) are removed and mass balance is maintained. Hydrogen ion combines with hydroxide ion (OH^{-}) to produce water.

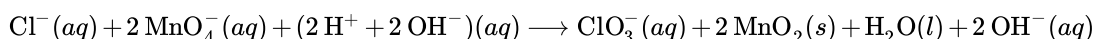
Let us now try a basic equation. We will start with the following basic reaction:

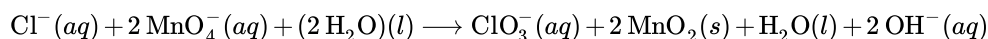


Balancing this as acid gives

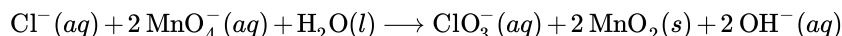


In this case, it is necessary to add two hydroxide ions to each side of the equation to convert the two hydrogen ions on the left into water:





Note that both sides of the equation show water. Simplifying should be done when necessary, and gives the desired equation. In this case, it is necessary to remove one H_2O from each side of the reaction arrows.



Again, check each side of the overall equation to make sure there are no errors:

Cl: Does $(1 \times 1) = (1 \times 1)$? Yes.

Mn: Does $(2 \times 1) = (2 \times 1)$? Yes.

H: Does $(1 \times 2) = (2 \times 1)$? Yes.

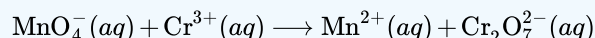
O: Does $(2 \times 4 + 1 \times 1) = (3 \times 1 + 2 \times 2 + 2 \times 1)$? Yes.

Charge: Does $[1 \times (-1) + 2 \times (-1)] = [1 \times (-1) + 2 \times (-1)]$? Yes.

Everything checks, so this is the overall equation in basic solution.

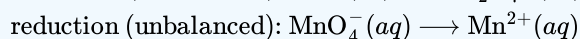
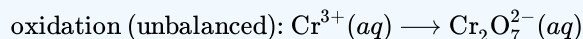
✓ Example 17.1.1: Balancing Acidic Oxidation-Reduction Reactions

Balance the following reaction equation in acidic solution:

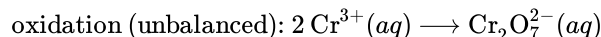


Solution

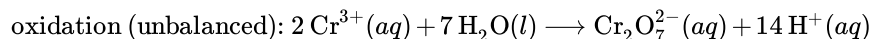
This is an oxidation-reduction reaction, so start by collecting the species given into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction.



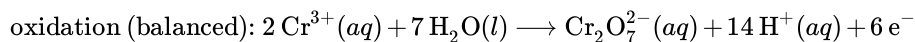
Starting with the oxidation half-reaction, we can balance the chromium



In acidic solution, we can use or generate hydrogen ions (H^{+}). Adding seven water molecules to the left side provides the necessary oxygen; the “left over” hydrogen appears as 14H^{+} on the right:



The left side of the equation has a total charge of $[2 \times (+3) = +6]$, and the right side a total charge of $[-2 + 14 \times (+1) = +12]$. The difference is six; adding six electrons to the right side produces a mass- and charge-balanced oxidation half-reaction (in acidic solution):



Checking the half-reaction:

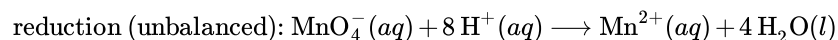
Cr: Does $(2 \times 1) = (1 \times 2)$? Yes.

H: Does $(7 \times 2) = (14 \times 1)$? Yes.

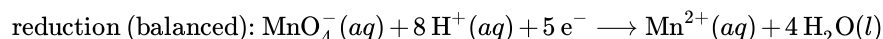
O: Does $(7 \times 1) = (1 \times 7)$? Yes.

Charge: Does $[2 \times (+3)] = [1 \times (-2) + 14 \times (+1) + 6 \times (-1)]$? Yes.

Now work on the reduction. It is necessary to convert the four oxygen atoms in the permanganate into four water molecules. To do this, add eight H^{+} to convert the oxygen into four water molecules:



Then add five electrons to the left side to balance the charge:



Make sure to check the half-reaction:

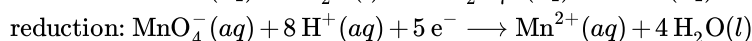
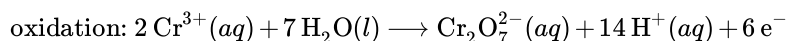
Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.

H: Does $(8 \times 1) = (4 \times 2)$? Yes.

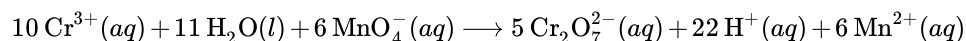
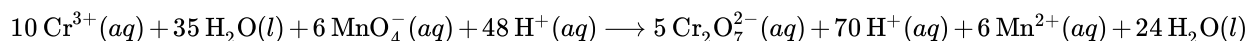
O: Does $(1 \times 4) = (4 \times 1)$? Yes.

Charge: Does $[1 \times (-1) + 8 \times (+1) + 5 \times (-1)] = [1 \times (+2)]$? Yes.

Collecting what we have so far:



The least common multiple for the electrons is 30, so multiply the oxidation half-reaction by five, the reduction half-reaction by six, combine, and simplify:



Checking each side of the equation:

Mn: Does $(6 \times 1) = (6 \times 1)$? Yes.

Cr: Does $(10 \times 1) = (5 \times 2)$? Yes.

H: Does $(11 \times 2) = (22 \times 1)$? Yes.

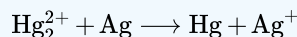
O: Does $(11 \times 1 + 6 \times 4) = (5 \times 7)$? Yes.

Charge: Does $[10 \times (+3) + 6 \times (-1)] = [5 \times (-2) + 22 \times (+1) + 6 \times (+2)]$? Yes.

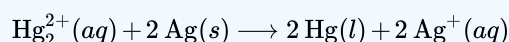
This is the balanced equation in acidic solution.

? Exercise 17.1.1

Balance the following equation in acidic solution:

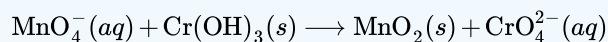


Answer



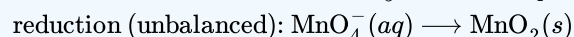
✓ Example 17.1.2: Balancing Basic Oxidation-Reduction Reactions

Balance the following reaction equation in basic solution:



Solution

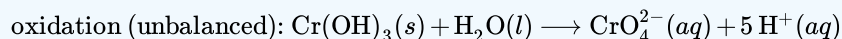
This is an oxidation-reduction reaction, so start by collecting the species given into an unbalanced oxidation half-reaction and an unbalanced reduction half-reaction



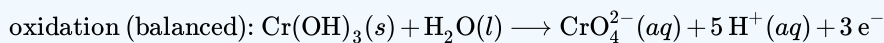
Starting with the oxidation half-reaction, we can balance the chromium



In acidic solution, we can use or generate hydrogen ions (H^+). Adding one water molecule to the left side provides the necessary oxygen; the “left over” hydrogen appears as five H^+ on the right side:



The left side of the equation has a total charge of [0], and the right side a total charge of $[-2 + 5 \times (+1) = +3]$. The difference is three, adding three electrons to the right side produces a mass- and charge-balanced oxidation half-reaction (in acidic solution):



Checking the half-reaction:

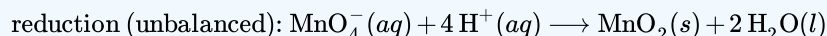
Cr: Does $(1 \times 1) = (1 \times 1)$? Yes.

H: Does $(1 \times 3 + 1 \times 2) = (5 \times 1)$? Yes.

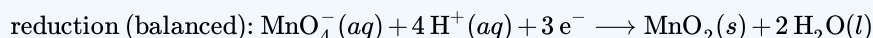
O: Does $(1 \times 3 + 1 \times 1) = (4 \times 1)$? Yes.

Charge: Does $[0 = [1 \times (-2) + 5 \times (+1) + 3 \times (-1)]]$? Yes.

Now work on the reduction. It is necessary to convert the four O atoms in the MnO_4^- minus the two O atoms in MnO_2 into two water molecules. To do this, add four H^+ to convert the oxygen into two water molecules:



Then add three electrons to the left side to balance the charge:



Make sure to check the half-reaction:

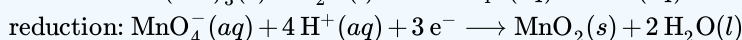
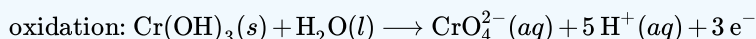
Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.

H: Does $(4 \times 1) = (2 \times 2)$? Yes.

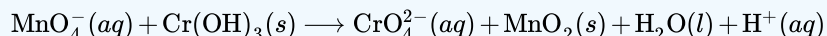
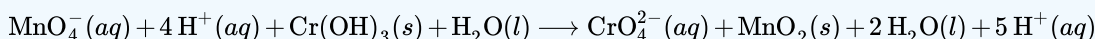
O: Does $(1 \times 4) = (1 \times 2 + 2 \times 1)$? Yes.

Charge: Does $[1 \times (-1) + 4 \times (+1) + 3 \times (-1)] = [0]$? Yes.

Collecting what we have so far:



In this case, both half reactions involve the same number of electrons; therefore, simply add the two half-reactions together.



Checking each side of the equation:

Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.

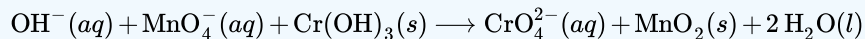
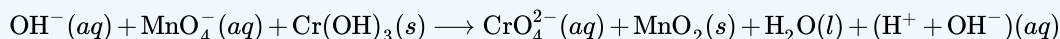
Cr: Does $(1 \times 1) = (1 \times 1)$? Yes.

H: Does $(1 \times 3) = (2 \times 1 + 1 \times 1)$? Yes.

O: Does $(1 \times 4 + 1 \times 3) = (1 \times 4 + 1 \times 2 + 1 \times 1)$? Yes.

Charge: Does $[1 \times (-1)] = [1 \times (-2) + 1 \times (+1)]$? Yes.

This is the balanced equation in acidic solution. For a basic solution, add one hydroxide ion to each side and simplify:



Checking each side of the equation:

Mn: Does $(1 \times 1) = (1 \times 1)$? Yes.

Cr: Does $(1 \times 1) = (1 \times 1)$? Yes.

H: Does $(1 \times 1 + 1 \times 3) = (2 \times 2)$? Yes.

O: Does $(1 \times 1 + 1 \times 4 + 1 \times 3) = (1 \times 4 + 1 \times 2 + 2 \times 1)$? Yes.

Charge: Does $[1 \times (-1) + 1 \times (-1)] = [1 \times (-2)]$? Yes.

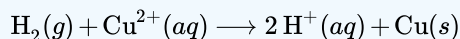
This is the balanced equation in basic solution.

? Exercise 17.1.2

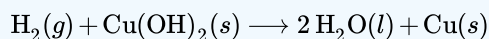
Balance the following in the type of solution indicated.

- $\text{H}_2 + \text{Cu}^{2+} \longrightarrow \text{Cu}$ (acidic solution)
- $\text{H}_2 + \text{Cu}(\text{OH})_2 \longrightarrow \text{Cu}$ (basic solution)
- $\text{Fe} + \text{Ag}^+ \longrightarrow \text{Fe}^{2+} + \text{Ag}$
- Identify the oxidizing agents in reactions (a), (b), and (c).
- Identify the reducing agents in reactions (a), (b), and (c).

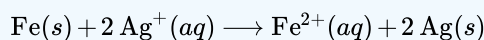
Answer a



Answer b



Answer c



Answer d

oxidizing agent = species reduced: Cu^{2+} , $\text{Cu}(\text{OH})_2$, Ag^+

Answer e

reducing agent = species oxidized: H_2 , H_2 , Fe .

Summary

An electric current consists of moving charge. The charge may be in the form of electrons or ions. Current flows through an unbroken or closed circular path called a circuit. The current flows through a conducting medium as a result of a difference in electrical potential between two points in a circuit. Electrical potential has the units of energy per charge. In SI units, charge is measured in coulombs (C), current in amperes $\left(\text{A} = \frac{\text{C}}{\text{s}}\right)$, and electrical potential in volts $\left(\text{V} = \frac{\text{J}}{\text{C}}\right)$.

Oxidation is the loss of electrons, and the species that is oxidized is also called the reducing agent. Reduction is the gain of electrons, and the species that is reduced is also called the oxidizing agent. Oxidation-reduction reactions can be balanced using the half-reaction method. In this method, the oxidation-reduction reaction is split into an oxidation half-reaction and a reduction half-reaction. The oxidation half-reaction and reduction half-reaction are then balanced separately. Each of the half-reactions must have the same number of each type of atom on both sides of the equation *and* show the same total charge on each side of the equation. Charge is balanced in oxidation half-reactions by adding electrons as products; in reduction half-reactions, charge is balanced by adding electrons as reactants. The total number of electrons gained by reduction must exactly equal the number of electrons lost by oxidation when combining the two half-reactions to give the overall balanced equation. Balancing oxidation-reduction reaction equations in aqueous solutions frequently requires that oxygen or hydrogen be added or removed from a reactant. In acidic solution, hydrogen is added by adding hydrogen ion (H^+) and removed by producing hydrogen ion; oxygen is removed by adding hydrogen ion and producing water, and added by adding water and producing hydroxide ion. A balanced equation in basic solution can be obtained by first balancing the equation in acidic solution, and then adding hydroxide ion to each side of the balanced equation in such numbers that all the hydrogen ions are converted to water.

Glossary

circuit

path taken by a current as it flows because of an electrical potential difference

current

flow of electrical charge; the SI unit of charge is the coulomb (C) and current is measured in amperes $\left(1\text{ A} = 1\frac{\text{C}}{\text{s}}\right)$

electrical potential

energy per charge; in electrochemical systems, it depends on the way the charges are distributed within the system; the SI unit of electrical potential is the volt $\left(1 \text{ V} = 1 \frac{\text{J}}{\text{C}}\right)$

half-reaction method

method that produces a balanced overall oxidation-reduction reaction by splitting the reaction into an oxidation “half” and reduction “half,” balancing the two half-reactions, and then combining the oxidation half-reaction and reduction half-reaction in such a way that the number of electrons generated by the oxidation is exactly canceled by the number of electrons required by the reduction

oxidation half-reaction

the “half” of an oxidation-reduction reaction involving oxidation; the half-reaction in which electrons appear as products; balanced when each atom type, as well as the charge, is balanced

reduction half-reaction

the “half” of an oxidation-reduction reaction involving reduction; the half-reaction in which electrons appear as reactants; balanced when each atom type, as well as the charge, is balanced

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