The cell electromotive force, or cell EMF, is the net voltage between the oxidation and reduction half-reactions taking place between two redox half-reactions. Cell EMF is used to determine whether or not the cell is galvanic. This example problem shows how to calculate the cell EMF using standard reduction potentials.  
The [Table of Standard Reduction Potentials](https://www.thoughtco.com/table-of-common-standard-reduction-potentials-603964) is needed for this example. In a homework problem, you should be given these values or else access to the table.

Sample EMF Calculation

Consider the redox reaction:

* Mg(s) + 2 H+(aq) → Mg2+(aq) + H2(g)
  + a) Calculate the cell EMF for the reaction.
  + b) Identify if the reaction is galvanic.
* **Solution:**
  + **Step 1:** Break the redox [reaction into reduction and oxidation half-reactions](https://www.thoughtco.com/oxidation-reduction-reactions-604037).  
    Hydrogen ions, H+ gain electrons when [forming hydrogen](https://www.thoughtco.com/hydrogen-facts-element-1-or-h-607917) gas, H2. The hydrogen atoms are reduced by the half-reaction:  
    2 H+ + 2 e- → H2  
    Magnesium loses two electrons and is oxidized by the half-reaction:  
    Mg → Mg2+ + 2 e-
  + **Step 2:** Find the standard reduction potentials for the half-reactions.  
    Reduction: E0 = 0.0000 V  
    The table shows reduction half-reactions and standard reduction potentials. To find E0 for an oxidation reaction, reverse the reaction.
  + [**Reversed reaction**](https://www.thoughtco.com/definition-of-reversible-reaction-and-examples-605617)**:**  
    Mg2+ + 2 e- → Mg  
    This reaction has a E0 = -2.372 V.  
    E0Oxidation = - E0Reduction  
    E0Oxidation = - (-2.372 V) = + 2.372 V
  + **Step 3:** Add the two E0 together to find the total cell EMF, E0cell  
    E0cell = E0reduction + E0oxidation  
    E0cell = 0.0000 V + 2.372 V = +2.372 V
  + **Step 4:** Determine if the reaction is galvanic. Redox reactions with a positive E0cell value are galvanic.  
    This reaction's E0cell is positive and therefore galvanic.
* **Answer:**The cell EMF of the reaction is +2.372 Volts and is galvanic.

The electromotive force of a cell or EMF of a cell is the maximum potential difference between two electrodes of a cell. It can also be defined as the net voltage between the oxidation and reduction half-reactions. The EMF of a cell is mainly used to determine whether an electrochemical cell is galvanic or not.

We shall learn more about this topic including important formulas and how to calculate the EMF of an electrochemical cell in this lesson.

What is an Electrochemical Cell?

An electrochemical cell is a device that generates electricity from a chemical reaction. Essentially, it can be defined as a device that converts chemical energy into electrical energy. A chemical reaction that involves the exchange of electrons is required for an electrochemical cell to operate. Such reactions are called redox reactions.

A cell is characterized by its voltage. A particular kind of cell generates the same voltage irrespective of the size of the cell. The only thing that depends on the cell voltage is the chemical composition of the cell, given the cell is operated at ideal conditions.

Normally, the cell voltage may be different from this ideal value, due to several factors like temperature difference, change in concentration, etc. [Nernst equation](https://byjus.com/jee/nernst-equation/) formulated by Walther Nernst can be used to calculate the EMF value of a given cell, provided the standard cell potential of the cell.

Types of Electrochemical Cell

Galvanic Cell

Galvanic Cell is named after Luigi Galvani an Italian scientist. A galvanic cell is an important electrochemical cell that forms the base of many other electrochemical cells like the Daniell cell. It constitutes of two different metallic conductors called electrodes immersed in their own ionic solutions. Each of these arrangements is a half cell. Alone, a half cell is not able to generate a potential difference. But combined, they generate a potential difference. A salt bridge is used to combine the two cells chemically. It serves the required amount of electrons to the electron-deficient half cell and accepts electrons from the electron-rich half cell.

**Read More:** [Galvanic Cell](https://byjus.com/chemistry/galvanic-cell/)

For ease of understanding, let’s look at the theory of the Daniell cell and derive the Nernst equation for the same.

Daniell Cell

Daniell cell is an adaptation of the galvanic cell. It is constituted of zinc and copper electrodes immersed in zinc sulfate and copper sulfate solutions respectively. Two half cells are connected together using a salt bridge. The zinc electrode as anode and copper act as cathode.

The zinc metal is top in the electrochemical series when comparing to the copper metal, owing to the higher value of the oxidation potential of the metal. Hence, zinc undergoes oxidation, consequently, two electrons and a zinc ion are generated. This electrode acquires a negative potential due to the release of electrons when comparing to the other electrode. We call it an anode.

However, copper undergoes reduction, owing to its higher reduction potential. The copper ion in the solution of the copper half cell accepts two electrons from the electrode and becomes copper metal and gets deposited in the electrode. As this electrode uses up electrons, we consider this electrode as a positive electrode, and we call it cathode.

Anode reaction is represented as follows:

Zn(s) → Zn2+ (aq) + 2e–

The cathode reaction is represented as follows:

Cu2+ (aq) +2e– → Cu(s)

The combined cell reaction or overall cell reaction is as follows:

Zn(s) + Cu2+(aq) → Zn2+ (aq) + Cu(s)



Electrode Potential

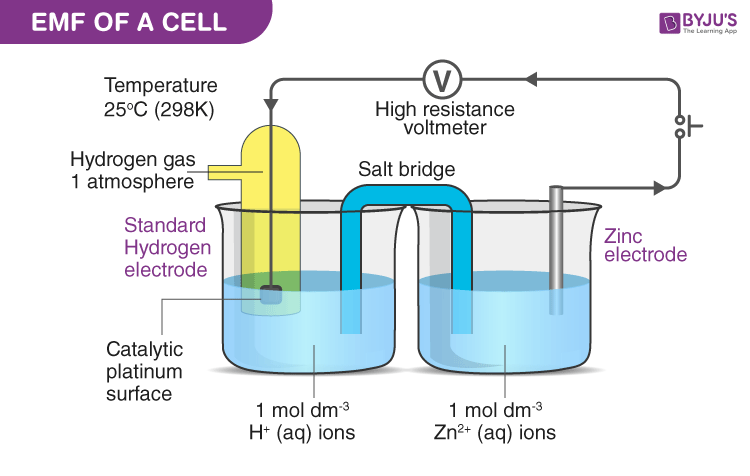
When a metal electrode is immersed in a solution containing its own ions, a potential difference is set up across the interface. This potential difference is called the electrode potential.

Consider the case of the zinc electrode immersed in a zinc sulfate solution. The zinc metal gets oxidized by releasing two electrons and becomes and is dissipated in the solution. The presence of electrons in the electrode and ions in the solution creates a potential difference. Same way, copper develops a positive potential. The combination of these two cells owing to the cell potential.

In reality, we are not able to determine the potential of a single half cell alone. To determine the potential of a single half cell, we always need a standard half cell whose potential value is already known. This standard half cell is then connected with the unknown half cell to determine the overall potential.

This overall potential is the difference between the potentials of the two half cells. The standard hydrogen electrode (SHE) is an example of such a standard half cell. The potential value of SHE is inherently set to zero volts. The standard hydrogen electrode is connected with an unknown half cell and the potential difference is measured. As SHE has zero volts, the measured value will be the potential difference of the unknown half cell.

The picture below represents the method to find the standard electrode potential of zinc.



Electrochemical Series

Likewise, the standard potential values of different metals are calculated and arranged in the increasing order of the potential, we obtain the [electrochemical series](https://byjus.com/jee/electrochemical-series/).

Electrochemical series are essential for the determination of cell potential. It also helps in selecting electrode metals for the construction of a cell.

The electrochemical series table shows the arrangement of a few elements based on the increasing order of their reduction potential. Lithium usually has the least reduction potential and fluorine has the most. Hydrogen has a zero reduction potential. This is because all other elements are compared against hydrogen to obtain their standard electrode potential.

Representation of an Electrochemical Cell

An electrochemical cell can be represented using special notations. This is useful in understanding the composition as well as it’s quantity in the cell.

The above-given Daniell cell can be represented as follows;

Zn | Zn2+ (1M) || Cu2+ (1M) | Cu

Let us break down this and understand its components:

● The left side of the notation represents the anode. At the anode, Zn is converted to by releasing a set of two electrons per zinc atom. As the solution used is of 1M concentration, we include that too in the representation

Zn | Zn2+ (1M)

● On the right side, we have the cathode. Here from the electrolyte absorbs a pair of electrons from the electrode and gets converted to Cu metal. Same as before, we are using a 1M copper sulfate solution.

Cu2+ (1M) | Cu

● These two half-cells are combined using a salt bridge. The salt bridge is represented using the two vertical bars.

Zn | Zn2+ (1M) || Cu2+ (1M) | Cu

Finding the Cell Potential of an Electrochemical Cell

The cell potential or EMF of the electrochemical cell can be calculated by taking the values of electrode potentials of the two half – cells. There are usually three methods that can be used for the calculation:

* By taking into account the oxidation potential of anode and reduction potential of cathode.
* By considering the reduction potentials of both electrodes.
* By taking the oxidation potentials of both electrodes.

The standard cell potential (ΔEo) of a galvanic cell can be calculated by considering the standard reduction potentials of the two half cells Eo.

Eocell = Eored + Eoox

Or

Eocell = EoCathode + EoAnode

The cell potential of a galvanic cell = Potential of the half cell on the right side (cathode) – Potential of the half cell on the left (anode).

In the case of Daniell cell;

The cell potential of Daniell cell = Ecell = Ecu2+ |Cu – Ezn |Zn2+

Nernst equation relates the equilibrium state potential of a half cell with the standard electrode potential of the half cell, temperature, reaction coefficients as well as activity of the reacting species.

For an electrode reaction Mn+ + n e– → M(s);

The equilibrium state EMF is given by;



Where EMn+|M is the half cell potential, EOMn+|M is the standard electrode potential of the half cell, [ M ] is the molar concentration of the metal, [ Mn+ ] is the molar concentration of the metal ion, R is the universal gas constant (8.314 J/K/mole), T is the temperature in kelvin, n is the number of electrons involved in the reaction and F is the Faraday’s constant (96500 C/mole).

**Also Read:** [Electrochemistry](https://byjus.com/jee/electrochemistry/)

The molar concentration of metallic solid is conventionally taken as one. Hence;

[ M ] = 1

Now, substitute the values of R, F, T = 298K (room temperature) to the above equation and we obtain a new equation;

EMn+|M = , EOMn+|M – 0.059 / n X log 1 / [ Mn+ ]

Let us consider an arbitrary cell having two metals M and N. Also let us assume that M has more reduction potential than N. Hence, M forms the cathode and N forms the anode.

Hence, Anode reaction;

N → Nn+ + ne–

Cathode reaction;

Mn+ + ne– → M

We know;

The cell potential of a galvanic cell = Potential of the half cell on the right side(cathode) – Potential of the half cell on the left(anode).

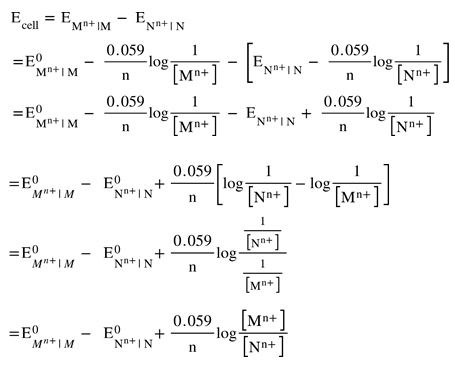
EMF of cathode half cell;

EMn+|M = , EOMn+|M – 0.059 / n X log 1 / [ Mn+ ]

EMF of anode half cell;

ENn+|N = , EONn+|N – 0.059 / n X log 1 / [ Nn+ ]

Hence, the cell potential of the Galvanic cell is;



We have;

EOMn+|M – EONn+|N = EOcell

This is the standard cell potential of a galvanic cell at STP conditions.

Hence we rewrite this as;

Ecell = EOcell + 0.059 / n X log [ Mn+ ] / [ Nn+ ]

For the Daniell cell:

The number of electrons involved in the process is 2, hence n = 2.

Ecell = EOcell + 0.059 / 2 X log [ Cu2+ ] / [ Zn2+ ]

From the electrochemical series;

EOcell = EOcathode – EOanode = ECu2+|Cu = , EOZn2+|Zn = 0.34 – (-0.76) = 1.1 V

Substitute this value and we get;

Ecell = 1.1 + 0.059 / 2 X log [ Cu2+ ] / [ Zn2+ ]

Solved Examples

**1. Calculate the EMF of the below redox reaction.**

**Mg (s) + 2H+ (aq) → Mg2+ (aq) + H2(g)**

**Solution:**

Step 1: Break the reaction into oxidation and reduction half cell reaction

**2H+ + 2e– → H2**

Hydrogen ion takes an electron to form hydrogen gas (reduction reaction).

Magnesium undergo oxidation by loosing two electrons

**Mg → Mg2+ + 2 e–**

Step 2: Find the standard reduction potential of the half-cell reaction

E0(Reduction) = 0.0000 V

E0(Oxidation) = -2.372 V

E0(Oxidation) = – E0(Reduction)

= +2.372 V

Step 3: Calculate the total EMF of the cell

E0 (Cell) = E0(Reduction) + E0(Oxidation)

E0 (Cell) =  0.0000 V + 2.372 V

E0 (Cell) = 2.372 V

The EMF of the redox reaction is +2.372 volts.

**2. Calculate the potential of the following redox reaction?**

**Ag|Ag+||Li+|Li**

**Solution:**

**Step 1:** Break the reaction into oxidation and reduction half cell reaction

Li+ + e– → Li (reduction reaction)

Ag → Ag+ + e–(Oxidation reaction)

**Step 2:** Find the standard reduction potential of the half-cell reaction

E0(Reduction) = -3.045 V

E0(Oxidation) = −0.799 V

**Step 3:** Calculate the total EMF of the cell

E0 (Cell) = E0(Reduction) + E0(Oxidation)

E0 (Cell) =  -3.045 V −0.799 V

E0 (Cell) = -3.844 V

The total potential of the cell is -3.844 V and the negative potential inndicates the sponteneous reverse reaction.

**3. Consider a redox reaction**

**2Ag++ Cd → 2Ag + Cd2+**

**The satndard electrode potential of reduction and oxidation reactions are + 0.80 V and -0.40 V  respectively. Calculate the standard potentiol for the reaction.**

**Solution:**

**Step 1:** Consider a half cell reactions

2Ag++ 2e– → 2Ag (Reduction)

EoAg+/Ag =0.80  V

Cd → Cd2+  + 2e– (Oxidation)

EoCd+/Cd = -0.40 V

**Step 2:** Total EMF of the cell

Eo= E (Reduction) + E (Oxidation)

Eo= 0.40 V + +0.80 V

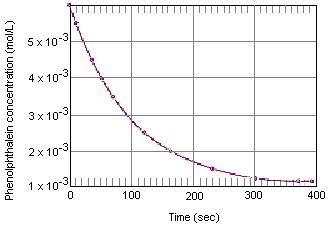
Eo= 1.20 V

The total EMF of the redox reaction is 1.20 V.

***Chemical Kinetics***

You may be familiar with acid-base titrations that use phenolphthalein as the endpoint indicator. You might not have noticed, however, what happens when a solution that contains phenolphthalein in the presence of excess base is allowed to stand for a few minutes. Although the solution initially has a pink color, it gradually turns colorless as the phenolphthalein reacts with the OH- ion in a strongly basic solution.

The table below shows what happens to the concentration of phenolphthalein in a solution that was initially 0.005 *M* in phenolphthalein and 0.61 *M* in OH- ion. As you can see when these data are plotted in the graph below, the phenolphthalein concentration decreases by a factor of 10 over a period of about four minutes.



*Experimental Data for the Reaction Between Phenolphthalein and Excess Base*

|  |  |  |
| --- | --- | --- |
| Concentration of Phenolphthalein (M) |  | *Time (s)* |
| 0.0050 |  | 0.0 |
| 0.0045 |  | 10.5 |
| 0.0040 |  | 22.3 |
| 0.0035 |  | 35.7 |
| 0.0030 |  | 51.1 |
| 0.0025 |  | 69.3 |
| 0.0020 |  | 91.6 |
| 0.0015 |  | 120.4 |
| 0.0010 |  | 160.9 |
| 0.00050 |  | 230.3 |
| 0.00025 |  | 299.6 |
| 0.00015 |  | 350.7 |
| 0.00010 |  | 391.2 |

Experiments such as the one that gave us the data in the above table are classified as measurements of **chemical kinetics** (from a Greek stem meaning "to move"). One of the goals of these experiments is to describe the **rate of reaction--**the rate at which the reactants are transformed into the products of the reaction.

The term *rate* is often used to describe the change in a quantity that occurs per unit of time. The rate of inflation, for example, is the change in the average cost of a collection of standard items per year. The rate at which an object travels through space is the distance traveled per unit of time, such as miles per hour or kilometers per second. In chemical kinetics, the distance traveled is the change in the concentration of one of the components of the reaction. The rate of a reaction is therefore the change in the concentration of one of the reactants**--delta**(*X*)**--**that occurs during a given period of time**--delta***t*.

equation

|  |
| --- |
| ***Practice Problem 1:***  Use the data in the above table to calculate the rate at which phenolphthalein reacts with the OH- ion during each of the following periods:  (a) During the first time interval, when the phenolphthalein concentration falls from 0.0050 *M* to 0.0045 *M*.  (b) During the second interval, when the concentration falls from 0.0045 *M* to 0.0040 *M*.  (c) During the third interval, when the concentration falls from 0.0040 *M* to 0.0035 *M*.  [***Click here to check your answer to Practice Problem 1.***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch22/problems/ex22_1a.html)  [***Click here to see a solution to Practice Problem 1.***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch22/problems/ex22_1s.html) |

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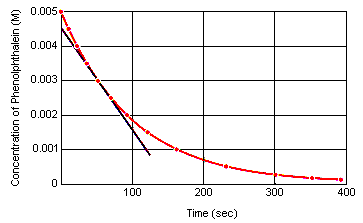
***Instantaneous Rates of Reaction and the Rate Law for a Reaction***

The rate of the reaction between phenolphthalein and the OH- ion isn't constant; it changes with time. Like most reactions, the rate of this reaction gradually decreases as the reactants are consumed. This means that the rate of reaction changes while it is being measured.

To minimize the error this introduces into our measurements, it seems advisable to measure the rate of reaction over periods of time that are short compared with the time it takes for the reaction to occur. We might try, for example, to measure the infinitesimally small change in concentration--*d*(*X*)--that occurs over an infinitesimally short period of time--*dt*. The ratio of these quantities is known as the **instantaneous rate of reaction**.

equation

The instantaneous rate of reaction at any moment in time can be calculated from a graph of the concentration of the reactant (or product) versus time. The graph below shows how the rate of reaction for the decomposition of phenolphthalein can be calculated from a graph of concentration versus time. The rate of reaction at any moment in time is equal to the slope of a tangent drawn to this curve at that moment.



The instantaneous rate of reaction can be measured at any time between the moment at which the reactants are mixed and the reaction reaches equilibrium. Extrapolating these data back to the instant at which the reagents are mixed gives the *initial instantaneous rate of reaction*.

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***Rate Laws and Rate Constants***

An interesting result is obtained when the instantaneous rate of reaction is calculated at various points along the curve in the [graph](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch22/rate.php#graph_1) in the previous section. The rate of reaction at every point on this curve is directly proportional to the concentration of phenolphthalein at that moment in time.

*Rate = k(phenolphthalein)*

Because this equation is an experimental law that describes the rate of the reaction, it is called the **rate law** for the reaction. The proportionality constant, *k*, is known as the **rate constant**.

|  |
| --- |
| ***Practice Problem 2:***  Calculate the rate constant for the reaction between phenolphthalein and the OH- ion if the instantaneous rate of reaction is 2.5 x 10-5 mole per liter per second when the concentration of phenolphthalein is 0.0025 *M*.  [***Click here to check your answer to Practice Problem 2.***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch22/problems/ex22_2a.html)  ***[Click here to see a solution to Practice Problem 2.](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch22/problems/ex22_2s.html)*** |

|  |
| --- |
| ***Practice Problem 3:***  Use the rate constant for the reaction between phenolphthalein and the OH- ion to calculate the initial instantaneous rate of reaction for the experimental data listed in the preceding table.  [***Click here to check your answer to Practice Problem 3.***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch22/problems/ex22_3a.html)  [***Click here to see a solution to Practice Problem 3.***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch22/problems/ex22_3s.html) |

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***Different Ways of Expressing the Rate of Reaction***

There is usually more than one way to measure the rate of a reaction. We can study the decomposition of hydrogen iodide, for example, by measuring the rate at which either H2 or I2 is formed in the following reaction or the rate at which HI is consumed.

2 HI(*g*) <----> H2(*g*) + I2(*g*)

Experimentally we find that the rate at which I2 is formed is proportional to the square of the HI concentration at any moment in time.

equation

What would happen if we studied the rate at which H2 is formed? The balanced equation suggests that H2 and I2 must be formed at exactly the same rate.

equation

What would happen, however, if we studied the rate at which HI is consumed in this reaction? Because HI is consumed, the change in its concentration must be a negative number. By convention, the rate of a reaction is always reported as a positive number. We therefore have to change the sign before reporting the rate of reaction for a reactant that is consumed in the reaction.



The negative sign does two things. Mathematically, it converts a negative change in the concentration of HI into a positive rate. Physically, it reminds us that the concentration of the reactant decreases with time.

What is the relationship between the rate of reaction obtained by monitoring the formation of H2 or I2 and the rate obtained by watching HI disappear? The stoichiometry of the reaction says that two HI molecules are consumed for every molecule of H2 or I2 produced. This means that the rate of decomposition of HI is twice as fast as the rate at which H2 and I2 are formed. We can translate this relationship into a mathematical equation as follows.

equation

As a result, the rate constant obtained from studying the rate at which H2 and I2 are formed in this reaction (*k*) is not the same as the rate constant obtained by monitoring the rate at which HI is consumed (*k'*)

|  |
| --- |
| ***Practice Problem 4:***  Calculate the rate at which HI disappears in the following reaction at the moment when I2 is being formed at a rate of 1.8 x 10-6 moles per liter per second:  2 HI(*g*) <----> H2(*g*) + I2(*g*)  [***Click here to check your answer to Practice Problem 4.***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch22/problems/ex22_4a.html)  [***Click here to see a solution to Practice Problem 4.***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch22/problems/ex22_4s.html) |

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***The Rate Law Versus the Stoichiometry of a Reaction***

In the 1930s, Sir Christopher Ingold and coworkers at the University of London studied the kinetics of substitution reactions such as the following.

CH3Br(*aq*) + OH-(*aq*) <----> CH3OH(*aq*) + Br-(*aq*)

They found that the rate of this reaction is proportional to the concentrations of both reactants.

Rate = *k*(CH3Br)(OH-)

When they ran a similar reaction on a slightly different starting material, they got similar products.

(CH3)3CBr(*aq*) + OH-(*aq*) <----> (CH3)3COH(*aq*) + Br-(*aq*)

But now the rate of reaction was proportional to the concentration of only one of the reactants.

Rate = *k*((CH3)3CBr)

These results illustrate an important point: **The rate law for a reaction cannot be predicted from the stoichiometry of the reaction; it must be determined experimentally**. Sometimes, the rate law is consistent with what we expect from the stoichiometry of the reaction.

|  |  |  |
| --- | --- | --- |
| 2 HI(*g*) <----> H2(*g*) + I2(*g*) |  | Rate = *k*(HI)2 |

Often, however, it is not.

|  |  |  |
| --- | --- | --- |
| 2 N2O5(*g*) ---> 4 NO2(*g*) + O2(*g*) |  | Rate = *k*(N2O5) |

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***Order of Molecularity***

Some reactions occur in a single step. The reaction in which a chlorine atom is transferred from ClNO2 to NO to form NO2 and ClNO is a good example of a one-step reaction.

ClNO2(*g*) + NO(*g*) <-----> NO2(*g*) + ClNO(*g*)

Other reactions occur by a series of individual steps. N2O5, for example, decomposes to NO2 and O2 by a three-step mechanism.

|  |  |  |
| --- | --- | --- |
| **Step 1:** |  | N2O5 <----> NO2 + NO3 |
| **Step 2:** |  | NO2 + NO3 <----> NO2 + NO + O2 |
| **Step 3:** |  | NO + NO3 <----> 2 NO2 |

The steps in a reaction are classified in terms of **molecularity**, which describes the number of molecules consumed. When a single molecule is consumed, the step is called **unimolecular**. When two molecules are consumed, it is **bimolecular**.

|  |
| --- |
| ***Practice Problem 5:***  Determine the molecularity of each step in the reaction by which N2O5 decomposes to NO2 and O2.  [***Click here to check your answer to Practice Problem 5.***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch22/problems/ex22_5a.html)  [***Click here to see a solution to Practice Problem 5.***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch22/problems/ex22_5s.html) |

Reactions can also be classified in terms of their **order**. The decomposition of N2O5 is a **first-order reaction** because the rate of reaction depends on the concentration of N2O5 raised to the first power.

Rate = *k*(N2O5)

The decomposition of HI is a **second-order reaction** because the rate of reaction depends on the concentration of HI raised to the second power.

Rate = *k*(HI)2

When the rate of a reaction depends on more than one reagent, we classify the reaction in terms of the order of each reagent.

|  |
| --- |
| ***Practice Problem 6:***  Classify the order of the reaction between NO and O2 to form NO2:  2 NO(*g*) + O2(*g*) <----> 2 NO2(*g*)  Assume the following rate law for this reaction:  Rate = *k*(NO)2(O2)  [***Click here to check your answer to Practice Problem 6.***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch22/problems/ex22_6a.html) |

    The difference between the molecularity and the order of a reaction is important. The molecularity of a reaction, or a step within a reaction, describes what happens on the molecular level. The order of a reaction describes what happens on the macroscopic scale. We determine the order of a reaction by watching the products of a reaction appear or the reactants disappear. The molecularity of the reaction is something we deduce to explain these experimental results.

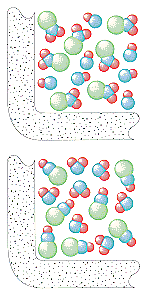
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***Collision Theory Model of Chemical Reactions***

The **collision theory model**of chemical reactions can be used to explain the observed rate laws for both one-step and multi-step reactions. This model assumes that the rate of any step in a reaction depends on the frequency of collisions between the particles involved in that step.

The figure below provides a basis for understanding the implications of the collision theory model for simple, one-step reactions, such as the following.

ClNO2(*g*) + NO(*g*) <----> NO2(*g*) + ClNO(*g*)



The kinetic molecular theory assumes that the number of collisions per second in a gas depends on the number of particles per liter. The rate at which NO2 and ClNO are formed in this reaction should therefore be directly proportional to the concentrations of both ClNO2 and NO.

Rate = *k*(ClNO2)(NO)

The collision theory model suggests that the rate of any step in a reaction is proportional to the concentrations of the reagents consumed in that step. The rate law for a one-step reaction should therefore agree with the stoichiometry of the reaction.

The following reaction, for example, occurs in a single step.

CH3Br(*aq*) + OH-(*aq*) <----> CH3OH(*aq*) + Br-(*aq*)

When these molecules collide in the proper orientation, a pair of nonbonding electrons on the OH- ion can be donated to the carbon atom at the center of the CH3Br molecule, as shown in the figure below.

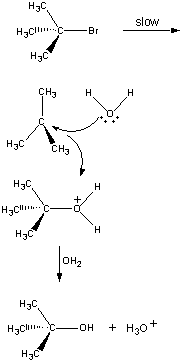
reaction

When this happens, a carbon-oxygen bond forms at the same time that the carbon-bromine bond is broken. The net result of this reaction is the substitution of an OH- ion for a Br - ion. Because the reaction occurs in a single step, which involves collisions between the two reactants, the rate of this reaction is proportional to the concentration of both reactants.

Rate = *k*(CH3Br)(OH-)

Not all reactions occur in a single step. The following reaction occurs in three steps, as shown in the figure below.

(CH3)3CBr(*aq*) + OH-(*aq*) <----> (CH3)3COH(*aq*) + Br-(*aq*)



In the first step, the (CH3)3CBr molecule dissociates into a pair of ions.

|  |  |  |
| --- | --- | --- |
| First step |  | reaction |

The positively charged (CH3)3C+ ion then reacts with water in a second step.

|  |  |  |
| --- | --- | --- |
| Second step |  | reaction |

The product of this reaction then loses a proton to either the OH- ion or water in the final step.

|  |  |  |
| --- | --- | --- |
| Third step |  | reaction |

The second and third steps in this reaction are very much faster than first.

|  |  |  |
| --- | --- | --- |
| (CH3)3CBr <----> (CH3)3C+ + Br- |  | Slow step |
| (CH3)3C+ + H2O <----> (CH3)3COH2+ |  | Fast step |
| (CH3)3COH2+ + OH- <----> (CH3)3COH + H3O |  | Fast step |

The overall rate of reaction is therefore more or less equal to the rate of the first step. The first step is therefore called the **rate-limiting step** in this reaction because it literally limits the rate at which the products of the reaction can be formed. Because only one reagent is involved in the rate-limiting step, the overall rate of reaction is proportional to the concentration of only this reagent.

Rate = *k*((CH3)3CBr)

The rate law for this reaction therefore differs from what we would predict from the stoichiometry of the reaction. Although the reaction consumes both (CH3)3CBr and OH-, the rate of the reaction is only proportional to the concentration of (CH3)3CBr.

The rate laws for chemical reactions can be explained by the following general rules.

* The rate of any step in a reaction is directly proportional to the concentrations of the reagents consumed in that step.
* The overall rate law for a reaction is determined by the sequence of steps, or the **mechanism**, by which the reactants are converted into the products of the reaction.
* The overall rate law for a reaction is dominated by the rate law for the slowest step in the reaction.

[**20.1: Oxidation States**](https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/20%3A_Electrochemistry/20.01%3A_Oxidation_States_and_Redox_Reactions)

**Q20.1.1**

Identify the oxidation state of the atoms in the following compounds:

1. *PCl*3
2. *CO*2−3
3. *H*2*S*
4. *S*8
5. *SCl*2
6. *Na*2*SO*3
7. *SO*2−4

**S20.1.1**

1. An atom’s oxidation state is representative of the number of electrons that a specific atom has lost or gained when binding to another atom. This allows us to determine the changes that cause in redox reactions as well as balance redox reactions.

Below are some of the rules to determining an atom’s oxidation number:

1. The oxidation state of an element that is not combined with another element Fe, H2, O2, P4, S8 is zero (0).
2. The oxidation state of oxygen in a compounds is -2, except for when it is in peroxides like H2O2, and Na2O2, in this case the oxidation state for O is -1.
3. The oxidation state of hydrogen is +1 in its compounds, except for metal hydrides, such as NaH and LiH, where the oxidation state for H is -1.
4. The net charge on a molecule of ion is equal to the algebraic sum of the oxidation state of all the atoms present in the species.
   * +1 for alkali metals (Group 1): (Li, Na, K, Rb, Cs)
   * +2 for alkaline earth metals (Group 2): (Be, Mg, Ca, Sr, Ba)
   * The oxidation number of fluorine is always –1. Chlorine, bromine, and iodine usually have an oxidation number of –1, unless they are combined with an oxygen or fluorine atom
5. The oxidation number of a monatomic ion is equal to the charge on the ion
6. *Solution:*

a) PCl3

According to Rule #5 above, chlorine has an oxidation state of -1. There are 3 chlorine atoms present in this compound and so chlorine has a total oxidation state of (-1)3=-3. Because this is a neutral compound, we know that the net charge of the molecule must equal to 0 (Rule #4). Therefore we can find the oxidation state of phosphorous because :

O.S.(P)+O.S(Cl)=net charge

O.S.(P)+(-3)=0

O.S.(P)=+3

**Oxidation state of chlorine atom=-1, total oxidation state of Chlorine atoms: -3**

**Oxidation state of phosphorous atom=+3**

b) CO32−

According to Rule #2, oxygen has an oxidation number of -2. Since there are 3 oxygen atoms, the overall oxidation state of the oxygens is (-2)3=-6 Because the overall molecule has a net charge of 2- , carbon must have an oxidation state of (-2)-(-6)=+4.

**Oxidation state of oxygen atom=-2**

**Oxidation state of carbon atom=+4**

c) H2S

According to Rule #3, hydrogen has an oxidation state of +1. Since there are two hydrogen atoms, the total oxidation state of the hydrogens is (+1)2=+2. The overall molecule has a net charge of 0, and so the oxidation state of the sulfur atom is 0-(+2)=-2.

**Oxidation state of hydrogen atom=+1**

**Oxidation state of sulfur atom=-2**

d) S8

Since this is an elemental form of sulfur, according to Rule #1, the sulfur atom would have an oxidation state of 0.

**Oxidation state of sulfur atom=0**

e) SCl2

According to Rule #5 above, chlorine has an oxidation state of -1. There are 2 chlorine atoms present in this compound and so chlorine has a total oxidation state of (-1)2=-2. This is a neutral compound, so the net charge of the molecule is equal to 0. Therefore, the oxidation state of the sulfur atom is 0-(-2)-+2.

**Oxidation state of chlorine atom=-1**

**Oxidation state of sulfur atom=+2**

f) Na2SO3

Sodium is an alkali metal, and so one Na atom has an oxidation state of +1; the overall oxidation state of the two sodium atoms in this compound is equal to (+1)2=+2. Oxygen atom has an oxidation state of -2, and since there are 3 oxygen atoms, the total oxidation state of the oxygen atoms in this compound is (-2)3=-6. This is a neutral molecule with a net charge of 0, and so the oxidation state of the sulfur atom is 0-(+2)-(-6)=+4.

**Oxidation state of sodium atom=+1**

**Oxidation state of sulfur atom=+4**

**Oxidation state of oxygen atom=-2**

g) SO42−

According to Rule #2, the oxidation state of an oxygen atom is -2. The overall oxidation state of 4 atoms of oxygen is (-2)4=-8. The net charge of the compound is 2-, and so the oxidation state of the sulfur atom is -2-(-8)=+6.

**Oxidation state of sulfur atom=+6**

**Oxidatin state of oxygen atom=-2**

**A20.1.1**

a)

**Oxidation state of chlorine atom=-1**

**Oxidation state of phosphorous atom=+3**

b)

**Oxidation state of oxygen atom=-2**

**Oxidation state of carbon atom=+4**

c)

**Oxidation state of hydrogen atom=+1**

**Oxidation state of sulfur atom=-2**

d)

**Oxidation state of sulfur atom=0**

e)

**Oxidation state of chlorine atom=-1**

**Oxidation state of sulfur atom=+2**

f)

**Oxidation state of sodium atom=+1**

**Oxidation state of sulfur atom=+4**

**Oxidation state of oxygen atom=-2**

***Electrical Work From Spontaneous Oxidation-Reduction Reactions***

The following rule can be used to predict whether an oxidation-reduction reaction should occur. **Oxidation-reduction reactions should occur when they convert the stronger of a pair of oxidizing agents and the stronger of a pair of reducing agents into a weaker oxidizing agent and a weaker reducing agent.**

|  |
| --- |
| ***Practice Problem 1:***  Predict whether zinc metal should dissolve in acid.  [***Click here to check your answer to Practice Problem 1***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/problems/ex20_2a.html) |

We can test this prediction by adding a few chunks of mossy zinc to a beaker of concentrated hydrochloric acid. Within a few minutes, the zinc metal dissolves, and significant amounts of hydrogen gas are liberated.

The reaction in Practice Problem 1 has some of the characteristic features of oxidation-reduction reactions.

* It is exothermic, in this case giving off 153.89 kilojoules per mole of zinc consumed.
* The equilibrium constant for the reaction is very large (*Kc* = 6 x 1025), and chemists often write the equation for this reaction as if essentially all of the reactants were converted to products.

Zn(*s*) + 2 H+(*aq*) -----> Zn2+(*aq*) + H2(*g*)

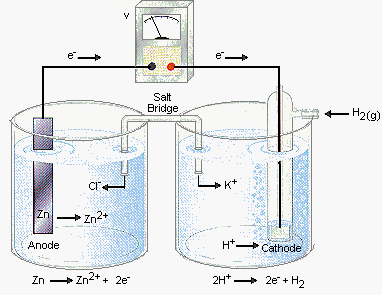
* It can be formally divided into separate oxidation and reduction half-reactions.

|  |  |  |
| --- | --- | --- |
| Oxidation: |  | Zn -----> Zn2+ + 2 e- |
| Reduction: |  | 2 H+ + 2 e- -----> H2 |

* By separating the two half-reactions, the energy given off by this reaction can be used to do work.

According to the first law of thermodynamics, the energy given off in a chemical reaction can be converted into heat, work, or a mixture of heat and work. By running the half-reactions in separate containers, we can force the electrons to flow from the oxidation to the reduction half-reaction through an external wire, which allows us to capture as much as possible of the energy given off in the reaction as electrical work.

We can start by immersing a strip of zinc metal into a 1 *M* Zn2+ ion solution, as shown in the figure below. We then immerse a piece of platinum wire in a second beaker filled with 1 *M* HCl and bubble H2 gas over the Pt wire. Finally, we connect the zinc metal and platinum wire to form an electric circuit.



We've now made a system in which electrons can flow from one half-reaction, or **half-cell,**to another. The same driving force that makes zinc metal react with acid when the two are in contact should operate in this system. Zinc atoms on the metal surface lose electrons to form Zn2+ ions, which go into solution.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Oxidation: |  | Zn | -----> | Zn2+ + 2 e- |

The electrons given off in this half-reaction flow through the circuit and eventually accumulate on the platinum wire to give this wire a net negative charge. The H+ ions from the hydrochloric acid are attracted to this negative charge and migrate toward the platinum wire. When the H+ ions touch the platinum wire, they pick up electrons to form hydrogen atoms, which immediately combine to form H2 molecules.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Reduction: |  | 2 H+ + 2 e- | -----> | H2 |

The oxidation of zinc metal releases Zn2+ ions into the Zn/Zn2+ half-cell. This half-cell therefore picks up a positive charge that interferes with the transfer of more electrons. The reduction of H+ ions in the H2/H+ half-cell leads to a net negative charge as these H+ ions are removed from the solution. This negative charge also interferes with the transfer of more electrons.

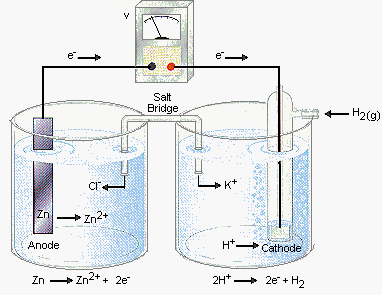
To overcome this problem, we complete the circuit by adding a U-tube filled with a saturated solution of a soluble salt such as KCl. Negatively charged Cl- ions flow out of one end of the U-tube to balance the positive charge on the Zn2+ ions created in one half-cell. Positively charged K+ ions flow out of the other end of the tube to replace the H+ ions consumed in the other half cell. The U-tube is called a **salt bridge**, because it contains a solution of a salt that literally serves as a bridge to complete the electric circuit.

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***Voltaic Cells***

Electrochemical cells that use an oxidation-reduction reaction to generate an electric current are known as **galvanic** or **voltaic cells**. Because the potential of these cells to do work by driving an electric current through a wire is measured in units of *volts*, we will refer to the cells that generate this potential from now on as *voltaic cells*.

Let's take another look at the voltaic cell in the figure below.



Within each half-cell, reaction occurs on the surface of the metal electrode. At the zinc electrode, zinc atoms are oxidized to form Zn2+ ions, which go into solution. The electrons liberated in this reaction flow through the zinc metal until they reach the wire that connects the zinc electrode to the platinum wire. They then flow through the platinum wire, where they eventually reduce an H+ ion in the neighboring solution to a hydrogen atom, which combines with another hydrogen atom to form an H2 molecule.

The electrode at which oxidation takes place in a electrochemical cell is called the **anode**. The electrode at which reduction occurs is called the **cathode**. The identity of the cathode and anode can be remembered by recognizing that positive ions, or **cations**, flow toward the cathode, while negative ions, or **anions**, flow toward the anode. In the voltaic cell shown above, H+ ions flow toward the cathode, where they are reduced to H2 gas. On the other side of the cell, Cl- ions are released from the salt bridge and flow toward the anode, where the zinc metal is oxidized.

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***Standard-State Cell Potentials for Voltaic Cells***

The **cell potential** for a voltaic cell is literally the potential of the cell to do work on its surroundings by driving an electric current through a wire. By definition, one joule of energy is produced when one coulomb of electrical charge is transported across a potential of one volt.

1V = 1 J/1 C

The potential of a voltaic cell depends on the concentrations of any species present in solution, the partial pressures of any gases involved in the reaction, and the temperature at which the reaction is run. To provide a basis for comparing the results of one experiment with another, the following set of **standard-state conditions** for electrochemical measurements has been defined.

* All solutions are 1 *M*.
* All gases have a partial pressure of 0.1 MPa (0.9869 atm).

Although standard-state measurements can be made at any temperature, they are often taken at 25oC.

Cell potentials measured under standard-state conditions are represented by the symbol *E*o. The standard-state cell potential, *E*o, measures the strength of the driving force behind the chemical reaction. The larger the difference between the oxidizing and reducing strengths of the reactants and products, the larger the cell potential. To obtain a relatively large cell potential, we have to react a strong reducing agent with a strong oxidizing agent.

Example: The experimental value for the standard-state cell potential for the reaction between zinc metal and acid is 0.76 volts.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Zn(*s*) + 2 H+(*aq*) ----> Zn2+(*aq*) + H2(*g*) |  |  | *E*o = 0.76 V |  |

The cell potential for this reaction measures the *relative* reducing power of zinc metal compared with hydrogen gas. But it doesn't tell us anything about the *absolute* value of the reducing power for either zinc metal or H2.

We therefore arbitrarily define the standard-state potential for the reduction of H+ ions to H2 gas as exactly zero volts.

|  |  |  |  |
| --- | --- | --- | --- |
| 2 H+ + 2 e- ----> H2 |  |  | *E*o = 0.000... V |

We will then use this reference point to calibrate the potential of any other half-reaction.

The key to using this reference point is recognizing that the overall cell potential for a reaction must be the sum of the potentials for the oxidation and reduction half-reactions.

*Eooverall* = *E*o*ox* + *E*o*red*

If the overall potential for the reaction between zinc and acid is 0.76 volts, and the half-cell potential for the reduction of H+ ions is 0 volts, then the half-cell potential for the oxidation of zinc metal must be 0.76 volts.

|  |  |
| --- | --- |
| Zn ----> Zn2+ + ~~2 e~~- | *E*o*ox* = 0.76 V |
| + 2 H+ + ~~2 e~~- ----> H2 | *E*o*red* = 0.00 V |
|  |  |
| Zn + 2 H+ ----> Zn2+ + H2 | *E*o = *E*o*ox* + *E*o*red* = 0.76 V |

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***Predicting Spontaneous Redox Reactions From the Sign of Eo***

The *magnitude* of the cell potential is a measure of the driving force behind a reaction. The larger the value of the cell potential, the further the reaction is from equilibrium. The *sign* of the cell potential tells us the direction in which the reaction must shift to reach equilibrium.

Consider the reaction between zinc and acid, for example.

|  |  |  |  |
| --- | --- | --- | --- |
| Zn(*s*) + 2 H+(*aq*) ----> Zn2+(*aq*) + H2(*g*) |  |  | *E*o = 0.76 V |

The fact that *E*o is positive tells us that when this system is present at standard-state conditions, it has to shift to the right to reach equilibrium. Reactions for which *E*o is positive therefore have equilibrium constants that favor the products of the reaction. It is tempting to describe these reactions as "spontaneous."

What happens to the cell potential when we reverse the direction in which a reaction is written? Turning the reaction around doesn't change the relative strengths of the oxidizing or reducing agents. The *magnitude* of the potential must remain the same. But turning the equation around changes the *sign* of the cell potential, and can therefore turn an unfavorable reaction into one that is spontaneous, or vice versa.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| ***Practice Problem 2:***  Use the overall cell potentials to predict which of the following reactions are spontaneous.   |  |  |  | | --- | --- | --- | | (a) Cu(*s*) + 2 Ag+(*aq*)Cu2+(*aq*) + 2 Ag(*s*) |  | *E*o = 0.46 V | | (b) 2 Fe3+(*aq*) + 2 Cl-(*aq*)2 Fe2+(*aq*) + Cl2(*g*) |  | *E*o = -0.59 V | | (c) 2 Fe3+(*aq*) + 2 I-(*aq*)2 Fe2+(*aq*) + I2(*aq*) |  | *E*o = 0.24 V | | (d) 2 H2O2(*aq*)2 H2O(*l*) + O2(*aq*) |  | *E*o = 1.09 V | | (e) Cu(*s*) + 2 H+(*aq*)Cu2+(*aq*) + H2(*g*) |  | *E*o = -0.34 V |   [***Click here to check your answer to Practice Problem 2***](https://chemed.chem.purdue.edu/~genchem/topicreview/bp/ch20/problems/ex20_3a.html) |

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| ***Practice Problem 3:***  Use the standard-state cell potential for the following reaction   |  |  |  |  | | --- | --- | --- | --- | | Cu(*s*) + 2 H+(*aq*) -----> Cu2+(*aq*) + H2(*g*) |  |  | *E*o = -0.34 V |   to predict the standard-state cell potential for the opposite reaction.   |  |  |  |  | | --- | --- | --- | --- | | Cu2+(*aq*) + H2(*g*) -----> Cu(*s*) + 2 H+(*aq*) |  |  | *E*o = ? |   [***Click here to check your answer to Practice Problem 3***](https://chemed.chem.purdue.edu/~genchem/topicreview/bp/ch20/problems/ex20_4a.html) |

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***Standard-State Reduction Half-Cell Potentials***

The standard-state cell potentials for some common half-reactions are given in the table below.

*Standard-State Reduction Potentials, Eored*

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  |  | *Half-Reaction* |  | *Eored* |  |  |
|  |  | K+ + e- <-----> K |  | -2.924 |  | Best |
|  |  | Ba2+ + 2 e- <-----> Ba |  | -2.90 |  | reducing |
|  |  | Ca2+ + 2 e- <-----> Ca |  | -2.76 |  | agents |
|  |  | Na+ + e- <-----> Na |  | -2.7109 |  |  |
|  |  | Mg2+ + 2 e- <-----> Mg |  | -2.375 |  |  |
|  |  | H2 + 2 e- <-----> 2 H- |  | -2.23 |  |  |
|  |  | Al3+ + 3 e- <-----> Al |  | -1.706 |  |  |
|  |  | Mn2+ + 2 e- <-----> Mn |  | -1.04 |  |  |
|  |  | Zn2+ + 2 e- <-----> Zn |  | -0.7628 |  |  |
|  |  | Cr3+ + 3 e- <-----> Cr |  | -0.74 |  |  |
|  |  | S + 2 e- <-----> S2- |  | -0.508 |  |  |
|  |  | 2 CO2 + 2 H+ + 2 e- <-----> H2C2O4 |  | -0.49 |  |  |
|  |  | Cr3+ + e- <-----> Cr2+ |  | -0.41 |  |  |
|  |  | Fe2+ + 2 e- <-----> Fe |  | -0.409 |  |  |
|  |  | Co2+ + 2 e- <-----> Co |  | -0.28 |  |  |
|  |  | Ni2+ + 2 e- <-----> Ni |  | -0.23 |  |  |
|  |  | Sn2+ + 2 e- <-----> Sn |  | -0.1364 |  |  |
|  |  | Pb2+ + 2 e- <-----> Pb |  | -0.1263 |  |  |
|  |  | Fe3+ + 3 e- <-----> Fe |  | -0.036 |  |  |
|  |  | 2 H+ + 2 e- <-----> H2 |  | 0.0000... |  |  |
|  |  | S4O62- + 2 e- <-----> 2 S2O32- |  | 0.0895 |  |  |
| Oxidizing |  | Sn4+ + 2 e- <-----> Sn2+ |  | 0.15 |  | up |
| power |  | Cu2+ + e- <-----> Cu+ |  | 0.158 |  | Reducing |
| increases |  | Cu2+ + 2 e-<-----> Cu |  | 0.3402 |  | power |
| down |  | O2 + 2 H2O + 4 e- <-----> 4 OH- |  | 0.401 |  | increases |
|  |  | Cu+ + e- <-----> Cu |  | 0.522 |  |  |
|  |  | I3- + 2 e- <-----> 3 I- |  | 0.5338 |  |  |
|  |  | MnO4- + 2 H2O + 3 e- <-----> MnO2 + 4 OH- |  | 0.588 |  |  |
|  |  | O2 + 2 H+ + 2 e- <-----> H2O2 |  | 0.682 |  |  |
|  |  | Fe3+ + e- <-----> Fe2+ |  | 0.770 |  |  |
|  |  | Hg22+ + 2 e- <-----> Hg |  | 0.7961 |  |  |
|  |  | Ag+ + e- <-----> Ag |  | 0.7996 |  |  |
|  |  | Hg2+ + 2 e- <-----> Hg |  | 0.851 |  |  |
|  |  | H2O2 + 2 e- <-----> 2 OH- |  | 0.88 |  |  |
|  |  | HNO3 + 3 H+ + 3 e- <-----> NO + 2 H2O |  | 0.96 |  |  |
|  |  | Br2(*aq*) + 2 e- <-----> 2 Br- |  | 1.087 |  |  |
|  |  | 2 IO3- + 12 H+ + 10 e- <-----> I2 + 6 H2O |  | 1.19 |  |  |
|  |  | CrO42- + 8 H+ + 3 e- <-----> Cr3+ + 4 H2O |  | 1.195 |  |  |
|  |  | Pt2+ + 2 e- <-----> Pt |  | 1.2 |  |  |
|  |  | MnO2 + 4 H+ + 2 e- <-----> Mn2+ + 2 H2O |  | 1.208 |  |  |
|  |  | O2 + 4 H+ + 4 e- <-----> 2 H2O |  | 1.229 |  |  |
|  |  | Cr2O72- + 14 H+ + 6 e- <-----> 2 Cr3+ + 7 H2O |  | 1.33 |  |  |
|  |  | Cl2(*g*) + 2 e- <-----> 2 Cl- |  | 1.3583 |  |  |
|  |  | PbO2 + 4 H+ + 2 e- <-----> Pb2+ + 2 H2O |  | 1.467 |  |  |
|  |  | MnO4- + 8 H+ + 5 e- <-----> Mn2+ + 4 H2O |  | 1.491 |  |  |
|  |  | Au+ + e- <-----> Au |  | 1.68 |  |  |
|  |  | H2O2 + 2 H+ + 2 e- <-----> 2 H2O |  | 1.776 |  |  |
|  |  | Co3+ + e-<-----> Co2+ |  | 1.842 |  |  |
| Best |  | S2O82- + 2 e- <-----> 2 SO42- |  | 2.05 |  |  |
| oxidizing |  | O3(*g*) + 2 H+ + 2 e- <-----> O2(*g*) + H2O |  | 2.07 |  |  |
| agents |  | F2(*g*) + 2 H+ + 2 e- <-----> 2 HF(*aq*) |  | 3.03 |  |  |

There is no need to remember that reducing agents become stronger toward the upper right corner of this table, or that the strength of the oxidizing agents increases toward the bottom left corner. All you have to do is remember some of the chemistry of the elements at the top and bottom of this table.

Take a look at the half-reaction at the top of the table.

|  |  |  |  |
| --- | --- | --- | --- |
| K+ + e- <-----> K |  |  | *E*o*red* = -2.924 V |

What do we know about potassium metal? Potassium is one of the most reactive metals--it bursts into flame when added to water, for example. Furthermore, we know that metals are reducing agents in all of their chemical reactions. When we find potassium in this table, we can therefore conclude that it is listed among the strongest reducing agents.

Conversely, look at the last reaction in the table.

|  |  |  |  |
| --- | --- | --- | --- |
| F2 + 2 e- <-----> 2 F- |  |  | *E*o*red* = 3.03 V |

Fluorine is the most electronegative element in the periodic table. It shouldn't be surprising to find that F2 is the strongest oxidizing agent in the above table.

Referring to either end of this table can also help you remember the sign convention for cell potentials. The previous section introduced the following rule: **Oxidation-reduction reactions that have a positive overall cell potential are spontaneous**. This is consistent with the data in the above table. We know that fluorine wants to gain electrons to form fluoride ions, and the half-cell potential for this reaction is positive.

|  |  |  |  |
| --- | --- | --- | --- |
| F2 + 2 e- <-----> 2 F- |  |  | *E*o*red* = 3.03 V |

We also know that potassium is an excellent reducing agent. Thus, the potential for the reduction of K+ ions to potassium metal is negative

|  |  |  |  |
| --- | --- | --- | --- |
| K+ + e- <-----> K |  |  | *E*o*red* = -2.924 V |

but the potential for the oxidation of potassium metal to K+ ions is positive.

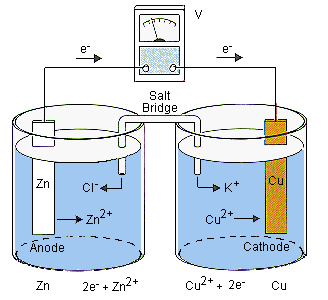
|  |  |  |  |
| --- | --- | --- | --- |
| K <-----> K+ + e- |  |  | *E*o*ox* = -(-2.924 V) = 2.924 V |

|  |
| --- |
| ***Practice Problem 4:***  Which of the following is the strongest oxidizing agent?  (a) H2O2 in acid  (b) H2O2 in base  (c) MnO4- in acid  (d) MnO4- in base  (e) CrO42- in acid  [***Click here to check your answer to Practice Problem 4***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/problems/ex20_5a.html) |

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***Predicting Standard-State Cell Potentials***

A voltaic cell stable enough to be used as a battery is called a Daniell cell. For our purposes, we will work with the idealized Daniell cell in the figure below.



We can use the known values of the standard-state reduction potentials for the Cu/Cu2+ and Zn/Zn2+ half-cells to predict the overall potential for the Daniell cell and to determine which electrode is the anode and which is the cathode.

We start by writing a balanced chemical equation for the reaction that occurs in this cell. The [table of standard-state reduction potentials](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/electro.php#table)suggests that zinc is a better reducing agent than copper and that the Cu2+ ion is a better oxidizing agent than the Zn2+ ion. The overall reaction therefore involves the reduction of Cu2+ ions by zinc metal.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Zn(*s*)** | **+** | **Cu2+(*aq*)** | **--->** | **Zn2+(*aq*)** | **+** | **Cu(*s*)** |
| stronger reducing agent |  | stronger oxidizing agent |  | weaker oxidizing agent |  | weaker reducing agent |

We then divide the reaction into separate oxidation and reduction half-reactions.

|  |  |  |  |
| --- | --- | --- | --- |
| **Reduction**: |  |  | Cu2+ + 2 e- ---> Cu |
| **Oxidation**: |  |  | Zn ---> Zn2+ + 2 e- |

The potential for the reduction of Cu2+ ions to copper metal can be found in the [table of standard-state reduction potentials](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/electro.php#table). To find the potential for the oxidation of zinc metal, we have to reverse the sign on the potential for the Zn/Zn2+ couple in this table.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Reduction**: |  | Cu2+ + 2 e- ---> Cu |  |  | *E*o*red* = 0.34 V |
| **Oxidation**: |  | Zn ---> Zn2+ + 2 e- |  |  | *E*o*ox* = -(-0.76 V) = 0.76 V |

The overall potential for this cell is the sum of the potentials for the two half-cells.

|  |  |  |
| --- | --- | --- |
| Cu2+ + ~~2 e~~- ---> Cu |  | *E*o*red* = 0.34 V |
| + Zn ---> Zn2+ + ~~2 e~~- |  | *E*o*ox* = 0.76 V |
|  |  |  |
| Zn + Cu2+ ---> Zn2+ + Cu |  | *E*o = *E*o*red* + *E*o*ox* = 1.10 V |

Oxidation always occurs at the anode and reduction always occurs at the cathode of an electrochemical cell. The Zn/Zn2+ half-cell is therefore the anode, and the Cu2+/Cu half-cell is the cathode, as shown in the figure of the Daniell cell.

|  |  |  |  |
| --- | --- | --- | --- |
| ***Practice Problem 5:***  Use cell potential data to explain why copper metal does not dissolve in a typical strong acid, such as hydrochloric acid,   |  |  | | --- | --- | | Cu(*s*) + 2 H+(*aq*) | --/---> |   but will dissolve in 1 *M* nitric acid.   |  | | --- | | 3 Cu(*s*) + 2 HNO3(*aq*) + 6 H+(*aq*) --->3 Cu2+(*aq*) + 2 NO(*g*) + 4 H2O(*l*) |   [***Click here to check your answer to Practice Problem 5***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/problems/ex20_6a.html) |

The units of half-cell potentials are volts, not volts per mole or volts per electron. All we do when combining half-reactions is add the two half-cell potentials. We do not multiply these potentials by the integers used to balance the number of electrons transferred in the reaction.

|  |
| --- |
| ***Practice Problem 6:***  Use cell potentials to explain why hydrogen peroxide disproportionates to form oxygen and water.  2 H2O2(*aq*) ---> 2 H2O(*l*) + O2(*g*)  [***Click here to check your answer to Practice Problem 6***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/problems/ex20_7a.html) |

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***Line Notation For Voltaic Cells***

Voltaic cells can be described by a line notation based on the following conventions.

* A single vertical line indicates a change in state or phase.
* Within a half-cell, the reactants are listed before the products.
* Concentrations of aqueous solutions are written in parentheses after the symbol for the ion or molecule.
* A double vertical line is used to indicate the junction between the half-cells.
* The line notation for the anode (oxidation) is written before the line notation for the cathode (reduction).

The line notation for a standard-state Daniell cell is written as follows.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Zn | | | Zn2+(1.0 *M*) | || | Cu2+(1.0 *M*) | | | Cu |
|  |  | anode (oxidation) |  | cathode (reduction) |  |  |

Electrons flow from the anode to the cathode in a voltaic cell. (They flow from the electrode at which they are given off to the electrode at which they are consumed.) Reading from left to right, this line notation therefore corresponds to the direction in which electrons flow.

|  |
| --- |
| ***Practice Problem 7:***  Write the line notation for the cell shown in the figure below.  diagram  [***Click here to check your answer to Practice Problem 7***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/problems/ex20_8a.html) |

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***The Nernst Equation***

What happens when the [Daniell cell](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/electro.php" \l "daniell) is used to do work?

* The zinc electrode becomes lighter as zinc atoms are oxidized to Zn2+ ions, which go into solution.
* The copper electrode becomes heavier as Cu2+ ions in the solution are reduced to copper metal.
* The concentration of Zn2+ ions at the anode increases and the concentration of the Cu2+ ions at the cathode decreases.
* Negative ions flow from the salt bridge toward the anode to balance the charge on the Zn2+ ions produced at this electrode.
* Positive ions flow from the salt bridge toward the cathode to compensate for the Cu2+ ions consumed in the reaction.

An important property of the cell is missing from this list. Over a period of time, the cell runs down, and eventually has to be replaced. Let's assume that our cell is initially a standard-state cell in which the concentrations of the Zn2+ and Cu2+ ions are both 1 molar.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Zn | | | Zn2+(1.0 *M*) | || | Cu2+(1.0 *M*) | | | Cu |

As the reaction goes forward--as zinc metal is consumed and copper metal is produced--the driving force behind the reaction must become weaker. Therefore, the cell potential must become smaller.

This raises an interesting question: When does the cell potential become zero?

The cell potential is zero if and only if the reaction is at equilibrium.

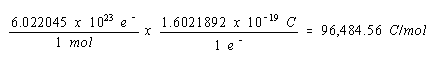
When the reaction is at equilibrium, there is no net change in the amount of zinc metal or copper ions in the system, so no electrons flow from the anode to the cathode. If there is no longer a net flow of electrons, the cell can no longer do electrical work. Its potential for doing work must therefore be zero.

In 1889 Hermann Walther Nernst showed that the potential for an electrochemical reaction is described by the following equation.

nernst equation

In the **Nernst equation**, *E* is the cell potential at some moment in time, *E*o is the cell potential when the reaction is at standard-state conditions, *R* is the ideal gas constant in units of joules per mole, *T* is the temperature in kelvin, *n* is the number of moles of electrons transferred in the balanced equation for the reaction, *F* is the charge on a mole of electrons, and *Qc* is the reaction quotient at that moment in time. The symbol *ln* indicates a natural logarithm, which is the log to the base *e*, where *e* is an irrational number equal to 2.71828...

Three terms in the Nernst equation are constants: *R*, *T*, and *F*. The ideal gas constant is 8.314 J/mol-K. The temperature is usually 25oC. The charge on a mole of electrons can be calculated from Avogadro's number and the charge on a single electron.



Substituting this information into the Nernst equation gives the following equation.

equation

Three of the remaining terms in this equation are characteristics of a particular reaction: *n*, *E*o, and *Qc*.

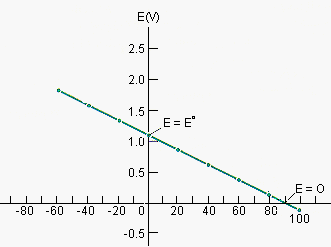
Example: The standard-state potential for the Daniell cell is 1.10 V. Two moles of electrons are transferred from zinc metal to Cu2+ ions in the balanced equation for this reaction, so *n* is 2 for this cell. Because we never include the concentrations of solids in either reaction quotient or equilibrium constant expressions, *Qc* for this reaction is equal to the concentration of the Zn2+ ion divided by the concentration of the Cu2+ ion.

equation

Substituting what we know about the Daniell cell into the Nernst equation gives the following result, which represents the cell potential for the Daniell cell at 25oC at any moment in time.

equation

The figure below shows a plot of the potential for the Daniell cell as a function of the natural logarithm of the reaction quotient.



When the reaction quotient is very small, the cell potential is positive and relatively large. This isn't surprising, because the reaction is far from equilibrium and the driving force behind the reaction should be relatively large. When the reaction quotient is very large, the cell potential is negative. This means that the reaction would have to shift back toward the reactants to reach equilibrium.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| ***Practice Problem 8:***  Calculate the potential in the following cell when 99.99% of the Cu2+ ions have been consumed.   |  |  |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | --- | --- | | Zn | | | Zn2+(1.00 *M*) | || | Cu2+(1.00 *M*) | | | Cu |  |   [***Click here to check your answer to Practice Problem 8***](https://chemed.chem.purdue.edu/~genchem/topicreview/bp/ch20/problems/ex20_9a.html)  [***Click here to see a solution to Practice Problem 8***](https://chemed.chem.purdue.edu/~genchem/topicreview/bp/ch20/problems/ex20_9s.html) |

Practice Problem 8 above raises an important point. The cell potential depends on the logarithm of the ratio of the concentrations of the products and the reactants. As a result, the potential of a cell or battery is more or less constant until virtually all of the reactants have been converted into products.

The Nernst equation can be used to calculate the potential of a cell that operates at non-standard-state conditions.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| ***Practice Problem 9:***  Calculate the potential at 25oC for the following cell.   |  |  |  |  |  |  |  | | --- | --- | --- | --- | --- | --- | --- | | Cu | | | Cu2+(0.024 *M*) | || | Ag+(0.0048 *M*) | | | Ag |   [***Click here to check your answer to Practice Problem 9***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/problems/ex20_10a.html)  [***Click here to see a solution to Practice Problem 9***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/problems/ex20_10s.html) |

The Nernst equation can help us understand a popular demonstration that uses glucose, C6H12O6, to reduce Ag+ ions to silver metal, thereby forming a silver mirror on the inner surface of the container. The standard-state half-cell potential for the reduction of Ag+ ions is approximately 0.800 volt.

|  |  |  |  |
| --- | --- | --- | --- |
| Ag+ + e----->Ag |  |  | *E*o*red* = 0.800 V |

The standard-state half-cell potential for the oxidation of glucose is -0.050 V.

|  |  |  |  |
| --- | --- | --- | --- |
| C6H12O6 + H2O ----> C6H12O7 + 2 H+ + 2 e- |  |  | *E*o*ox* = -0.050 V |

The overall standard-state cell potential for this reaction is therefore favorable.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| 2 (Ag+ + ~~e~~- ----> Ag) |  |  | *E*o*red* = 0.800 V |  |
| + C6H12O6 + H2O ----> C6H12O7 + 2 H+ + ~~2 e~~- |  |  | *E*o*ox* = -0.050 V |  |
|  |  |  |  |  |
| 2 Ag+ + C6H12O6 + H2O ----> 2 Ag + C6H12O7 + 2 H+ |  |  | *E*o = 0.750 V |  |

The reaction isn't run under standard-state conditions, however. It takes place in a solution to which aqueous ammonia has been added. Most of the silver is therefore present as the Ag(NH3)2+ complex ion. This is important, because the half-cell potential for the reduction of this complex is considerably smaller than the potential for the reduction of the Ag+ ion.

|  |  |  |  |
| --- | --- | --- | --- |
| Ag(NH3)2+ + e- ----> Ag + 2 NH3 |  |  | *E*o*red* = 0.373 V |

This leads to a significant *decrease* in the overall cell potential for the reaction because the Ag(NH3)2+ ion is a much weaker oxidizing agent than the Ag+ ion.

The fact that this reaction is run in an aqueous ammonia solution also has an effect on the potential for the oxidation of glucose, because this half-reaction contains a pair of H+ ions.

C6H12O6 + H2O ----> C6H12O7 + 2 H+ + 2 e-

The half-cell potential for this reaction therefore depends on the pH of the solution. Because two H+ ions are given off when glucose is oxidized, the reaction quotient for this reaction depends on the square of the H+ ion concentration. A change in this solution from standard-state conditions (pH = 0) to the pH of an aqueous ammonia solution (pH  11) therefore results in an *increase* of 0.650 volts in the half-cell potential for this reaction.

The increase in the reducing strength of glucose when the reaction is run at pH 11 more than compensates for the decrease in oxidizing strength that results from the formation of the Ag(NH3)2+ complex ion. Thus, the overall cell potential for the reduction of silver ions to silver metal is actually more favorable in aqueous ammonia than under standard-state conditions.

|  |  |  |  |
| --- | --- | --- | --- |
| 2 (Ag(NH3)2+ + ~~e~~-----> Ag + 2 NH3) |  |  | *E*o*red* = 0.373 V |
| + C6H12O6 + H2O ----> C6H12O7 + 2 H+ + ~~2 e~~- |  |  | *E*o*ox* = 0.600 V |
|  |  |  |  |
| 2 Ag(NH3)2+ + C6H12O6 + H2O ----> 2 Ag + C6H12O7 + 2 NH4+ |  |  | *E*o = 0.973 V |

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***Using the Nernst Equation to Measure Equilibrium Constants***

The Nernst equation can be used to measure the equilibrium constant for a reaction. To understand how this is done, we have to recognize what happens to the cell potential as an oxidation-reduction reaction comes to equilibrium. As the reaction approaches equilibrium, the driving force behind the reaction decreases, and the cell potential approaches zero.

|  |  |  |  |
| --- | --- | --- | --- |
| **At equilibrium**: |  |  | *E* = 0 |

What implications does this have for the Nernst equation?

equation

At equilibrium, the reaction quotient is equal to the equilibrium constant (*Qc* = *Kc*) and the overall cell potential for the reaction is zero (*E* = 0).

|  |  |  |  |
| --- | --- | --- | --- |
| **At equilibrium**: |  |  | equation |

Rearranging this equation gives the following result.

|  |  |  |  |
| --- | --- | --- | --- |
| **At equilibrium**: |  |  | equation |

According to this equation, we can calculate the equilibrium constant for any oxidation-reduction reaction from its standard-state cell potential:

equation

or, in a more useful arrangement:

equation

|  |
| --- |
| ***Practice Problem 10:***  Calculate the equilibrium constant at 25oC for the reaction between zinc metal and acid.  Zn(*s*) + 2 H+(*aq*) ----> Zn2+(*aq*) + H2(*g*)  [***Click here to check your answer to Practice Problem 10***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/problems/ex20_11a.html)  [***Click here to see a solution to Practice Problem 10***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/problems/ex20_11s.html) |

This technique used in Practice Problem 10 can even be used to calculate equilibrium constants for reactions that don't seem to involve oxidation-reduction.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| ***Practice Problem 11:***  Use the following standard-state cell potentials to calculate the complex formation equilibrium constant for the Zn(NH3)42+ complex ion.   |  |  |  |  | | --- | --- | --- | --- | | Zn(NH3)42+ + 2 e- <----> Zn + 4 NH3 |  |  | *E*o*red* = -1.04 V | | Zn2+ + 2 e- <----> Zn |  |  | *E*o*red* = -0.7628 V |   [***Click here to check your answer to Practice Problem 11***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/problems/ex20_12a.html)  ***[Click here to see a solution to Practice Problem 11](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/problems/ex20_12s.html)*** |

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| ***Practice Problem 12:***  Use the following standard-state cell potentials to calculate the solubility product at 25oC for Mg(OH)2.   |  |  |  |  | | --- | --- | --- | --- | | Mg(OH)2 + 2 e- <----> Mg + 2 OH- |  |  | *E*o*red* = -2.69 V | | Mg2+ + 2 e- <----> Mg |  |  | *E*o*red* = -2.375 V |   [***Click here to check your answer to Practice Problem 12***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/problems/ex20_13a.html)  [***Click here to see a solution to Practice Problem 12***](https://chemed.chem.purdue.edu/genchem/topicreview/bp/ch20/problems/ex20_13s.html) |

**Practice Problems Electrochemistry**

1. What is the difference between an oxidation-reduction reaction and a half-reaction?

**Answer**

Oxidation-reductions reactions always have an electron transfer from the oxidized species to the reduced species. When the oxidized species is separated from the reduced species, a balanced reaction can be written for each process (oxidation or reduction) that is called a *half-reaction*. All half-reactions must have electrons either as reactants (for reduction half-reactions) or products (for oxidation half-reactions).

2. What is the function of the salt bridge in an electrochemical cell?

**Answer**

The salt bridge completes the electrical circuit between the anode and cathode half–;cells. An effective salt bridge conducts current using ions (from an ionic *salt*) and not electrons.

3. What is the criterion for spontaneous chemical change based on cell potentials? Explain.

**Answer**

Spontaneous reactions occur when the Gibb's Free Energy is negative. Cell potentials are proportional to the Gibb's Free Energy but with a sign change. Thus, a *positive* cell potential indicates a spontaneous chemical change.

4. Complete and balance the following half–equations, and indicate whether oxidation or reduction is involved.

(**a**) ClO2(*g*) → ClO3–(*aq*) (acidic solution)

(**b**) MnO4–(*aq*) → MnO2(*s*) (acidic solution)

(**c**) SbH3(*g*) → Sb(*s*) (basic solution)

**Answer**

(**a**) ClO2(*g*) + H2O(*l*) → ClO3–(*aq*) + 2 H+(*aq*) + e– Oxidation

(**b**) MnO4–(*aq*) + 4 H+(*aq*) + 3 e– → MnO2(*s*) + 2 H2O(*l*) Reduction

(**c**) SbH3(*g*) + 3 OH–(*aq*) → Sb(*s*) + 3 H2O(*l*) + 3 e– Oxidation

5. Balance the following redox equations in acidic solution.

(**a**) Fe2+(*aq*) + Cr2O72–(*aq*) → Fe3+(*aq*) + Cr3+(*aq*)

(**b**) S8(*s*) + O2(*g*) → SO42–(*aq*)

(**c**) Fe3+(*aq*) + NH2OH2+(*aq*) → Fe2+(*aq*) + N2O(*g*)

**Answer**

(**a**) Fe2+(*aq*) + Cr2O72–(*aq*) → Fe3+(*aq*) + Cr3+(*aq*)

Oxidation: Fe2+(*aq*) → Fe3+(*aq*) + e–

Reduction: Cr2O72–(*aq*) + 14 H+(*aq*) + 6 e– → 2 Cr3+(*aq*) + 7 H2O(*l*)

Net: 6 Fe2+(*aq*) + Cr2O72–(*aq*) + 14 H+(*aq*) → 6 Fe3+(*aq*) + 2 Cr3+(*aq*) + 7 H2O(*l*)

(**b**) S8(*s*) + O2(*g*) → SO42–(*aq*)

Oxidation: S8(*s*) + 32 H2O(*l*) → 8 SO42–(*aq*) + 64 H+(*aq*) + 48 e–

Reduction: O2(*g*) + 4 H+(*aq*) + 4 e– → 2 H2O(*l*)

Net: S8(*s*) + 12 O2(*g*) + 8 H2O(*l*) → 8 SO42–(*aq*) + 16 H+(*aq*)

(**c**) Fe3+(*aq*) + NH2OH2+(*aq*) → Fe2+(*aq*) + N2O(*g*)

Oxidation: 2 NH2OH2+(*aq*) → N2O(*g*) + H2O(*l*) + 6 H+(*aq*) + 4 e–

Reduction: Fe3+(*aq*) + e– → Fe2+(*aq*)

Net: 4 Fe3+(*aq*) + 2 NH2OH2+(*aq*) → 4 Fe2+(*aq*) + N2O(*g*) + H2O(*l*) + 6 H+(*aq*)

6. Balance the following equations in acidic solution.

(**a**) Ag(*s*) + NO3–(*aq*) → Ag+(*aq*) + NO(*g*)

(**b**) H2O2(*aq*) + MnO4–(*aq*) → Mn2+(*aq*) + O2(*g*)

(**c**) Cl2(*g*) + I–(*aq*) → Cl–(*aq*) + IO3–(*aq*)

**Answer**

(**a**) Ag(*s*) + NO3–(*aq*) → Ag+(*aq*) + NO(*g*)

Oxidation: Ag(*s*) → Ag+(*aq*) + e–

Reduction: NO3–(*aq*) + 4 H+(*aq*) + 3 e– → NO(*g*) + 2 H2O(*l*)

Net: 3 Ag(*s*) + NO3–(*aq*) + 4 H+(*aq*) → 3 Ag+(*aq*) + NO(*g*) + 2 H2O(*l*)

(**b**) H2O2(*aq*) + MnO4–(*aq*) → Mn2+(*aq*) + O2(*g*)

Oxidation: H2O2(*aq*) → O2(*g*) + 2 H+(*aq*) + 2 e–

Reduction: MnO4–(*aq*) + 8 H+(*aq*) + 5 e– → Mn2+(*aq*) + 4 H2O(*l*)

Net: 5 H2O2(*aq*) + 2 MnO4–(*aq*) + 6 H+(*aq*) → 2 Mn2+(*aq*) + 5 O2(*g*) + 8 H2O(*l*)

(**c**) Cl2(*g*) + I–(*aq*) → Cl–(*aq*) + IO3–(*aq*)

Oxidation: I–(*aq*) + 3 H2O(*l*) → IO3–(*aq*) + 6 H+(*aq*) + 6 e–

Reduction: Cl2(*g*) + 2 e– → 2 Cl–(*aq*)

Net: 3 Cl2(*g*) + I–(*aq*) + 3 H2O(*l*) → 6 Cl–(*aq*) + IO3–(*aq*) + 6 H+(*aq*)

7. Balance the following equations in basic solution.

(**a**) Fe(OH)2(*s*) + O2(*g*) → Fe(OH)3(*s*)

(**b**) S8(*s*) → S2O32–(*aq*) + S2–(*aq*)

(**c**) CrI3(*s*) + H2O2(*aq*) → CrO42–(*aq*) + IO4–(*aq*)

**Answer**

(**a**) Fe(OH)2(*s*) + O2(*g*) → Fe(OH)3(*s*)

Oxidation: Fe(OH)2(*s*) + H2O(*l*) → Fe(OH)3(*s*) + H+(*aq*) + e–

Reduction: O2(*g*) + 4 H+(*aq*) + 4 e– → 2 H2O(*l*)

Net in acid: 4 Fe(OH)2(*s*) + O2(*g*) + 2 H2O(*l*) → 4 Fe(OH)3(*s*)

Neutralization: None

Net in base: 4 Fe(OH)2(*s*) + O2(*g*) + 2 H2O(*l*) → 4 Fe(OH)3(*s*)

(**b**) S8(*s*) → S2O32–(*aq*) + S2–(*aq*)

Oxidation: S8(*s*) + 12 H2O(*l*) → 4 S2O32–(*aq*) + 24 H+(*aq*) + 16 e–

Reduction: S8(*s*) + 16 e– → 8 S2–(*aq*)

Net in acid: 2 S8(*s*) + 12 H2O(*l*) → 4 S2O32–(*aq*) + 8 S2–(*aq*) + 24 H+(*aq*)

Neutralization: 24 H+(*aq*) + 24 OH–(*aq*) → 24 H2O(*l*)

Net in base: 2 S8(*s*) + 24 OH–(*aq*) → 4 S2O32–(*aq*) + 8 S2–(*aq*) + 12 H2O(*l*)

(**c**) CrI3(*s*) + H2O2(*aq*) → CrO42–(*aq*) + IO4–(*aq*)

Oxidation: CrI3(*s*) + 16 H2O(*l*) → CrO42–(*aq*) + 3 IO4–(*aq*) + 32 H+(*aq*) + 27 e–

Reduction: H2O2(*aq*) + 2 H+(*aq*) + 2 e– → 2 H2O(*l*)

Net in acid: 2 CrI3(*s*) + 27 H2O2(*aq*) → 2 CrO42–(*aq*) + 6 IO4–(*aq*) + 10 H+(*aq*) + 22 H2O(*l*)

Neutralization: 10 H+(*aq*) + 10 OH–(*aq*) → 10 H2O(*l*)

Net in base: 2 CrI3(*s*) + 27 H2O2(*aq*) + 10 OH–(*aq*) → 2 CrO42–(*aq*) + 6 IO4–(*aq*) + 32 H2O(*l*)

8. Balance the following equations in basic solution.

(**a**) CrO42–(*aq*) + AsH3(*g*) → Cr(OH)3(*s*) + As(*s*)

(**b**) CH3OH(*aq*) + MnO4–(*aq*) → HCOO–(*aq*) + MnO2(*s*)

(**c**) [Fe(CN)6]3–(*aq*) + N2H4(*aq*) → [Fe(CN)6]4–(*aq*) + N2(*g*)

**Answer**

(**a**) CrO42–(*aq*) + AsH3(*g*) → Cr(OH)3(*s*) + As(*s*)

Oxidation: AsH3(*g*) → As(*s*) + 3 H+(*aq*) + 3 e–

Reduction: CrO42–(*aq*) + 5 H+(*aq*) + 3 e– → Cr(OH)3(*s*) + H2O(*l*)

Net in acid: CrO42–(*aq*) + AsH3(*g*) + 2 H+(*aq*) → Cr(OH)3(*s*) + As(*s*) + H2O(*l*)

Neutralization: 2 H2O(*l*) → 2 H+(*aq*) + 2 OH–(*aq*)

Net in base: CrO42–(*aq*) + AsH3(*g*) + H2O(*l*) → Cr(OH)3(*s*) + As(*s*) + 2 OH–(*aq*)

(**b**) CH3OH(*aq*) + MnO4–(*aq*) → HCOO–(*aq*) + MnO2(*s*)

Oxidation: CH3OH(*aq*) + H2O(*l*) → HCOO–(*aq*) + 5 H+(*aq*) + 4 e–

Reduction: MnO4–(*aq*) + 4 H+(*aq*) + 3 e– → MnO2(*s*) + 2 H2O(*l*)

Net in acid: 3 CH3OH(*aq*) + 4 MnO4–(*aq*) + H+(*aq*) → 3 HCOO–(*aq*) + 4 MnO2(*s*) + 5 H2O(*l*)

Neutralization: H2O(*l*) → H+(*aq*) + OH–(*aq*)

Net in base: 3 CH3OH(*aq*) + 4 MnO4–(*aq*) → 3 HCOO–(*aq*) + 4 MnO2(*s*) + 4 H2O(*l*) + OH–(*aq*)

(**c**) [Fe(CN)6]3–(*aq*) + N2H4(*aq*) → [Fe(CN)6]4–(*aq*) + N2(*g*)

Oxidation: N2H4(*aq*) → N2(*g*) + 4 H+(*aq*) + 4 e–

Reduction: [Fe(CN)6]3–(*aq*) + e– → [Fe(CN)6]4–(*aq*)

Net in acid: 4 [Fe(CN)6]3–(*aq*) + N2H4(*aq*) → 4 [Fe(CN)6]4–(*aq*) + N2(*g*) + 4 H+(*aq*)

Neutralization: 4 H+(*aq*) + 4 OH–(*aq*) → 4 H2O(*l*)

Net in base: 4 [Fe(CN)6]3–(*aq*) + N2H4(*aq*) + 4 OH–(*aq*) → 4 [Fe(CN)6]4–(*aq*) + N2(*g*) + 4 H2O(*l*)

9. Write balanced equations for

(**a**) the reaction of oxalic acid (HOOCCOOH) and permanganate ion in acid solution to produce manganese(II) ion and carbon dioxide gas

(**b**) the reaction of Cr2O72– and UO2+ to produce UO22+ and Cr3+ in an acidic aqueous environment

(**c**) the reaction in basic solution of nitrate ion and zinc to produce zinc(II) ion and gaseous ammonia.

**Answer**

(**a**) the reaction of oxalic acid (HOOCCOOH) and permanganate ion in acid solution to produce manganese(II) ion and carbon dioxide gas

Oxidation: HOOCCOOH(*aq*) → 2 CO2(*g*) + 2 H+(*aq*) + 2 e–

Reduction: MnO4–(*aq*) + 8 H+(*aq*) + 5 e– → Mn2+(*aq*) + 4 H2O(*l*)

Net: 5 HOOCCOOH(*aq*) + 2 MnO4–(*aq*) + 6 H+(*aq*) → 10 CO2(*g*) + 2 Mn2+(*aq*) + 8 H2O(*l*)

(**b**) the reaction of Cr2O72– and UO2+ to produce UO22+ and Cr3+ in an acidic aqueous environment

Oxidation: UO2+(*aq*) + H2O(*l*) → UO22+(*aq*) + 2 H+(*aq*) + 2 e–

Reduction: Cr2O72–(*aq*) + 14 H+(*aq*) + 6 e– → 2 Cr3+(*aq*) + 7 H2O(*l*)

Net: Cr2O72–(*aq*) + 3 UO2+(*aq*) + 8 H+(*aq*) → 2 Cr3+(*aq*) + 3 UO22+(*aq*) + 4 H2O(*l*)

(**c**) the reaction in basic solution of nitrate ion and zinc to produce zinc(II) ion and gaseous ammonia.

Oxidation: Zn(*s*) → Zn2+(*aq*) + 2 e–

Reduction: NO3–(*aq*) + 9 H+(*aq*) + 8 e– → NH3(*aq*) + 3 H2O(*l*)

Net in acid: 4 Zn(*s*) + NO3–(*aq*) + 9 H+(*aq*) → 4 Zn2+(*aq*) + NH3(*aq*) + 3 H2O(*l*)

Neutralization: 9 H2O(*l*) → 9 H+(*aq*) + 9 OH–(*aq*)

Net in base: 4 Zn(*s*) + NO3–(*aq*) + 6 H2O(*l*) → 4 Zn2+(*aq*) + NH3(*aq*) + 9 OH–(*aq*)

10. For the reaction

2 CuI(*s*) + Cd(*s*) → Cd2+(*aq*) + 2 I–(*aq*) + 2 Cu(*s*) E°cell = +0.23 V

given that E°Cd2+/Cd = –0.403 V, determine E° for the half–reaction

2 CuI(*s*) + 2 e– → 2 Cu(*s*) + 2 I–(*aq*)

**Answer**

The two half–reactions for the cell are:

2 CuI(*s*) + 2 e– → 2 Cu(*s*) + 2 I–(*aq*) E°reduction = ?

Cd(*s*) → Cd2+(*aq*) + 2 e– E°oxidation = –E°reduction = –(–0.403) = +0.403 V

For the net cell, E°cell = E°reduction + E°oxidation = +0.23 V

Substituting, +0.23 = E°reduction + 0.403

E°reduction = –0.17 V

11. E°cell = 1.47 V for the voltaic cell

V(*s*) | V2+(1 M) || Cu2+(1 M) | Cu(*s*)

Determine the value of E°V2+//V.

**Answer**

The cell is set up at standard conditions so the question can be answered using standard potentials.

The anode reaction is:

V(*s*) → V2+(*aq*) + 2 e–

with E°oxidation = – E°anode being the unknown potential.

The cathode reaction is:

Cu2+(*aq*) + 2 e– → Cu(*s*)

with E°reduction = E°cathode = +0.340 V from the [Table of Standard Reduction Potentials](https://www.chm.uri.edu/weuler/chm112/refmater/redpottable.html).

The net reaction is:

V(*s*) + Cu2+(*aq*) → V2+(*aq*) + Cu(*s*)

with a cell potential = E°cell = E°reduction + E°oxidation = E°cathode – E°anode

E°cell = +0.340 V – E°anode = +1.47 V

E°anode = E°V2+/V = 0.340 – 1.47 = –1.13 V

12. Write equations for the half–reactions and the overall cell reaction, and calculate E°cell for each of the voltaic cells diagrammed below.

(**a**) Pt | I2(*s*) | I–(*aq*) || Cl–(*aq*) | Cl2(*g*) | Pt

(**b**) Pt | PbO2(*s*) | Pb2+(*aq*), H+(*aq*) || S2O82–(*aq*),SO42–(*aq*) | Pt

**Answer**

Split each cell into it's half–;reactions, find the potential for the half–reaction from the [Table of Standard Reduction Potentials](https://www.chm.uri.edu/weuler/chm112/refmater/redpottable.html), then use these to find the cell voltage.

(**a**) Pt | I2(*s*) | I–(*aq*) || Cl–(*aq*) | Cl2(*g*) | Pt

Anode (oxidation) reaction: 2 I–(*aq*) → I2(*s*) + 2 e–

E°oxidation = –E°reduction =–(0.535) = –0.535 V

Cathode (reduction) reaction: Cl2(*g*) + 2 e– → 2 Cl–(*aq*)

E°reduction = +1.358 V

Overall cell reaction: Cl2(*g*) + 2 I–(*aq*) → I2(*s*) + 2 Cl–(*aq*)

E°cell = E°oxidation + E°reduction = –0.535 + 1.358 = +0.823 V

(**b**) Pt | PbO2(*s*) | Pb2+(*aq*), H+(*aq*) || S2O82–(*aq*),SO42–(*aq*) | Pt

Anode (oxidation) reaction: Pb2+(*aq*) + 2 H2O(*l*) → PbO2(*s*) + 4 H+(*aq*) + 2 e–

E°oxidation = –E°reduction =–(1.455) = –1.455 V

Cathode (reduction) reaction: S2O82–(*aq*) + 2 e– → 2 SO42–(*aq*)

E°reduction = +2.01 V

Overall cell reaction: Pb2+(*aq*) + 2 H2O(*l*) + S2O82–(*aq*) → PbO2(*s*) + 4 H+(*aq*) + 2 SO42–(*aq*)

E°cell = E°oxidation + E°reduction = –1.455 + 2.01 = +0.56 V

13. Predict whether a spontaneous reaction will occur in the forward direction in each of the following. Assume that all reactants and products are in their standard states.

(**a**) Sn(*s*) + Co2+(*aq*) → Sn2+(*aq*) + Co(*s*)

(**b**) 6 Br–(*aq*) + Cr2O72–(*aq*) + 14 H+(*aq*) → 2 Cr3+(*aq*) + 7 H2O(*l*) + 3 Br2(*l*)

**Answer**

(**a**) Sn(*s*) + Co2+(*aq*) → Sn2+(*aq*) + Co(*s*)

Sn(*s*) → Sn2+(*aq*) + 2 e–  E°oxidation = +0.137 V

Co2+(*aq*) + 2 e– → Co(*s*)  E°reduction = –0.277 V

E°cell = +0.137 + –0.277 = –0.140 V < 0, therefore nonspontaneous.

(**b**) 6 Br–(*aq*) + Cr2O72–(*aq*) + 14 H+(*aq*) → 2 Cr3+(*aq*) + 7 H2O(*l*) + 3 Br2(*l*)

2 Br–(*aq*) → Br2(*l*) + 2 e–  E°oxidation = –1.065 V

Cr2O72–(*aq*) + 14 H+(*aq*) + 6 e– → 2 Cr3+(*aq*) + 7 H2O(*l*)  E°reduction = +1.33 V

E°cell = –1.065 + 1.33 = +0.27 V > 0, therefore spontaneous.

14. Rhodium is a rare metal used as a catalyst. The metal does not react with HCl(*aq*), but it does react with HNO3(*aq*), producing Rh3+(*aq*) and NO(*g*). Copper will displace Rh3+ from aqueous solution, but silver will not. Estimate a value of E°Rh3+/Rh.

**Answer**

Consider the potentials for the reactions described:

(**1**)

Rh(*s*) + HCl(*aq*) → NR  E°cell < 0

E°cell = E°oxidation + E°reduction = – E°Rh3+/Rh + E°H+/H2 < 0

Since 2 H+(*aq*) + 2 e– → H2(*g*)  E°reduction = 0.00 V, then E°Rh3+/Rh > 0 V.

(**2**)

Rh(*s*) + HNO3(*aq*) + 3 H+(*aq*) → Rh3+(*aq*) + NO(*g*) + 2 H2O(*l*)  E°cell > 0

E°cell = E°oxidation + E°reduction = – E°Rh3+/Rh + E°HNO3/NO > 0

Since HNO3(*aq*) + 3 H+(*aq*) + 3 e– → NO(*g*) + 2 H2O(*l*)

E°reduction = 0.956 V, then E°Rh3+/Rh < 0.956 V.

(**3**)

Rh3+(*aq*) + Cu(*s*) → Rh(*s*) + Cu2+(*aq*) E°cell > 0.

E°cell = E°oxidation + E°reduction = E°Rh3+/Rh + –E°Cu2+/Cu > 0

Since Cu(*s*) → Cu2+(*aq*) + 2 e–  E°oxidation = –0.340 V, then E°Rh3+/Rh > 0.340 V.

(**4**)

Rh3+(*aq*) + Ag(*s*) → NR  E°cell < 0.

E°cell = E°oxidation + E°reduction = E°Rh3+/Rh + –E°Ag+/Ag < 0

Since Ag(*s*) → Ag+(*aq*) + e–  E°oxidation = –0.800 V, then E°Rh3+/Rh < 0.800 V.

Net conclusion:

0.340 V < E°Rh3+/Rh < 0.800 V

15. Determine the values of E°cell and ΔG° for the following reactions.

(**a**) O2(*g*) + 4 I–(*aq*) + 4 H+(*aq*) → 2 H2O(*l*) + 2 I2(*s*)

(**b**) Cr2O72–(*aq*) + 3 Cu(*s*) + 14 H+(*aq*) → 2 Cr3+(*aq*) + 3 Cu2+(*aq*) + 7 H2O(*l*)

**Answer**

(**a**) O2(*g*) + 4 I–(*aq*) + 4 H+(*aq*) → 2 H2O(*l*) + 2 I2(*s*)

Reduction: O2(*g*) + 4 H+(*aq*) + 4 e– → 2 H2O(*l*)     E°red = +1.229 V

Oxidation: 4 I–(*aq*) → 2 I2(*s*) + 4 e–    E°ox = –0.535 V

E°cell = +1.229 + –0.535 = +0.694 V

ΔG° = –nFE° = –(4)(96485)(0.694) = –26800 J = –26.8 kJ

(**b**) Cr2O72–(*aq*) + 3 Cu(*s*) + 14 H+(*aq*) → 2 Cr3+(*aq*) + 3 Cu2+(*aq*) + 7 H2O(*l*)

Reduction: Cr2O72–(*aq*) + 14 H+(*aq*) + 6 e– → 2 Cr3+(*aq*) + 7 H2O(*l*)    E°red = +1.33 V

Oxidation: Cu(*s*) → Cu2+(*aq*) + 2 e–    E°ox = –0.340 V

E°cell = +1.33 + –0.340 = +0.99 V

ΔG° = –nFE° = –(6)(96485)(0.99) = –570000 J = –570 kJ

16. Determine the values of E°cell and ΔG° for the following reactions.

(**a**) Al(*s*) + 3 Ag+(*aq*) → Al3+(*aq*) + 3 Ag(*s*)

(**b**) 4 IO3–(*aq*) + 4 H+(*aq*) → 2 I2(*s*) + 2 H2O(*l*) + 5 O2(*g*)

**Answer**

(**a**) Al(*s*) + 3 Ag+(*aq*) → Al3+(*aq*) + 3 Ag(*s*)

Al(*s*) → Al3+(*aq*) + 3 e–  E°oxidation = +1.676 V

Ag+(*aq*) + e– → Ag(*s*)  E°reduction = +0.800 V

E°cell = E°oxidation + E°reduction = 1.676 + 0.800 = 2.476 V

ΔG° = –nFE°cell = –(3)(96485)(2.476) = –716700 J = –716.7 kJ

(**b**) 4 IO3–(*aq*) + 4 H+(*aq*) → 2 I2(*s*) + 2 H2O(*l*) + 5 O2(*g*)

2 H2O(*l*) → O2(*g*) + 4 H+(*aq*) + 4 e–  E°oxidation = –1.229 V

2 IO3–(*aq*) + 12 H+(*aq*) + 10 e– → I2(*s*) + 6 H2O(*l*)   E°reduction = +1.20 V

E°cell = E°oxidation + E°reduction = –1.229 + 1.20 = –0.03 V

ΔG° = –nFE°cell = –(20)(96485)(–0.03) = +60000 J = +60 kJ

17. Write the equilibrium constant expression for each of the following reactions, and determine the numerical value of Keq at 25 °C.

**(a)** PbO2(*s*) + 4 H+(*aq*) + 2 Cl–(*aq*) → ← Pb2+(*aq*) + 2 H2O(*l*) + Cl2(*g*)

**(b)** 3 O2(*g*) + 2 Br–(*aq*) → ← 2 BrO3–(*aq*) (basic solution)

**Answer**

**(a)** PbO2(*s*) + 4 H+(*aq*) + 2 Cl–(*aq*) → ← Pb2+(*aq*) + 2 H2O(*l*) + Cl2(*g*)

The reaction is already balanced so the mass action expression for the equilibirum constant is easily found by inspection. Since a thermodynamic equilibrium constant is required, aqueous components are given as concentrations and gases are given as partial pressures (pure liquids and pure solids are ignored):

Keq = [Pb2+]ePCl2e/ [H+]e4[Cl–]e2

To find the value of this equilibrium constant, use the [Table of Standard Reduction Potentials](https://www.chm.uri.edu/weuler/chm112/refmater/redpottable.html) to find the cell potential and then use this value to find the equilibrium constant.

PbO2(*s*) + 4 H+(*aq*) + 2 e– → Pb2+(*aq*) + 2 H2O(*l*)E°red = 1.455 V

2 Cl–(*aq*) → Cl2(*g*) + 2 e–E°ox = –1.358 V

E°cell = 1.455 – 1.358 = 0.097 V

Keq = exp(nFE°cell/RT)

Keq = exp[(2)(96485)(0.097)/(8.314)(298)] = 1900

**(b)** 3 O2(*g*) + 2 Br–(*aq*) → ← 2 BrO3–(*aq*) (basic solution)

The reaction is already balanced so the mass action expression for the equilibirum constant is easily found by inspection. Since a thermodynamic equilibrium constant is required, aqueous components are given as concentrations and gases are given as partial pressures (pure liquids and pure solids are ignored):

Keq = [BrO3–]e2/ [Br–]e2PO2e3

To find the value of this equilibrium constant, use the [Table of Standard Reduction Potentials](https://www.chm.uri.edu/weuler/chm112/refmater/redpottable.html) to find the cell potential and then use this value to find the equilibrium constant.

O2(*g*) + 2 H2O(*l*) + 4 e– → 4 OH–(*aq*)E°red = 0.401 V

Br–(*aq*) + 6 OH–(*aq*) → BrO3–(*aq*) + 3 H2O(*l*) + 6 e–E°ox = –0.584 V

E°cell = 0.401 – 0.584 = –0.183 V

Keq = exp(nFE°cell/RT)

Keq = exp[(12)(96485)(–0.183)/(8.314)(298)] = 7×10–38

18. Write the equilibrium constant expression for each of the following reactions, and determine the numerical value of Keq at 25 °C.

**(a)** Ag+(*aq*) + Fe2+(*aq*) → ← Fe3+(*aq*) + Ag(*s*)

**(b)** MnO2(*s*) + 4 H+(*aq*) + 2 Cl–(*aq*) → ← Mn2+(*aq*) + 2 H2O(*l*) + Cl2(*g*)

**(c)** 2 OCl–(*aq*) → ← 2 Cl–(*aq*) + O2(*g*) (basic solution)

**Answer**

**(a)** Ag+(*aq*) + Fe2+(*aq*) → ← Fe3+(*aq*) + Ag(*s*)

Keq = [Fe3+]e/[Ag+]e[Fe2+]e

Ag+(*aq*) + e–→Ag(*s*)E°red = 0.800 V

Fe2+(*aq*)→ Fe3+(*aq*) + e–E°ox = –0.771 V

E°cell = 0.800 – 0.771 = 0.029 V

Keq = exp(nFE°cell/RT)

Keq = exp[(1)(96485)(0.029)/(8.314)(298)] = 3.1

**(b)** MnO2(*s*) + 4 H+(*aq*) + 2 Cl–(*aq*) → ← Mn2+(*aq*) + 2 H2O(*l*) + Cl2(*g*)

Keq = [Mn2+]ePCl2e/ [H+]e4[Cl–]e2

MnO2(*s*) + 4 H+(*aq*) + 2 e–→Mn2+(*aq*) + 2 H2O(*l*)E°red = 1.23 V

2 Cl–(*aq*) → Cl2(*g*) + 2 e–E°ox = –1.358 V

E°cell = 1.23 –1.358 = –0.13 V

Keq = exp(nFE°cell/RT)

Keq = exp[(2)(96485)(–0.13)/(8.314)(298)] = 4×10–5

**(c)** 2 OCl–(*aq*) → ← 2 Cl–(*aq*) + O2(*g*) (basic solution)

Keq = [Cl–]e2PO2e/ [OCl–]e2

OCl–(*aq*) + H2O(*l*) + 2 e–→Cl–(*aq*) + 2 OH–(*aq*)E°red = 0.890 V

4 OH–(*aq*)→ O2(*g*) + 2 H2O(*l*) + 4 e–E°ox = –0.401 V

E°cell = 0.890 –0.401 = 0.489 V

Keq = exp(nFE°cell/RT)

Keq = exp[(4)(96485)(0.489)/(8.314)(298)] = 1×1033

19. What is the value of Ecell of each of the following reactions when carried out in a voltaic cell?

(**a**) Fe(*s*) + 2 Ag+(*aq*, 0.0015 M) → Fe2+(*aq*, 1.33 M) + 2 Ag(*s*)

(**b**) 4 VO2+(*aq*, 0.050 M) + O2(*g*, 0.25 atm) + 2 H2O(*l*) → 4 VO2+(*aq*, 0.75 M) + 4 H+(*aq*, 0.30 M)

**Answer**

Assume 25 °C = 298 K

(**a**) Fe(*s*) + 2 Ag+(*aq*, 0.0015 M) → Fe2+(*aq*, 1.33 M) + 2 Ag(*s*)

Fe(*s*) → Fe2+(*aq*) + 2 e–    E°ox = +0.440 V

Ag+(*aq*) + e– → Ag(*s*)    E°red = +0.800 V

E°cell = E°ox + E°red = 0.440 + 0.800 = 1.240 V

Use the Nernst equation: Ecell = E°cell – (RT/nF)ln([Fe3+]/[Ag+]2) = 1.240 – (8.314×298/2×96485)ln(1.33/(0.0015)2) = +1.069 V

(**b**) 4 VO2+(*aq*, 0.050 M) + O2(*g*, 0.25 atm) + 2 H2O(*l*) → 4 VO2+(*aq*, 0.75 M) + 4 H+(*aq*, 0.30 M)

VO2+(*aq*) + H2O(*l*) → VO2+(*aq*) + 2 H+(*aq*) + e–    E°ox = –1.000 V

O2(*g*) + 4 H+(*aq*) + 4 e– → 2 H2O(*l*)    E°red = +1.229 V

E°cell = E°ox + E°red = –1.000 + 1.229 = 0.229 V

Use the Nernst equation: Ecell = E°cell – (RT/nF)ln([VO2+]4[H+]4/ [VO2+]4)PO2

Ecell = 0.229 – (8.314×298/4×96485)ln((0.75)4(0.30)4/(0.050)4)(0.25) = +0.181 V

20. What is Ecell for the voltaic cell diagrammed below?

Pt | H2(*g*, 1 atm) | 0.0025 M HCl || H+ (1 M) | H2(*g*, 1 atm) | Pt

**Answer**

Anode (oxidation) reaction: H2(*g*) → 2 H+(*aq*) + 2 e–    E°ox = 0.000 V

Cathode (reduction) reaction: 2 H+(*aq*) + 2 e– → H2(*g*)    E°red = 0.000 V

Net reaction: 2 H+(*aq*) + H2(*g*) → 2 H+(*aq*) + H2(*g*)    E°cell = 0.000 V

Ecell = E°cell – (RT/nF)ln([H+]2anodePH2cathode)/ [H+]2cathodePH2anode)

Ecell = 0.000 – (8.314×298/2×96485)ln((0.0025)2(1)/(1)2(1))

Ecell = +0.15 V

21. How many coulombs of electric charge are required to deposit 25.0 g of Cu(*s*) at the cathode in the electrolysis of CuSO4(*aq*)?

**Answer**

25.0 g Cu(*s*) = 25.0/63.5 g/mol = 0.394 mol

Cu2+(*aq*) + 2 e– → Cu(*s*)

so 0.394 mol Cu requires 2×0.394 = 0.788 mol electrons

coulombs = mols electrons × Faraday's constant = 0.788 × 96485 = 7.60×104 coulombs.

22. Balance the following redox equations.

(**a**) B2Cl4(*aq*) + OH–(*aq*) → BO2–(*aq*) + Cl–(*aq*) + H2O(*l*) + H2(*g*)

(**b**) CH3CH2ONO2(*aq*) + Sn(*s*) + H+(*aq*) → CH3CH2OH(*aq*) + NH2OH(*aq*) + Sn2+(*aq*) + H2O(*l*)

(**c**) F5SeOF(*aq*) + OH–(*aq*) → SeO42–(*aq*) + F–(*aq*) + H2O(*l*) + O2(*g*)

(**d**) As2S3(*s*) + OH–(*aq*) + H2O2(*aq*) → AsO43–(*aq*) + SO42–(*aq*) + H2O(*l*)

(**e**) XeF6(*s*) + OH–(*aq*) → XeO64–(*aq*) + F–(*aq*) + H2O(*l*) + Xe(*g*) + O2(*g*)

**Answer**

(**a**) B2Cl4(*aq*) + OH–(*aq*) → BO2–(*aq*) + Cl–(*aq*) + H2O(*l*) + H2(*g*)

Oxidation: B2Cl4(*aq*) + 4 H2O(*l*) → 2 BO2–(*aq*) + 4 Cl–(*aq*) + 8 H+(*aq*) + 2 e–

Reduction: OH–(*aq*) + 3 H+(*aq*) + 2 e– → H2O(*l*) + H2(*g*)

Net in acid: B2Cl4(*aq*) + OH–(*aq*) + 3 H2O(*l*) → 2 BO2–(*aq*) + 4 Cl–(*aq*) + 5 H+(*aq*) + H2(*g*)

Neutralization: 5 H+(*aq*) + 5 OH–(*aq*) → 5 H2O(*l*)

Net in base: B2Cl4(*aq*) + 6 OH–(*aq*) → 2 BO2–(*aq*) + 4 Cl–(*aq*) + 2 H2O(*l*) + H2(*g*)

(**b**) CH3CH2ONO2(*aq*) + Sn(*s*) + H+(*aq*) → CH3CH2OH(*aq*) + NH2OH(*aq*) + Sn2+(*aq*) + H2O(*l*)

Oxidation: Sn(*s*) → Sn2+(*aq*) + 2 e–

Reduction: CH3CH2ONO2(*aq*) + 6 H+(*aq*) + 6 e– → CH3CH2OH(*aq*) + NH2OH(*aq*) + H2O(*l*)

Net in acid: CH3CH2ONO2(*aq*) + 3 Sn(*s*) + 6 H+(*aq*) → CH3CH2OH(*aq*) + NH2OH(*aq*) + 3 Sn2+(*aq*) + H2O(*l*)

(**c**) F5SeOF(*aq*) + OH–(*aq*) → SeO42–(*aq*) + F–(*aq*) + H2O(*l*) + O2(*g*)

Oxidation: OH–(*aq*) + H2O(*l*) → O2(*g*) + 3 H+(*aq*) + 4 e–

Reduction: F5SeOF(*aq*) + 3 H2O(*l*) + 2 e– → SeO42–(*aq*) + 6 F–(*aq*) + 6 H+(*aq*)

Net in acid: 2 F5SeOF(*aq*) + OH–(*aq*) + 7 H2O(*l*) → 2 SeO42–(*aq*) + 12 F–(*aq*) + O2(*g*) + 15 H+(*aq*)

Neutralization: 15 H+(*aq*) + 15 OH–(*aq*) → 15 H2O(*l*)

Net in base: 2 F5SeOF(*aq*) + 16 OH–(*aq*) → 2 SeO42–(*aq*) + 12 F–(*aq*) + 8 H2O(*l*) + O2(*g*)

(**d**) As2S3(*s*) + OH–(*aq*) + H2O2(*aq*) → AsO43–(*aq*) + SO42–(*aq*) + H2O(*l*)

Oxidation: As2S3(*s*) + 20 H2O(*l*) → 2 AsO43–(*aq*) + 3 SO42–(*aq*) + 40 H+(*aq*) + 28 e–

Reduction: H2O2(*aq*) + 2 H+(*aq*) + 2 e– → 2 H2O(*l*)

Net in acid: As2S3(*s*) + 14 H2O2(*aq*) → 2 AsO43–(*aq*) + 3 SO42–(*aq*) + 12 H+(*aq*) + 8 H2O(*l*)

Neutralization: 12 H+(*aq*) + 12 OH–(*aq*) → 12 H2O(*l*)

Net in base: As2S3(*s*) + 12 OH–(*aq*) + 14 H2O2(*aq*) → 2 AsO43–(*aq*) + 3 SO42–(*aq*) + 20 H2O(*l*)

(**e**) XeF6(*s*) + OH–(*aq*) → XeO64–(*aq*) + F–(*aq*) + H2O(*l*) + Xe(*g*) + O2(*g*)

Oxidation: OH–(*aq*) + H2O(*l*) → O2(*g*) + 3 H+(*aq*) + 4 e–

Reduction: 2 XeF6(*s*) + 6 H2O(*l*) + 4 e– → XeO64–(*aq*) + 12 F–(*aq*) + Xe(*g*) + 12 H+(*aq*)

Net in acid: 2 XeF6(*s*) + OH–(*aq*) + 7 H2O(*l*) → XeO64–(*aq*) + 12 F–(*aq*) + Xe(*g*) + O2(*g*) + 15 H+(*aq*)

Neutralization: 15 H+(*aq*) + 15 OH–(*aq*) → 15 H2O(*l*)

Net in base: 2 XeF6(*s*) + 16 OH–(*aq*) → XeO64–(*aq*) + 12 F–(*aq*) + 8 H2O(*l*) + Xe(*g*) + O2(*g*)