

Lecture – 6 Electrochemistry

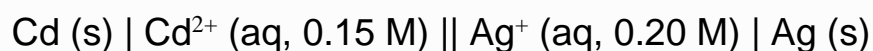
Cell Notation Rules:

1. The anode half-cell is described first; the cathode half-cell follows. Within a given half-cell, the **reactants** are specified first and the **products** last. The description of the oxidation reaction is first, and the reduction reaction is last; when you read it, your eyes move in the direction of electron flow. **Spectator ions** are not included.

2. A single vertical line (|) is drawn between two chemical species that are in different phases but in physical contact with each other (e.g., solid electrode | liquid with **electrolyte**). A double vertical line (||) represents a salt bridge or porous membrane separating the individual half-cells.

3. The phase of each chemical (s, l, g, aq) is shown in parentheses. If the electrolytes in the cells are not at standard conditions, concentrations and/or pressure, they are included in parentheses with the phase notation. If no concentration or pressure is noted, the electrolytes in the cells are assumed to be at standard conditions (1.00 M or 1.00 atm and 298 K).

Using these rules, the notation for the cell we put together is:



The cell potential E_{cell} is related to the free energy of the reaction ΔG by

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

If the reactants and products are in their standard states, the resulting cell potential is called the standard cell potential.

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} = -RT \ln K_{\text{eq}}$$

The Relationship between Cell Potential and the Equilibrium Constant

We can use the relationship between ΔG° and the equilibrium constant K , to obtain a relationship between E_{cell}° and K . Recall that for a general reaction of the type $aA + bB \rightarrow cC + dD$, the standard free-energy change and the equilibrium constant are related by the following equation:

$$\Delta G^{\circ} = -RT \ln K \quad (20.3.17)$$

Given the relationship between the standard free-energy change and the standard cell potential (Equation $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$), we can write

$$- n F E^{\circ}_{\text{cell}} = - R T \ln K \quad (20.3.18)$$

Rearranging this equation,

$$E^{\circ}_{\text{cell}} = \left(\frac{RT}{nF} \right) \ln K \quad (20.3.19)$$

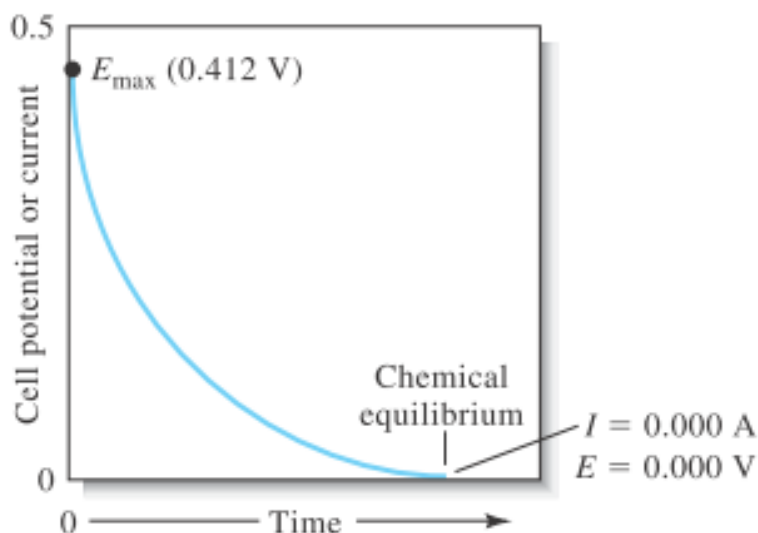
For T = 298 K, Equation 20.3.19 can be simplified as follows:

$$E^{\circ}_{\text{cell}} = \left(\frac{RT}{nF} \right) \ln K = \left[\frac{[8.314 \text{ J}/(\text{mol} \cdot \text{K})(298 \text{ K})]}{n[96,486 \text{ J}/(\text{V} \cdot \text{mol})]} \right] 2.303 \log K = \left(\frac{0.0591 \text{ V}}{n} \right) \log K \quad (20.3.20)$$

Thus E°_{cell} is directly proportional to the logarithm of the equilibrium constant. This means that large equilibrium constants correspond to large positive values of E°_{cell} and vice versa.

Discharging a Galvanic Cell

Cell potential in the galvanic cell as a function of time. The cell current, which is directly related to the cell potential, also decreases with the same time behavior.



The Standard Hydrogen Reference Electrode (SHE)

Although it is impossible to measure the potential of any electrode directly, we can choose a reference electrode whose potential is defined as 0 V under standard conditions. The **standard hydrogen electrode (SHE)** is universally used for this purpose and is assigned a standard potential of 0 V. It consists of a strip of platinum wire in contact with an aqueous solution containing 1 M H⁺. The [H⁺] in solution is in equilibrium with H₂ gas at a pressure of 1 atm at the Pt-solution interface (Figure 20.2.2). Protons are reduced or hydrogen molecules are oxidized at the Pt surface according to the following equation:



One especially attractive feature of the SHE is that the Pt metal electrode is not consumed during the reaction.

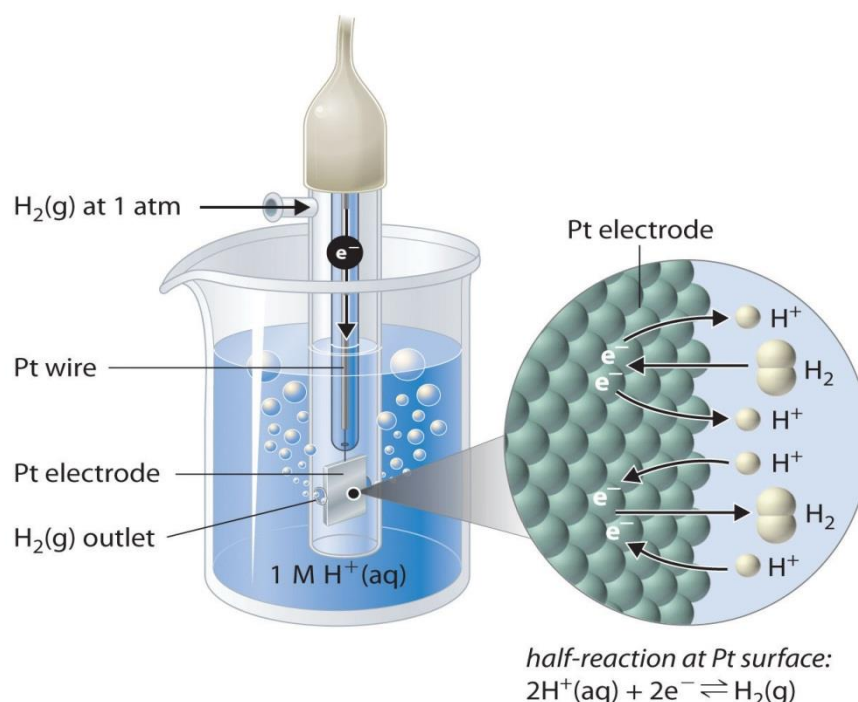
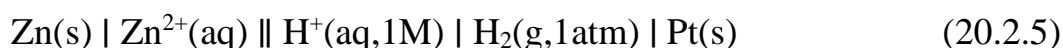
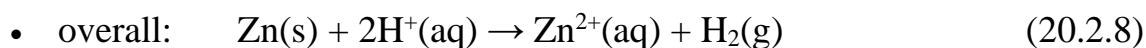
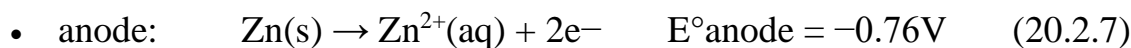
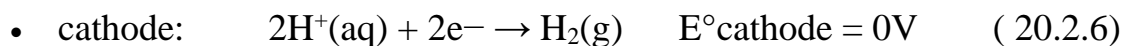


Figure 20.2.2: The Standard Hydrogen Electrode. The SHE consists of platinum wire that is connected to a Pt surface in contact with an aqueous solution containing 1 M H⁺ in equilibrium with H₂ gas at a pressure of 1 atm. In the molecular view, the Pt surface catalyzes the oxidation of hydrogen molecules to protons or the reduction of protons to hydrogen gas. (Water is omitted for clarity.) The standard potential of the SHE is arbitrarily assigned a value of 0 V.

Figure 20.2.3 shows a galvanic cell that consists of a SHE in one beaker and a Zn strip in another beaker containing a solution of Zn²⁺ ions. When the circuit is closed, the voltmeter indicates a potential of 0.76 V. The zinc electrode begins to dissolve to form Zn²⁺, and H⁺ ions are reduced to H₂ in the other compartment. Thus the hydrogen electrode is the cathode, and the zinc electrode is the anode. The diagram for this galvanic cell is as follows:



The half-reactions that actually occur in the cell and their corresponding electrode potentials are as follows:



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.76\text{V} \quad (20.2.9)$$

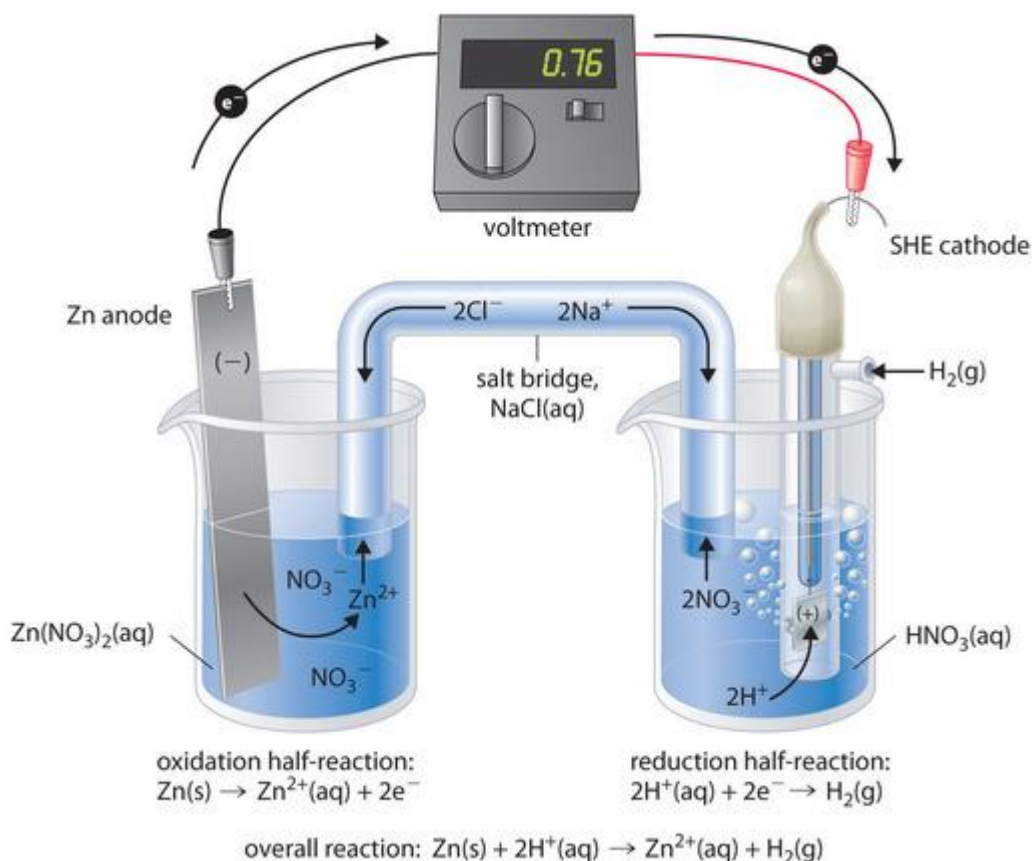


Figure 20.2.3: Determining a Standard Electrode Potential Using a Standard Hydrogen Electrode. The voltmeter shows that the standard cell potential of a galvanic cell consisting of a SHE and a Zn/Zn²⁺ couple is $E^\circ_{\text{cell}} = 0.76\text{V}$. Because the zinc electrode in this cell dissolves spontaneously to form Zn²⁺(aq) ions while H⁺(aq) ions are reduced to H₂ at the platinum surface, the standard electrode potential of the Zn²⁺/Zn couple is -0.76 V.

Although the reaction at the anode is an oxidation, by convention its tabulated E° value is reported as a reduction potential. The potential of a half-reaction measured against the SHE under standard conditions is called the **standard electrode potential** for that half-reaction. In this example, the

standard reduction potential for $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Zn}(\text{s})$ is reaction that occurs at the anode, the oxidation of Zn to Zn^{2+} , often called the Zn/Zn²⁺ redox couple, or the Zn/Zn²⁺ couple, is $-(-0.76 \text{ V}) = 0.76 \text{ V}$. We must therefore subtract E°_{anode} from $E^{\circ}_{\text{cathode}}$ to obtain

$$E^{\circ}_{\text{cell}}: 0 - (-0.76 \text{ V}) = 0.76 \text{ V}.$$

Because electrical potential is the energy needed to move a charged particle in an electric field, standard electrode potentials for half-reactions are intensive properties and do not depend on the amount of substance involved. Consequently, E° values are independent of the stoichiometric coefficients for the half-reaction, and, most important, the coefficients used to produce a balanced overall reaction do not affect the value of the cell potential.

Note: E° values do **NOT** depend on the stoichiometric coefficients for a half-reaction, because it is an *intensive* property.

Calculating Standard Cell Potentials

The standard cell potential for a redox reaction (E°_{cell}) is a measure of the tendency of reactants in their standard states to form products in their standard states; consequently, it is a measure of the driving force for the reaction, which earlier we called voltage. We can use the two standard electrode potentials we found earlier to calculate the standard potential for the Zn/Cu cell represented by the following cell diagram:



We know the values of E°_{anode} for the reduction of Zn^{2+} and $E^{\circ}_{\text{cathode}}$ for the reduction of Cu^{2+} , so we can calculate E°_{cell} :

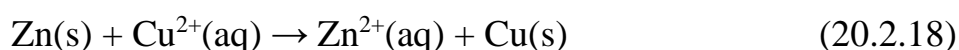
- cathode:



- anode:



overall:



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} = 1.10\text{V} \quad (20.2.19)$$

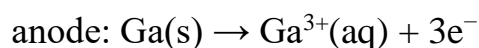
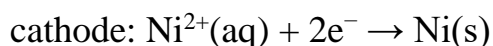
This is the same value that is observed experimentally. If the value of E°_{cell} is positive, the reaction will occur spontaneously as written. If the value of E°_{cell} is negative, then the reaction is not spontaneous, and it will not occur as written under standard conditions; it will, however, proceed spontaneously in the opposite direction. As we shall see, this does

not mean that the reaction cannot be made to occur at all under standard conditions. With a sufficient input of electrical energy, virtually any reaction can be forced to occur. Example 4 and its corresponding exercise illustrate how we can use measured cell potentials to calculate standard potentials for redox couples.

Note: A positive E°_{cell} means that the reaction will occur spontaneously as written. A negative E°_{cell} means that the reaction will proceed spontaneously in the opposite direction.

Example 20.2.2

A galvanic cell with a measured standard cell potential of 0.27 V is constructed using two beakers connected by a salt bridge. One beaker contains a strip of gallium metal immersed in a 1 M solution of GaCl_3 , and the other contains a piece of nickel immersed in a 1 M solution of NiCl_2 . The half-reactions that occur when the compartments are connected are as follows:



If the potential for the oxidation of Ga to Ga^{3+} is 0.55 V under standard conditions, what is the potential for the oxidation of Ni to Ni^{2+} ?

Given: galvanic cell, half-reactions, standard cell potential, and potential for the oxidation half-reaction under standard conditions

Asked for: standard electrode potential of reaction occurring at the cathode

Strategy:

- Write the equation for the half-reaction that occurs at the anode along with the value of the standard electrode potential for the half-reaction.
- Use Equation 20.2.2 to calculate the standard electrode potential for the half-reaction that occurs at the cathode. Then reverse the sign to obtain the potential for the corresponding oxidation half-reaction under standard conditions.

Solution:

A. We have been given the potential for the oxidation of Ga to Ga^{3+} under standard conditions, but to report the standard electrode potential, we must reverse the sign. For the reduction reaction $\text{Ga}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Ga}(\text{s})$, $E^\circ_{\text{anode}} = -0.55 \text{ V}$.

B. Using the value given for E°_{cell} and the calculated value of E°_{anode} , we can calculate the standard potential for the reduction of Ni^{2+} to Ni from Equation 20.2.2:

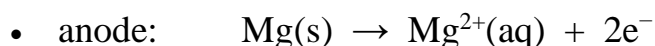
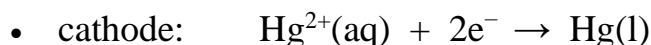
$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ 0.27 \text{ V} &= E^\circ_{\text{cathode}} - (-0.55 \text{ V}) \end{aligned}$$

$$E^{\circ}_{\text{cathode}} = -0.28 \text{ V}$$

This is the standard electrode potential for the reaction $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Ni}(\text{s})$. Because we are asked for the potential for the oxidation of Ni to Ni^{2+} under standard conditions, we must reverse the sign of $E^{\circ}_{\text{cathode}}$. Thus $E^{\circ} = -(-0.28 \text{ V}) = 0.28 \text{ V}$ for the oxidation. With three electrons consumed in the reduction and two produced in the oxidation, the overall reaction is not balanced. Recall, however, that standard potentials are independent of stoichiometry.

Exercise 20.2.2

A galvanic cell is constructed with one compartment that contains a mercury electrode immersed in a 1 M aqueous solution of mercuric acetate $\text{Hg}(\text{CH}_3\text{CO}_2)_2$ and one compartment that contains a strip of magnesium immersed in a 1 M aqueous solution of MgCl_2 . When the compartments are connected, a potential of 3.22 V is measured and the following half-reactions occur:



If the potential for the oxidation of Mg to Mg^{2+} is 2.37 V under standard conditions, what is the standard electrode potential for the reaction that occurs at the anode? **(Answer: 0.85 V)**

We can use this procedure described to measure the standard potentials for a wide variety of chemical substances, some of which are listed in Table P2. These data allow us to compare the oxidative and reductive strengths of a variety of substances. The half-reaction for the standard hydrogen electrode (SHE) lies more than halfway down the list in Table 20.2.1. All reactants that lie below the SHE in the table are stronger oxidants than H^{+} , and all those that lie above the SHE are weaker. The strongest oxidant in the table is F_2 , with a standard electrode potential of 2.87 V. This high value is consistent with the high electronegativity of fluorine and tells us that fluorine has a stronger tendency to accept electrons (it is a stronger oxidant) than any other element.

Table 20.2.1: Standard Potentials for Selected Reduction Half-Reactions at 25°C

Half-Reaction	E° (V)
$\text{Li}^{+}(\text{aq}) + \text{e}^{-} \rightleftharpoons \text{Li}(\text{s})$	-3.040
$\text{Be}^{2+}(\text{aq}) + 2\text{e}^{-} \rightleftharpoons \text{Be}(\text{s})$	-1.99

Table 20.2.1: Standard Potentials for Selected Reduction Half-Reactions at 25°C

Half-Reaction	E° (V)
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightleftharpoons \text{Al}(\text{s})$	-1.676
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$	-0.7618
$\text{Ag}_2\text{S}(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{Ag}(\text{s}) + \text{S}^{2-}(\text{aq})$	-0.71
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Fe}(\text{s})$	-0.44
$\text{Cr}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cr}^{2+}(\text{aq})$	-0.424
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cd}(\text{s})$	-0.4030
$\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightleftharpoons \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$	-0.356
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ni}(\text{s})$	-0.257
$2\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	-0.25
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Sn}(\text{s})$	-0.14
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$	0.00
$\text{Sn}^{4+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Sn}^{2+}(\text{aq})$	0.154
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Cu}^+(\text{aq})$	0.159
$\text{AgCl}(\text{s}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	0.2223
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$	0.3419
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightleftharpoons 4\text{OH}^-(\text{aq})$	0.401
$\text{H}_2\text{SO}_3(\text{aq}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightleftharpoons \text{S}(\text{s}) + 3\text{H}_2\text{O}(\text{l})$	0.45
$\text{I}_2(\text{s}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(\text{aq})$	0.5355
$\text{MnO}_4^{2-}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) + 2\text{e}^- \rightleftharpoons \text{MnO}_2(\text{s}) + 4\text{OH}^-(\text{aq})$	0.60
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2\text{O}_2(\text{aq})$	0.695
$\text{H}_2\text{SeO}_3(\text{aq}) + 4\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Se}(\text{s}) + 3\text{H}_2\text{O}(\text{l})$	0.74
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Fe}^{2+}(\text{aq})$	0.771
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$	0.7996
$\text{NO}_3^-(\text{aq}) + 3\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$	0.94
$\text{Br}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Br}^-(\text{aq})$	1.087
$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	1.23
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	1.229
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightleftharpoons 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	1.36
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-(\text{aq})$	1.396
$\text{Ce}^{4+}(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ce}^{3+}(\text{aq})$ (20.2.53)	1.44
$\text{PbO}_2(\text{s}) + \text{HSO}_4^-(\text{aq}) + 3\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	1.690
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}(\text{l})$	1.763
$\text{F}_2(\text{g}) + 2\text{e}^- \rightleftharpoons 2\text{F}^-(\text{aq})$	2.87

Similarly, all species in Table 20.2.1 that lie above H_2 are stronger reductants than H_2 , and those that lie below H_2 are weaker. The strongest reductant in the table is thus metallic lithium, with a standard electrode potential of -3.04 V. This fact might be surprising

because cesium, not lithium, is the least electronegative element. The apparent anomaly can be explained by the fact that electrode potentials are measured in aqueous solution, where intermolecular interactions are important, whereas ionization potentials and electron affinities are measured in the gas phase. Due to its small size, the Li^+ ion is stabilized in aqueous solution by strong electrostatic interactions with the negative dipole end of water molecules. These interactions result in a significantly greater $\Delta H_{\text{hydration}}$ for Li^+ compared with Cs^+ . Lithium metal is therefore the strongest reductant (most easily oxidized) of the alkali metals in aqueous solution.

Note: Species in Table 20.2.1 (or Table P2) that lie above H_2 are stronger reducing agents (more easily oxidized) than H_2 . Species that lie below H_2 are stronger oxidizing agents.

Because the half-reactions shown in Table 20.2.1 are arranged in order of their E° values, we can use the table to quickly predict the relative strengths of various oxidants and reductants. Any species on the left side of a half-reaction will spontaneously oxidize any species on the right side of another half-reaction that lies below it in the table. Conversely, any species on the right side of a half-reaction will spontaneously reduce any species on the left side of another half-reaction that lies above it in the table. We can use these generalizations to predict the spontaneity of a wide variety of redox reactions ($E^\circ_{\text{cell}} > 0$), as illustrated below.

The standard potential for the reaction is positive, indicating that under standard conditions, it will occur spontaneously as written. Hydrogen peroxide will reduce MnO_2 , and oxygen gas will evolve from the solution.

Exercise 20.2.4 / Use the data in Table 20.2.1 to determine whether each reaction is likely to occur spontaneously under standard conditions:

1. $2\text{Ce}^{4+}(\text{aq}) + 2\text{Cl}^{-}(\text{aq}) \rightarrow 2\text{Ce}^{3+}(\text{aq}) + \text{Cl}_2(\text{g})$
2. $4\text{MnO}_2(\text{s}) + 3\text{O}_2(\text{g}) + 4\text{OH}^{-}(\text{aq}) \rightarrow 4\text{MnO}_4^{-}(\text{aq}) + 2\text{H}_2\text{O}$

Answer

1. spontaneous ($E^\circ_{\text{cell}} = 0.36 \text{ V}$)
2. nonspontaneous ($E^\circ_{\text{cell}} = -0.20 \text{ V}$)

Although the sign of E°_{cell} tells us whether a particular redox reaction will occur spontaneously under standard conditions, it does not tell us to what extent the reaction proceeds, and it does not tell us what will happen under nonstandard conditions. To answer these questions requires a more quantitative understanding of the relationship between electrochemical cell potential and chemical thermodynamics.

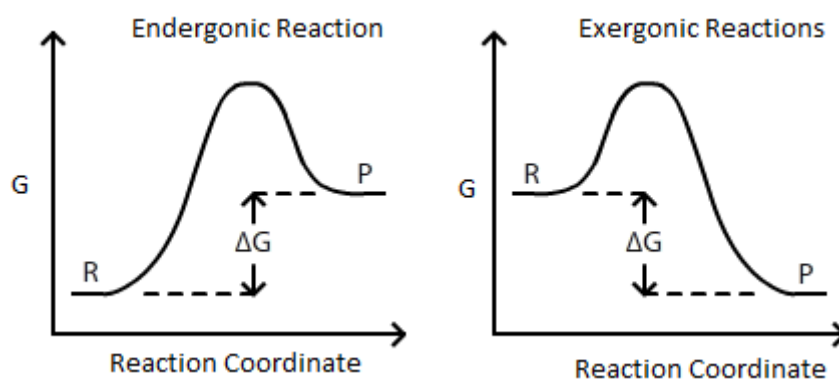
Connection between E_{cell} , ΔG , and K

The connection between cell potential, Gibbs energy and constant equilibrium are directly related in the following multi-part equation:

$$\Delta G^\circ = -RT \ln K_{eq} = -nFE^\circ_{cell}$$

ΔG : Gibbs Energy

ΔG is the change of Gibbs (free) energy for a system and ΔG° is the Gibbs energy change for a system under standard conditions (1 atm, 298K). On an energy diagram, ΔG can be represented as:



Where ΔG is the difference in the energy between reactants and products. In addition ΔG is unaffected by external factors that change the kinetics of the reaction. For example if E_a (activation energy) were to decrease in the presence of a catalyst or the kinetic energy of molecules increases due to a rise in temperature, the ΔG value would remain the same

E°_{cell} : Standard Cell Potential

E°_{cell} is the electromotive force (also called cell voltage or cell potential) between two half-cells. The greater the E°_{cell} of a reaction the greater the driving force of electrons through the system, the more likely the reaction will proceed (more spontaneous). E°_{cell} is measured in volts (V). The overall voltage of the cell = the half-cell potential of the reduction reaction + the half-cell potential of the oxidation reaction. To simplify,

$$E_{cell} = E_{reduction} + E_{oxidation} \quad (1)$$

or

$$E_{cell} = E_{cathode} + E_{anode} \quad (2)$$

The potential of an oxidation reduction (loss of electron) is the negative of the potential for a reduction potential (gain of electron). Most tables only record the standard reduction half-reactions. In other words, most tables only record the standard reduction potential; so in order to find the standard oxidation potential, simply reverse the sign of the standard reduction potential.