

19.4: Comparing Strengths of Oxidants and Reductants

Learning Objectives

- To know how to predict the relative strengths of various oxidants and reductants.

We can use the procedure described in [Section 19.2](#) to measure the standard potentials for a wide variety of chemical substances, some of which are listed in [Table 19.3.1](#) ([Table P1](#) contains a more extensive listing.) 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 19.3.1](#). All reactants that lie *above* the SHE in the table are stronger oxidants than H^+ , and all those that lie below 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 19.3.1 Standard Potentials for Selected Reduction Half-Reactions at 25°C

Half-Reaction	E° (V)
$F_2(g) + 2e^- \rightarrow 2F^-(aq)$	2.87
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(l)$	1.78
$Ce^{4+}(aq) + e^- \rightarrow Ce^{3+}(aq)$	1.72
$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$	1.69
$Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq)$	1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$	1.23
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O(l)$	1.23
$MnO_2(s) + 4H^+(aq) + 2e^- \rightarrow Mn^{2+}(aq) + 2H_2O(l)$	1.22
$Br_2(aq) + 2e^- \rightarrow 2Br^-(aq)$	1.09
$NO_3^-(aq) + 3H^+(aq) + 2e^- \rightarrow HNO_2(aq) + H_2O(l)$	0.93
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.80
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.77
$H_2SeO_3(aq) + 4H^+ + 4e^- \rightarrow Se(s) + 3H_2O(l)$	0.74
$O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O_2(aq)$	0.70
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4OH^-(aq)$	0.60
$MnO_4^{2-}(aq) + 2H_2O(l) + 2e^- \rightarrow MnO_2(s) + 4OH^-(aq)$	0.60
$I_2(s) + 2e^- \rightarrow 2I^-(aq)$	0.54
$H_2SO_3(aq) + 4H^+(aq) + 4e^- \rightarrow S(s) + 3H_2O(l)$	0.45
$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$	0.40
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.34
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	0.22
$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	0.15
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	0.15
$2H^+(aq) + 2e^- \rightarrow H_2(g)$	0.00

Half-Reaction	E° (V)
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14
$2\text{SO}_4^{2-}(\text{aq}) + 4\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{S}_2\text{O}_6^{2-}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	-0.22
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.26
$\text{PbSO}_4(\text{s}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$	-0.36
$\text{Cd}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.40
$\text{Cr}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Cr}^{2+}(\text{aq})$	-0.41
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.45
$\text{Ag}_2\text{S}(\text{s}) + 2\text{e}^- \rightarrow 2\text{Ag}(\text{s}) + \text{S}^{2-}(\text{aq})$	-0.69
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76
$\text{Al}^{3+}(\text{aq}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	-1.662
$\text{Be}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Be}(\text{s})$	-1.85
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.04

Similarly, all species in [Table 19.3.1](#) that lie *below* H_2 are stronger reductants than H_2 , and those that lie above 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 the Pattern

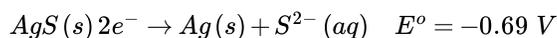
Species in [Table 19.3.1](#) that lie below H_2 are stronger reductants (more easily oxidized) than H_2 . Species that lie above H_2 are stronger oxidants.

Because the half-reactions shown in [Table 19.3.1](#) 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 in [Example 5](#).



Example 19.3.1

The black tarnish that forms on silver objects is primarily Ag_2S . The half-reaction for reversing the tarnishing process is as follows:



- Referring to [Table 19.3.1](#), predict which species— $\text{H}_2\text{O}_2(\text{aq})$, $\text{Zn}(\text{s})$, $\text{I}^-(\text{aq})$, $\text{Sn}^{2+}(\text{aq})$ —can reduce Ag_2S to Ag under standard conditions.
- Of these species— $\text{H}_2\text{O}_2(\text{aq})$, $\text{Zn}(\text{s})$, $\text{I}^-(\text{aq})$, $\text{Sn}^{2+}(\text{aq})$, identify which is the strongest reducing agent in aqueous solution and thus the best candidate for a commercial product.

3. From the data in [Table 19.3.1](#), suggest an alternative reducing agent that is readily available, inexpensive, and possibly more effective at removing tarnish.

Given: reduction half-reaction, standard electrode potential, and list of possible reductants

Asked for: reductants for Ag_2S , strongest reductant, and potential reducing agent for removing tarnish

Strategy:

A From their positions in [Table 19.3.1](#), decide which species can reduce Ag_2S . Determine which species is the strongest reductant.

B Use [Table 19.3.1](#) to identify a reductant for Ag_2S that is a common household product.

Solution:

We can solve the problem in one of two ways: (1) compare the relative positions of the four possible reductants with that of the $\text{Ag}_2\text{S}/\text{Ag}$ couple in [Table 19.3.1](#) or (2) compare E° for each species with E° for the $\text{Ag}_2\text{S}/\text{Ag}$ couple (-0.69 V).

- A** The species in [Table 19.3.1](#) are arranged from top to bottom in order of increasing reducing strength. Of the four species given in the problem, $\text{I}^-(\text{aq})$, $\text{Sn}^{2+}(\text{aq})$, and $\text{H}_2\text{O}_2(\text{aq})$ lie above Ag_2S , and one $[\text{Zn}(\text{s})]$ lies below it. We can therefore conclude that $\text{Zn}(\text{s})$ can reduce $\text{Ag}_2\text{S}(\text{s})$ under standard conditions, whereas $\text{I}^-(\text{aq})$, $\text{Sn}^{2+}(\text{aq})$, and $\text{H}_2\text{O}_2(\text{aq})$ cannot. $\text{Sn}^{2+}(\text{aq})$ and $\text{H}_2\text{O}_2(\text{aq})$ appear twice in the table: on the left side (oxidant) in one half-reaction and on the right side (reductant) in another.
- The strongest reductant is $\text{Zn}(\text{s})$, the species on the right side of the half-reaction that lies closer to the bottom of [Table 19.3.1](#) than the half-reactions involving $\text{I}^-(\text{aq})$, $\text{Sn}^{2+}(\text{aq})$, and $\text{H}_2\text{O}_2(\text{aq})$. (Commercial products that use a piece of zinc are often marketed as a “miracle product” for removing tarnish from silver. All that is required is to add warm water and salt for electrical conductivity.)
- B** Of the reductants that lie below $\text{Zn}(\text{s})$ in [Table 19.3.1](#), and therefore are stronger reductants, only one is commonly available in household products: $\text{Al}(\text{s})$, which is sold as aluminum foil for wrapping foods.

Exercise

Refer to [Table 19.3.1](#) to predict

- which species— $\text{Sn}^{4+}(\text{aq})$, $\text{Cl}^-(\text{aq})$, $\text{Ag}^+(\text{aq})$, $\text{Cr}^{3+}(\text{aq})$, and/or $\text{H}_2\text{O}_2(\text{aq})$ —can oxidize $\text{MnO}_2(\text{s})$ to MnO_4^- under standard conditions.
- which species— $\text{Sn}^{4+}(\text{aq})$, $\text{Cl}^-(\text{aq})$, $\text{Ag}^+(\text{aq})$, $\text{Cr}^{3+}(\text{aq})$, and/or $\text{H}_2\text{O}_2(\text{aq})$ —is the strongest oxidizing agent in aqueous solution.

Answer

- $\text{Ag}^+(\text{aq})$; $\text{H}_2\text{O}_2(\text{aq})$
- $\text{H}_2\text{O}_2(\text{aq})$

Example 19.3.2

Use the data in [Table 19.3.1](#) to determine whether each reaction is likely to occur spontaneously under standard conditions:

- $\text{Sn}(\text{s}) + \text{Be}^{2+}(\text{aq}) \rightarrow \text{Sn}^{2+}(\text{aq}) + \text{Be}(\text{s})$
- $\text{MnO}_2(\text{s}) + \text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow \text{O}_2(\text{g}) + \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$

Given: redox reaction and list of standard electrode potentials ([Table 19.3.1](#))

Asked for: reaction spontaneity

Strategy:

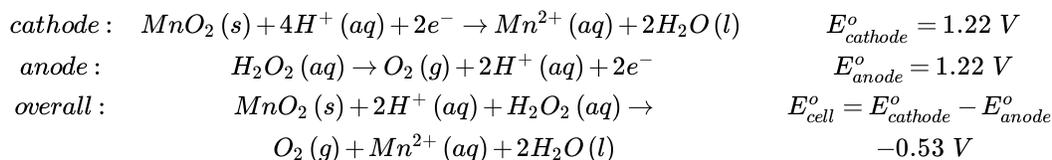
A Identify the half-reactions in each equation. Using [Table 19.3.1](#), determine the standard potentials for the half-reactions in the appropriate direction.

B Use [Equation 19.2.2](#) to calculate the standard cell potential for the overall reaction. From this value, determine whether the overall reaction is spontaneous.

Solution:

- A** Metallic tin is oxidized to $\text{Sn}^{2+}(\text{aq})$, and $\text{Be}^{2+}(\text{aq})$ is reduced to elemental beryllium. We can find the standard electrode potentials for the latter (reduction) half-reaction (-1.85 V) and for the former (oxidation) half-reaction (-0.14 V) directly from [Table 19.3.1](#).

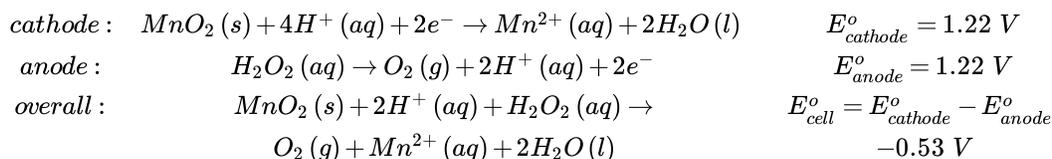
B Adding the two half-reactions gives the overall reaction:



The standard cell potential is quite negative, so the reaction will *not* occur spontaneously as written. That is, metallic tin cannot be used to reduce Be^{2+} to beryllium metal under standard conditions. Instead, the reverse process, the reduction of stannous ions (Sn^{2+}) by metallic beryllium, which has a positive value of E°_{cell} , will occur spontaneously.

2. A MnO_2 is the oxidant (Mn^{4+} is reduced to Mn^{2+}), while H_2O_2 is the reductant (O^{2-} is oxidized to O_2). We can obtain the standard electrode potentials for the reduction and oxidation half-reactions directly from [Table 19.2](#).

B The two half-reactions and their corresponding potentials are as follows:



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

Use the data in [Table 19.3.2](#) to determine whether each reaction is likely to occur spontaneously under standard conditions:

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

Answer

- spontaneous ($E^\circ_{\text{cell}} = 0.36 \text{ V}$)
- 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, as described in [Section 19.4](#).

Summary

The oxidative and reductive strengths of a variety of substances can be compared using standard electrode potentials. Apparent anomalies can be explained by the fact that electrode potentials are measured in aqueous solution, which allows for strong intermolecular electrostatic interactions, and not in the gas phase.

Key Takeaway

- The relative strengths of various oxidants and reductants can be predicted using E° values.

Conceptual Problems

- The order of electrode potentials cannot always be predicted by ionization potentials and electron affinities. Why? Do you expect sodium metal to have a higher or a lower electrode potential than predicted from its ionization potential? What is its approximate electrode potential?
- Without referring to tabulated data, of Br_2/Br^- , Ca^{2+}/Ca , O_2/OH^- , and Al^{3+}/Al , which would you expect to have the *least* negative electrode potential and which the *most* negative? Why?
- Because of the sulfur-containing amino acids present in egg whites, eating eggs with a silver fork will tarnish the fork. As a chemist, you have all kinds of interesting cleaning products in your cabinet, including a 1 M solution of oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$). Would you choose this solution to clean the fork that you have tarnished from eating scrambled eggs?

4. The electrode potential for the reaction $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{Cu}(\text{s})$ is 0.34 V under standard conditions. Is the potential for the oxidation of 0.5 mol of Cu equal to $-0.34/2$ V? Explain your answer.

Answer

- 1.
- 2.
3. No; $E^{\circ} = -0.691$ V for $\text{Ag}_2\text{S}(\text{s}) + 2\text{e}^{-} \rightarrow \text{Ag}(\text{s}) + \text{S}^{2-}(\text{aq})$, which is too negative for Ag_2S to be spontaneously reduced by oxalic acid [$E^{\circ} = 0.49$ V for $2\text{CO}_2(\text{g}) + 2\text{H}^{+}(\text{aq}) + 2\text{e}^{-} \rightarrow \text{H}_2\text{C}_2\text{O}_4(\text{aq})$]
- 4.

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