

CHM 3400 – Fundamentals of Physical Chemistry
Chapter 5 - Supplementary Material

1. Free energy and the equilibrium constant

The main reason for defining free energy is to have a thermodynamic function that makes it possible to easily decide whether or not a chemical reaction taking place at a particular temperature and pressure will or will not be spontaneous. The advantage of using free energy to do this is that finding the change in free energy only requires information about the system, and does not involve any calculations on the surroundings. For reactions where temperature and pressure do not change, we may say

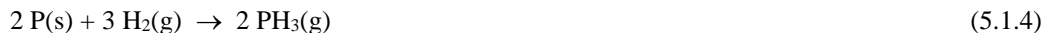
$$\Delta G_{\text{rxn}} < 0 \quad \text{reaction is spontaneous} \quad (5.1.1)$$

$$\Delta G_{\text{rxn}} = 0 \quad \text{reaction is at equilibrium} \quad (5.1.2)$$

$$\Delta G_{\text{rxn}} > 0 \quad \text{reaction is not spontaneous} \quad (5.1.3)$$

Note that if $\Delta G_{\text{rxn}} > 0$ then the reaction is not spontaneous as written but will be spontaneous if the direction of the reaction is reversed. This is a consequence of free energy being a state function.

To find a general expression for ΔG_{rxn} , consider the following specific example of a chemical reaction taking place at a particular temperature.



The free energy change per mole of reaction is given by the expression

$$\Delta G_{\text{rxn}} = [\Sigma (G(\text{products}))] - [\Sigma (G(\text{reactants}))] \quad (5.1.5)$$

Since the molar free energy (chemical potential) of a substance is (see Handout 4, Section 4)

$$G_{\text{m,A}} = \mu_{\text{A}} = \mu_{\text{A}}^{\circ} + RT \ln(a_{\text{A}}) \quad (5.1.6)$$

then we can use eq 5.1.6 to substitute into eq 5.1.5. The result is

$$\Delta G_{\text{rxn}} = [2 (\mu_{\text{PH}_3}^{\circ} + RT \ln(a_{\text{PH}_3}))] - [2 (\mu_{\text{P}}^{\circ} + RT \ln(a_{\text{P}})) + 3 (\mu_{\text{H}_2}^{\circ} + RT \ln(a_{\text{H}_2}))] \quad (5.1.7)$$

which, after rearrangement, can be written as

$$\Delta G_{\text{rxn}} = \{ [2 \mu_{\text{PH}_3}^{\circ}] - [2 \mu_{\text{P}}^{\circ} + 3 \mu_{\text{H}_2}^{\circ}] \} + \{ [2RT \ln(a_{\text{PH}_3})] - [2RT \ln(a_{\text{P}}) + 3RT \ln(a_{\text{H}_2})] \} \quad (5.1.8)$$

But the first term in eq 5.1.8 is simply the change in free energy for standard state conditions. So

$$[2 \mu_{\text{PH}_3}^{\circ}] - [2 \mu_{\text{P}}^{\circ} + 3 \mu_{\text{H}_2}^{\circ}] = \Delta G_{\text{rxn}}^{\circ} \quad (5.1.9)$$

For the second term in eq 5.1.8, if we factor out the common term RT and use the properties of logarithms, we get

$$[2RT \ln(a_{\text{PH}_3})] - [2RT \ln(a_{\text{P}}) + 3RT \ln(a_{\text{H}_2})] = RT \ln \frac{(a_{\text{PH}_3})^2}{(a_{\text{P}})^2 (a_{\text{H}_2})^3} = RT \ln(Q) \quad (5.1.10)$$

where Q , the reaction quotient, is the ratio of the activities of the products divided by the activities of the reactants. For this reaction, the reaction quotient is

$$Q = \frac{(a_{\text{PH}_3})^2}{(a_{\text{P}})^2 (a_{\text{H}_2})^3} \quad (5.1.11)$$

So for the reaction in eq 5.1.4 the change in free energy is

$$\Delta G_{\text{rxn}} = \Delta G^\circ_{\text{rxn}} + RT \ln(Q) \quad (5.1.12)$$

While eq 5.1.12 was derived for a specific reaction, it is a general result, and can be used to find the change in free energy for any chemical reaction as long as the thermodynamic data needed to find $\Delta G^\circ_{\text{rxn}}$ is available, and information for the activities of the products and reactants can be found, either by assuming ideal behavior or by other means. Note that activity has no units, and so Q also does not have units. Activities for common ideal and nonideal substances are given below

Substance	Activity (ideal)	Activity (nonideal)	Reference
gas	$a = p/p^\circ$	$a = \gamma p/p^\circ$	$p^\circ = 1 \text{ bar} + \text{ideal}$
pure liquid or solid	$a = 1$	$a = 1$	the pure solid or liquid
solvent	$a \cong 1$	$a \cong 1$	the pure solvent
solute, molarity	$a = [A]/(1 \text{ mol/L})$	$a = \gamma[A]/(1 \text{ mol/L})$	1 mol/L + ideal

For ideal gases and solutes we often do not show division of pressure or solute concentration by standard pressure or concentration, leaving the division implied. Nonideal behavior is accounted for by the activity coefficient (γ). Note that $\gamma = 1$ for ideal behavior. The larger the difference between the value of γ and 1 the more nonideal the behavior of the substance. Values for γ can be found both experimentally and, in some cases, from simple theories.

We will generally not consider activity for nonideal cases. The use of activity and activity coefficients does, however, provide a systematic way of discussing real systems exhibiting significant nonideal properties, such as seawater, where the high concentration of dissolved ions leads to deviations from ideal behavior.

Since eq 5.1.12 applies to all reactions at a fixed temperature and pressure, it applies for a reaction at equilibrium. At equilibrium $\Delta G_{\text{rxn}} = 0$. The equilibrium constant for a reaction, K , is defined the value for the reaction quotient for a reaction at equilibrium, and so $K = Q_{\text{eq}}$. Using this information to substitute into eq 5.1.12 gives, for a reaction at equilibrium

$$0 = \Delta G^\circ_{\text{rxn}} + RT \ln(K) \quad (5.1.13)$$

or, after rearrangement

$$\ln(K) = - \frac{\Delta G^\circ_{\text{rxn}}}{RT} \quad (5.1.14)$$

This is a powerful result. It tells us that for any reaction where the free energy of formation is known for all of the reactants and products we can find a numerical value for the equilibrium constant for the reaction.

As an example of the use of eq 5.1.14, consider the equilibrium between acetic acid and acetate ion in aqueous solution



The free energy change for the reaction in eq 5.1.15, for standard conditions, is

$$\Delta G^\circ_{\text{rxn}} = [\Delta G^\circ_f(\text{H}^+(\text{aq})) + \Delta G^\circ_f(\text{CH}_3\text{COO}^-(\text{aq}))] - [\Delta G^\circ_f(\text{CH}_3\text{COOH}(\text{aq}))] \quad (5.1.16)$$

At $T = 25.0\text{ }^\circ\text{C}$ and using the data in the Appendix of Atkins, this gives

$$\Delta G^\circ_{\text{rxn}} = [(0.00) + (-369.31)] - [(-396.46)] = +27.15\text{ kJ/mol} \quad (5.1.17)$$

So

$$\ln(K) = - \frac{(27150.\text{ J/mol})}{(8.3145\text{ J/mol}\cdot\text{K})(298.15\text{ K})} = -10.95 \quad K = e^{-10.95} = 1.8 \times 10^{-5} \quad (5.1.18)$$

Although we will not discuss this in detail, it is worth noting that for biological systems we often choose as the standard state for hydrogen ion a concentration $[\text{H}^+] = 1.0 \times 10^{-7}\text{ mol/L}$ (the concentration found for a neutral aqueous solution at $25.0\text{ }^\circ\text{C}$, $\text{pH} = 7.00$), rather than $[\text{H}^+] = 1.00\text{ mol/L}$, which would correspond to extremely acidic conditions. The choice $[\text{H}^+] = 1.0 \times 10^{-7}\text{ mol/L}$ is called the biological standard state for hydrogen ion. This is an example of a general strategy of choosing a standard state that is most useful in describing the thermodynamics of particular types of systems.

2. Temperature dependence of the equilibrium constant

We often need to know how the value for the equilibrium constant for a reaction changes with temperature. There are two ways we can proceed.

Method 1 – If we assume $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ are approximately independent of temperature, we can, starting with eq 5.1.14, derive the following result

$$\ln(K_2/K_1) = -(\Delta H^\circ_{\text{rxn}}/R) \{ (1/T_2) - (1/T_1) \} \quad (5.2.1)$$

In the above equation K_1 is the equilibrium constant for the reaction at a temperature T_1 (usually $25.0\text{ }^\circ\text{C}$), K_2 is the equilibrium constant at temperature T_2 , and $\Delta H^\circ_{\text{rxn}}$ is the enthalpy change for the reaction for standard conditions. Method 1 is approximate, but works well if T_1 and T_2 are close to one another.

Method 2 – For precise work, we proceed as follows. First, we find the value for $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ at some temperature T_1 . We then use the method outlined in the Chapter 3 Handout (Section 6) to find $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ at our new temperature T_2 . This requires that we know the constant pressure molar heat capacities of all of the reactants and products as a function of temperature. From the general relationship for free energy, we can then say

$$\Delta G^\circ_{\text{rxn}}(T_2) = \Delta H^\circ_{\text{rxn}}(T_2) - T_2 \Delta S^\circ_{\text{rxn}}(T_2) \quad (5.2.2)$$

where $\Delta G^\circ_{\text{rxn}}(T_2)$, $\Delta H^\circ_{\text{rxn}}(T_2)$, and $\Delta S^\circ_{\text{rxn}}(T_2)$ are the changes in free energy, enthalpy, and entropy for the reaction for standard conditions and at temperature T_2 . Substituting the values for $\Delta H^\circ_{\text{rxn}}(T_2)$ and $\Delta S^\circ_{\text{rxn}}(T_2)$ into eq 5.2.2 allows us to find the value for the $\Delta G^\circ_{\text{rxn}}(T_2)$. Equation 5.1.14 can then be used to find equilibrium constant for the reaction at temperature T_2 . This method is useful for finding more precise values for equilibrium constants or for cases where T_1 and T_2 are much different.

3. Galvanic cells – general review

A galvanic cell (battery) is an electrochemical system where a chemical reaction is used to generate a voltage. Galvanic cells have a variety of applications, such as power sources in electric cars, electronic devices, and light sources. In this section we review some conventions and general properties of galvanic cells.

Consider the galvanic cell in Figure 1. The left beaker contains an aqueous solution of zinc sulfate (ZnSO_4) and a zinc metal electrode. The right beaker contains an aqueous solution of copper II sulfate (CuSO_4) and a copper metal electrode. The electrodes serve as sites for the chemical reactions taking place in the galvanic cell, and in this case themselves participate in the reactions. The two beakers are connected by a salt bridge, typically composed of agar and containing potassium nitrate (KNO_3) or other unreactive salt, in the form of ions. The ions in the salt bridge provides a way for charge to move between the two beakers. A voltmeter (V) is used to measure the voltage generated by the galvanic cell.

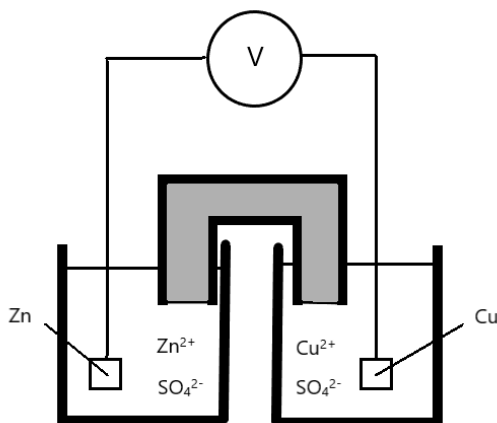
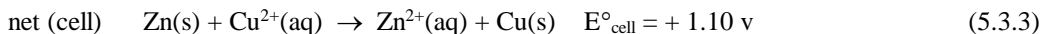
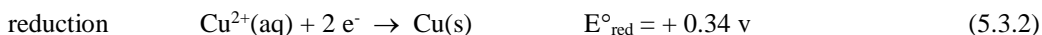


Figure 1. A galvanic cell.

The chemical reactions taking place in a galvanic cell include one oxidation reaction and one reduction reaction. By convention, the electrode where the oxidation reaction takes place is called the anode, and the electrode where the reduction reaction takes place is the cathode. We generally assume that the left electrode is the anode and the right electrode is the cathode.

The overall reaction taking place in a galvanic cell can be written as an oxidation half-reaction and a reduction half-reaction. For the cell in Figure 1, the half-reactions and net cell reaction are



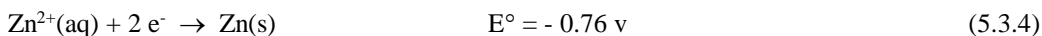
Note that before the two half-cell reactions can be combined to give the net cell reaction we must be sure that the number of moles of electrons generated in the oxidation reaction is the same as the number of moles of electrons consumed in the reduction reaction. This may require multiplying one or both of the half-cell reactions by a positive integer.

The voltage generated for a galvanic cell for standard conditions (and at $T = 25.0 \text{ }^{\circ}\text{C}$) can be found using a table of half-cell reduction potentials, such as Table 1 on the last page of this handout. The voltage generated by the net cell reaction is the sum of the voltage from the oxidation half-reaction and from the reduction half-reaction.

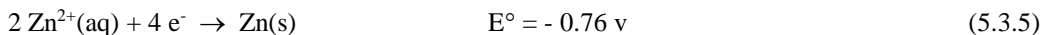
There are two important properties of the standard half-cell reduction potentials:

- 1) Multiplying a half-cell reduction reaction by a positive constant has no effect on the voltage.
- 2) Reversing the direction of a half-cell reduction reaction (which converts the reaction from reduction to oxidation) changes the sign of the potential, but not the magnitude.

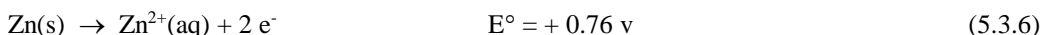
For example, from Table 1, the standard half-cell reduction potential for Zn^{2+} ion being reduced to zinc metal is



and so



and



Because it is tedious to draw a picture of a galvanic cell, such cells are often represented as a cell diagram. In a cell diagram, the substances in the cell are listed, in order, from anode to cathode. A single vertical line is used to indicate a change in phase (solid to solution, for example), and a double vertical line is used to indicate a salt bridge. Additional information, such as the activities or concentrations of substances in the cell, can also be indicated.

For the galvanic cell in Figure 1, the corresponding cell diagram is



Notice that spectator ions such as SO_4^{2-} , which are present in the cell but play no role in the cell reactions, are not listed in the cell diagram.

4. Thermodynamics of galvanic cells and the Nernst equation

Because we have spent time developing general thermodynamic relationships that apply to all systems, giving a thermodynamic analysis of a new system often means finding a connection between a property of the system and a thermodynamic function. Once such a connection is made, we may use all of the general relationships previously developed to produce a complete analysis of the thermodynamics of the new system.

One example of this process is in the discussion of the thermodynamics of galvanic cells. The connection between a property of a galvanic cell and thermodynamics is through the work done in moving a charge dQ through a potential difference V .

$$\delta w = V dQ \quad (5.4.1)$$

Because

$$dG = \delta w'_{\text{max}} \quad (5.4.2)$$

where $\delta w'_{\text{max}}$ represents the maximum amount of nonmechanical (non pressure-volume) work, we can combine eq 5.4.1 and 5.4.2 to get

$$\Delta G_{\text{cell}} = \int \delta w'_{\text{max}} = \int V dQ = -vFE_{\text{cell}} \quad (5.4.3)$$

In the above expression v represents the number of moles of electrons transferred per mole of the cell reaction. This can be found by looking at either the half-cell oxidation reaction or the half-cell reduction reaction of a galvanic cell, once these reactions have been adjusted so that the electrons cancel. For example, for the net cell reaction in eq 5.3.3, $v = 2$. E_{cell} is the voltage generated by the galvanic cell. F (Faraday's constant) is a conversion factor between

moles of charge and Coulombs of charge ($F = 96485$ Coulomb/mole). The negative sign in eq 5.4.3 is a consequence of the fact that the charge carriers in a galvanic cell are electrons (which have a negative charge). The conversion factor F is needed because of the relationship between electrical units and energy

$$(1 \text{ volt}) \cdot (1 \text{ Coulomb}) = 1 \text{ Joule} \quad (5.4.4)$$

Based on eq 5.4.3 and our knowledge of free energy, we can make the following general statements about cell potentials for galvanic cells operating at a particular temperature and pressure

$$\text{If } E_{\text{cell}} > 0 \text{ then } \Delta G_{\text{cell}} < 0, \text{ and the cell reaction is spontaneous} \quad (5.4.5)$$

$$\text{If } E_{\text{cell}} = 0 \text{ then } \Delta G_{\text{cell}} = 0, \text{ and the cell is at equilibrium} \quad (5.4.6)$$

$$\text{If } E_{\text{cell}} < 0 \text{ then } \Delta G_{\text{cell}} > 0, \text{ and the cell reaction is not spontaneous} \quad (5.4.7)$$

Note that if $E_{\text{cell}} < 0$ ($\Delta G_{\text{rxn}} > 0$) then the cell reaction is not spontaneous as written but will be spontaneous if the direction of the reaction is reversed. Essentially this corresponds to reversing the assignment of the anode and cathode in the cell. This result is a consequence of free energy being a state function.

Equation 5.4.3 makes the connection we need between a property of a galvanic cell and thermodynamics. Now all we have to do is use the general thermodynamic relationships previously derived to obtain a complete description of galvanic cells. For example, since

$$\Delta G_{\text{rxn}} = \Delta G^{\circ}_{\text{rxn}} + RT \ln(Q) \quad (5.4.8)$$

it follows, by use of eq 5.4.3 (and after some rearrangement of terms), that

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - (RT/vF) \ln(Q) \quad (5.4.9)$$

the Nernst equation. The Nernst equation allows us to find values for cell potentials for cases where the substances in the cell are not in their standard state.

When we use the Nernst equation to describe a galvanic cell at equilibrium (where $E_{\text{cell}} = 0$, $K = Q_{\text{eq}}$), we get

$$\ln(K) = \frac{vFE^{\circ}_{\text{cell}}}{RT} \quad (5.4.10)$$

Equation 5.4.10 can be used to find numerical values for equilibrium constants for reaction that can be represented by a galvanic cell, provided we have the half-cell potentials needed to find E°_{cell} . While useful, eq 5.3.10 is not as general a result as eq 5.1.14.

We can also find the values for other thermodynamic functions. Since

$$\Delta G^{\circ}_{\text{rxn}} = \Delta H^{\circ}_{\text{rxn}} - T \Delta S^{\circ}_{\text{rxn}} \quad (5.4.11)$$

and

$$(d\Delta G^{\circ}_{\text{rxn}}/dT)_p = - \Delta S^{\circ}_{\text{rxn}} \quad (5.4.12)$$

we can show, by combining eq 5.4.11 and 5.4.12 and assuming that both $\Delta H^{\circ}_{\text{rxn}}$ and $\Delta S^{\circ}_{\text{rxn}}$ are approximately independent of temperature, that

$$\Delta S^{\circ}_{\text{rxn}} = vF (dE^{\circ}_{\text{cell}}/dT) \quad (5.4.13)$$

and, (by substituting eq 5.4.3 and 5.4.13 into eq 5.4.11, and solving for $\Delta H^{\circ}_{\text{rxn}}$), that

$$\Delta H^{\circ}_{\text{rxn}} = \nu F \{ T (dE^{\circ}_{\text{cell}}/dT) - E^{\circ}_{\text{cell}} \} \quad (5.4.14)$$

What this means is that if we can measure the standard cell potential for a galvanic cell at several temperatures, we can use eq 5.4.3, 5.4.13, and 5.4.14 to find $\Delta G^{\circ}_{\text{rxn}}$, $\Delta S^{\circ}_{\text{rxn}}$, and $\Delta H^{\circ}_{\text{rxn}}$ for the corresponding cell reaction.

TABLE 1 – Table of standard half-cell reduction potentials, T = 25.0 °C

Reduction half-reaction	E°/V	Reduction half-reaction	E°/V
$\text{Ag}^+ + e^- \rightarrow \text{Ag}$	+0.80	$\text{I}_2 + 2e^- \rightarrow 2\text{I}^-$	+0.54
$\text{Ag}^{2+} + e^- \rightarrow \text{Ag}^+$	+1.98	$\text{I}_3^- + 2e^- \rightarrow 3\text{I}^-$	+0.53
$\text{AgBr} + e^- \rightarrow \text{Ag} + \text{Br}^-$	+0.0713	$\text{In}^+ + e^- \rightarrow \text{In}$	-0.14
$\text{AgCl} + e^- \rightarrow \text{Ag} + \text{Cl}^-$	+0.22	$\text{In}^{2+} + e^- \rightarrow \text{In}^+$	-0.40
$\text{Ag}_2\text{CrO}_4 + 2e^- \rightarrow 2\text{Ag} + \text{CrO}_4^{2-}$	+0.45	$\text{In}^{3+} + 2e^- \rightarrow \text{In}^+$	-0.44
$\text{AgF} + e^- \rightarrow \text{Ag} + \text{F}^-$	+0.78	$\text{In}^{3+} + 3e^- \rightarrow \text{In}$	-0.34
$\text{AgI} + e^- \rightarrow \text{Ag} + \text{I}^-$	-0.15	$\text{In}^{3+} + e^- \rightarrow \text{In}^{2+}$	-0.49
$\text{Al}^{3+} + 3e^- \rightarrow \text{Al}$	-1.66	$\text{K}^+ + e^- \rightarrow \text{K}$	-2.93
$\text{Au}^+ + e^- \rightarrow \text{Au}$	+1.69	$\text{La}^{3+} + 3e^- \rightarrow \text{La}$	-2.52
$\text{Au}^{3+} + 3e^- \rightarrow \text{Au}$	+1.50	$\text{Li}^+ + e^- \rightarrow \text{Li}$	-3.05
$\text{Ba}^{2+} + 2e^- \rightarrow \text{Ba}$	+2.91	$\text{Mg}^{2+} + 2e^- \rightarrow \text{Mg}$	-2.36
$\text{Be}^{2+} + 2e^- \rightarrow \text{Be}$	-1.85	$\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn}$	-1.18
$\text{Bi}^{3+} + 3e^- \rightarrow \text{Bi}$	+0.31	$\text{Mn}^{3+} + e^- \rightarrow \text{Mn}^{2+}$	+1.51
$\text{Br}_2 + 2e^- \rightarrow 2\text{Br}^-$	+1.09	$\text{MnO}_2 + 4\text{H}^+ + 2e^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	+1.23
$\text{BrO}^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{Br}^- + 2\text{OH}^-$	+0.76	$\text{MnO}_4^- + 8\text{H}^+ + 5e^- \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$	+1.51
$\text{Ca}^{2+} + 2e^- \rightarrow \text{Ca}$	-2.87	$\text{MnO}_4^- + e^- \rightarrow \text{MnO}_4^{2-}$	+0.56
$\text{Cd}(\text{OH})_2 + 2e^- \rightarrow \text{Cd} + 2\text{OH}^-$	-0.81	$\text{MnO}_4^{2-} + 2\text{H}_2\text{O} + 2e^- \rightarrow \text{MnO}_2 + 4\text{OH}^-$	+0.60
$\text{Cd}^{2+} + 2e^- \rightarrow \text{Cd}$	-0.40	$\text{Na}^+ + e^- \rightarrow \text{Na}$	-2.71
$\text{Ce}^{3+} + 3e^- \rightarrow \text{Ce}$	-2.48	$\text{Ni}^{2+} + 2e^- \rightarrow \text{Ni}$	-0.26
$\text{Ce}^{4+} + e^- \rightarrow \text{Ce}^{3+}$	+1.61	$\text{NiOOH} + \text{H}_2\text{O} + e^- \rightarrow \text{Ni}(\text{OH})_2 + \text{OH}^-$	+0.49
$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	+1.36	$\text{NO}_3^- + 2\text{H}^+ + e^- \rightarrow \text{NO}_2 + \text{H}_2\text{O}$	-0.80
$\text{ClO}^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{Cl}^- + 2\text{OH}^-$	+0.89	$\text{NO}_3^- + 4\text{H}^+ + 3e^- \rightarrow \text{NO} + 2\text{H}_2\text{O}$	+0.96
$\text{ClO}_4^- + 2\text{H}^+ + 2e^- \rightarrow \text{ClO}_3^- + \text{H}_2\text{O}$	+1.23	$\text{NO}_3^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{NO}_2^- + 2\text{OH}^-$	+0.10
$\text{ClO}_4^- + \text{H}_2\text{O} + 2e^- \rightarrow \text{ClO}_3^- + 2\text{OH}^-$	+0.36	$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$	+0.40
$\text{Co}^{2+} + 2e^- \rightarrow \text{Co}$	-0.28	$\text{O}_2 + 4\text{H}^+ + 4e^- \rightarrow 2\text{H}_2\text{O}$	+1.23
$\text{Co}^{3+} + e^- \rightarrow \text{Co}^{2+}$	+1.81	$\text{O}_2 + e^- \rightarrow \text{O}_2^-$	-0.56
$\text{Cr}^{2+} + 2e^- \rightarrow \text{Cr}$	-0.91	$\text{O}_2 + \text{H}_2\text{O} + 2e^- \rightarrow \text{HO}_2^- + \text{OH}^-$	-0.08
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	+1.33	$\text{O}_3 + 2\text{H}^+ + 2e^- \rightarrow \text{O}_2 + \text{H}_2\text{O}$	+2.07
$\text{Cr}^{3+} + 3e^- \rightarrow \text{Cr}$	-0.74	$\text{O}_3 + \text{H}_2\text{O} + 2e^- \rightarrow \text{O}_2 + 2\text{OH}^-$	+1.24
$\text{Cr}^{3+} + e^- \rightarrow \text{Cr}^{2+}$	-0.41	$\text{Pb}^{2+} + 2e^- \rightarrow \text{Pb}$	-0.13
$\text{Cs}^+ + e^- \rightarrow \text{Cs}$	-2.92	$\text{Pb}^{4+} + 2e^- \rightarrow \text{Pb}^{2+}$	+1.67
$\text{Cu}^+ + e^- \rightarrow \text{Cu}$	+0.52	$\text{PbSO}_4 + 2e^- \rightarrow \text{Pb} + \text{SO}_4^{2-}$	-0.36
$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$	+0.34	$\text{Pt}^{2+} + 2e^- \rightarrow \text{Pt}$	+1.20
$\text{Cu}^{2+} + e^- \rightarrow \text{Cu}^+$	+0.16	$\text{Pu}^{4+} + e^- \rightarrow \text{Pu}^{3+}$	+0.97
$\text{F}_2 + 2e^- \rightarrow 2\text{F}^-$	+2.87	$\text{Ra}^{2+} + 2e^- \rightarrow \text{Ra}$	-2.92
$\text{Fe}^{2+} + 2e^- \rightarrow \text{Fe}$	-0.44	$\text{Rb}^+ + e^- \rightarrow \text{Rb}$	-2.93
$\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe}$	-0.04	$\text{S} + 2e^- \rightarrow \text{S}^{2-}$	-0.48
$\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$	+0.77	$\text{S}_2\text{O}_8^{2-} + 2e^- \rightarrow 2\text{SO}_4^{2-}$	+2.01
$[\text{Fe}(\text{CN})_6]^{3-} + e^- \rightarrow [\text{Fe}(\text{CN})_6]^{4-}$	+0.36	$\text{Sc}^{3+} + 3e^- \rightarrow \text{Sc}$	-2.09
$2\text{H}^+ + 2e^- \rightarrow \text{H}_2$	0, by definition	$\text{Sn}^{2+} + 2e^- \rightarrow \text{Sn}$	-0.14
$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-$	-0.83	$\text{Sn}^{4+} + 2e^- \rightarrow \text{Sn}^{2+}$	+0.15
$2\text{HBrO} + 2\text{H}^+ + 2e^- \rightarrow \text{Br}_2 + 2\text{H}_2\text{O}$	+1.60	$\text{Sr}^{2+} + 2e^- \rightarrow \text{Sr}$	-2.89
$2\text{HClO} + 2\text{H}^+ + 2e^- \rightarrow \text{Cl}_2 + 2\text{H}_2\text{O}$	+1.63	$\text{Ti}^{2+} + 2e^- \rightarrow \text{Ti}$	-1.63
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O}$	+1.78	$\text{Ti}^{3+} + e^- \rightarrow \text{Ti}^{2+}$	-0.37
$\text{H}_4\text{XeO}_6 + 2\text{H}^+ + 2e^- \rightarrow \text{XeO}_3 + 3\text{H}_2\text{O}$	+3.0	$\text{Ti}^{4+} + e^- \rightarrow \text{Ti}^{3+}$	0.00
$\text{Hg}_2^{2+} + 2e^- \rightarrow 2\text{Hg}$	+0.79	$\text{Ti}^+ + e^- \rightarrow \text{Ti}$	-0.34
$\text{Hg}_2\text{Cl}_2 + 2e^- \rightarrow 2\text{Hg} + 2\text{Cl}^-$	+0.27	$\text{U}^{3+} + 3e^- \rightarrow \text{U}$	-1.79
$\text{Hg}_2^{2+} + 2e^- \rightarrow \text{Hg}$	+0.86	$\text{U}^{4+} + e^- \rightarrow \text{U}^{3+}$	-0.61
$2\text{Hg}^{2+} + 2e^- \rightarrow \text{Hg}_2^{2+}$	+0.92	$\text{V}^{2+} + 2e^- \rightarrow \text{V}$	-1.19
$\text{Hg}_2\text{SO}_4 + 2e^- \rightarrow 2\text{Hg} + \text{SO}_4^{2-}$	+0.62	$\text{V}^{3+} + e^- \rightarrow \text{V}^{2+}$	-0.26
		$\text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$	-0.76