

9.4: The Nernst Equation

Learning Objectives

- Relate cell potentials to free energy changes
- Use the Nernst equation to determine cell potentials at nonstandard conditions
- Perform calculations that involve converting between cell potentials, free energy changes, and equilibrium constants

We will now extend electrochemistry by determining the relationship between E_{cell}° and the thermodynamics quantities such as ΔG° (Gibbs free energy) and K (the equilibrium constant). In galvanic cells, chemical energy is converted into electrical energy, which can do work. The electrical work is the product of the charge transferred multiplied by the potential difference (voltage):

$$\text{electrical work} = \text{volts} \times (\text{charge in coulombs}) = J$$

The charge on 1 mole of electrons is given by Faraday's constant (F)

$$\begin{aligned} F &= \frac{6.022 \times 10^{23} e^{-}}{\text{mol}} \times \frac{1.602 \times 10^{-19} C}{e^{-}} \\ &= 9.648 \times 10^4 \frac{C}{\text{mol}} \\ &= 9.648 \times 10^4 \frac{J}{V \cdot \text{mol}} \end{aligned}$$

Therefore

$$\text{total charge} = (\text{number of moles of } e^{-}) \times F = nF$$

In this equation, n is the number of moles of electrons for the *balanced* oxidation-reduction reaction. The measured cell potential is the maximum potential the cell can produce and is related to the electrical work (w_{ele}) by

$$E_{\text{cell}} = \frac{-w_{\text{ele}}}{nF} \quad \text{or} \quad w_{\text{ele}} = -nFE_{\text{cell}}$$

The negative sign for the work indicates that the electrical work is done by the system (the galvanic cell) on the surroundings. In an earlier chapter, the free energy was defined as the energy that was available to do work. In particular, the change in free energy was defined in terms of the maximum work (w_{max}), which, for electrochemical systems, is w_{ele} .

$$\begin{aligned} \Delta G &= w_{\text{max}} = w_{\text{ele}} \\ &= -nFE_{\text{cell}} \end{aligned}$$

We can verify the signs are correct when we realize that n and F are positive constants and that galvanic cells, which have positive cell potentials, involve spontaneous reactions. Thus, spontaneous reactions, which have $\Delta G < 0$, must have $E_{\text{cell}} > 0$. If all the reactants and products are in their standard states, this becomes

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

This provides a way to relate standard cell potentials to equilibrium constants, since

$$\begin{aligned} \Delta G^{\circ} &= -RT \ln K \\ -nFE_{\text{cell}}^{\circ} &= -RT \ln K \end{aligned}$$

or

$$E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln K$$

Most of the time, the electrochemical reactions are run at standard temperature (298.15 K). Collecting terms at this temperature yields

$$\begin{aligned}
 E_{\text{cell}}^{\circ} &= \frac{RT}{nF} \ln K \\
 &= \frac{\left(8.314 \frac{\text{J}}{\text{K} \cdot \text{mol}}\right) (298.15 \text{ K})}{n \times 96,485 \text{ C/V} \cdot \text{mol}} \ln K \\
 &= \frac{0.0257 \text{ V}}{n} \ln K
 \end{aligned}$$

where n is the number of moles of electrons. The logarithm in equations involving cell potentials is often expressed using base 10 logarithms (i.e., \log_{10} or just \log), which changes the constant by a factor of 2.303:

$$E_{\text{cell}}^{\circ} = \frac{0.0592 \text{ V}}{n} \log K$$

Thus, if ΔG° , K , or E_{cell}° is known or can be calculated, the other two quantities can be readily determined. The relationships are shown graphically in Figure 9.4.1.

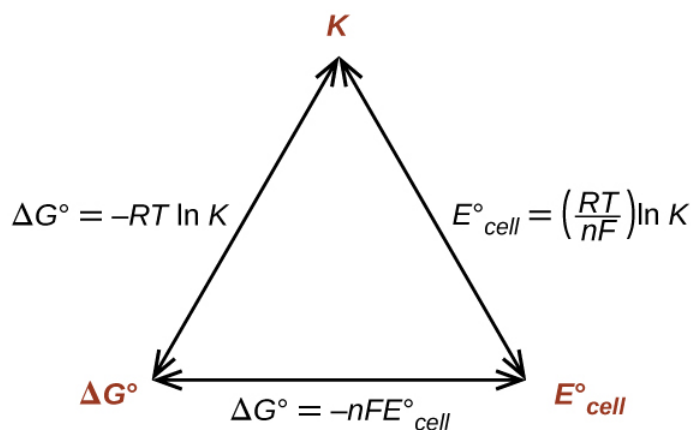


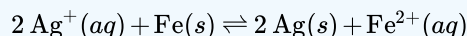
Figure 9.4.1: The relationships between ΔG° , K , and E_{cell}° . Given any one of the three quantities, the other two can be calculated, so any of the quantities could be used to determine whether a process was spontaneous.

A diagram is shown that involves three double headed arrows positioned in the shape of an equilateral triangle. The vertices are labeled in red. The top vertex is labeled “K.” The vertex at the lower left is labeled “delta G superscript degree symbol.” The vertex at the lower right is labeled “E superscript degree symbol subscript cell.” The right side of the triangle is labeled “E superscript degree symbol subscript cell equals (R T divided by n F) l n K.” The lower side of the triangle is labeled “delta G superscript degree symbol equals negative n F E superscript degree symbol subscript cell.” The left side of the triangle is labeled “delta G superscript degree symbol equals negative R T l n K.”

Given any one of the quantities, the other two can be calculated.

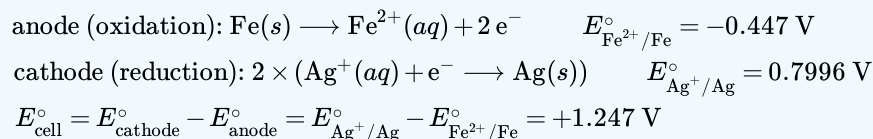
✓ Example 9.4.1: Equilibrium Constants, Potentials, & Free Energy Changes

What is the standard Gibbs free energy change and equilibrium constant for the following reaction at 25 °C?



Solution

The reaction involves an oxidation-reduction reaction, so the standard cell potential can be calculated using the data in Table P1.



Remember that the cell potential for the cathode is not multiplied by two when determining the standard cell potential. With $n = 2$, the equilibrium constant is then

$$E_{\text{cell}}^{\circ} = \frac{0.0592 \text{ V}}{n} \log K$$

$$K = 10^{n \times E_{\text{cell}}^{\circ} / 0.0592 \text{ V}}$$

$$= 10^{2 \times 1.247 \text{ V} / 0.0592 \text{ V}}$$

$$= 10^{42.128}$$

$$= 1.3 \times 10^{42}$$

The standard free energy is then

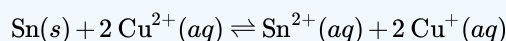
$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

$$\Delta G^{\circ} = -2 \times 96,485 \frac{\text{J}}{\text{V} \cdot \text{mol}} \times 1.247 \text{ V} = -240.6 \frac{\text{kJ}}{\text{mol}}$$

Check your answer: A positive standard cell potential means a spontaneous reaction, so the standard free energy change should be negative, and an equilibrium constant should be >1 .

? Exercise 9.4.1

What is the standard Gibbs free energy change and the equilibrium constant for the following reaction at room temperature? Is the reaction spontaneous?



Answer

Spontaneous; $n = 2$; $E_{\text{cell}}^{\circ} = +0.291 \text{ V}$; $\Delta G^{\circ} = -56.2 \frac{\text{kJ}}{\text{mol}}$; $K = 6.8 \times 10^9$.

Now that the connection has been made between the free energy and cell potentials, nonstandard concentrations follow. Recall that

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

where Q is the reaction quotient (see the chapter on equilibrium fundamentals). Converting to cell potentials:

$$-nFE_{\text{cell}} = -nFE_{\text{cell}}^{\circ} + RT \ln Q \quad (9.4.1)$$

or

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q \quad (9.4.2)$$

Equation 9.4.2 is the generalized Nernst equation that is applicable at any temperature. However, it can be simplified for reactions occurring at 25 °C (298.15 K) by rewriting it as

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0257 \text{ V}}{n} \ln Q \quad (9.4.3)$$

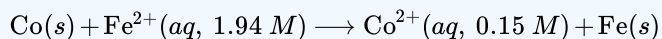
or

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log_{10} Q \quad (9.4.4)$$

If the temperature is not 298.15 K, it is necessary to recalculate the potential with Equation 9.4.2. With the Nernst equation, it is possible to calculate the cell potential at nonstandard conditions. This adjustment is necessary because potentials determined under different conditions will have different values.

✓ Example 9.4.2: Cell Potentials at Nonstandard Conditions

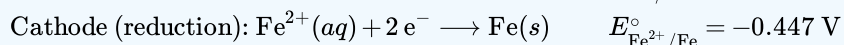
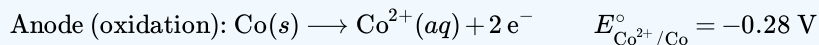
Consider the following reaction at room temperature:



Is the process spontaneous?

Solution

There are two ways to solve the problem. If the thermodynamic information in Table T1 were available, you could calculate the free energy change. If the free energy change is negative, the process is spontaneous. The other approach, which we will use, requires information like that given in Table P1. Using those data, the cell potential can be determined. If the cell potential is positive, the process is spontaneous. Collecting information from Table P1 and the problem,



$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = -0.447 \text{ V} - (-0.28 \text{ V}) = -0.17 \text{ V}$$

The process is not spontaneous under standard conditions. Using the Nernst equation and the concentrations stated in the problem and $n = 2$,

$$Q = \frac{[\text{Co}^{2+}]}{[\text{Fe}^{2+}]} = \frac{0.15 M}{1.94 M} = 0.077$$

Now we can insert these into the Nernst Equation at room temperature (Equation 9.4.4)

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{n} \log Q \\ &= -0.17 \text{ V} - \frac{0.0592 \text{ V}}{2} \log 0.077 \\ &= -0.17 \text{ V} + 0.033 \text{ V} = -0.14 \text{ V} \end{aligned}$$

The process is (still) nonspontaneous.

? Exercise 9.4.2

What is the cell potential for the following reaction at room temperature?



What are the values of n and Q for the overall reaction? Is the reaction spontaneous under these conditions?

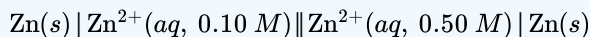
Answer

$n = 6$; $Q = 1440$; $E_{\text{cell}} = +1.97 \text{ V}$, spontaneous.

Finally, we will take a brief look at a special type of cell called a concentration cell. In a concentration cell, the electrodes are the same material and the half-cells differ only in concentration. Since one or both compartments is not standard, the cell potentials will be unequal; therefore, there will be a potential difference, which can be determined with the aid of the Nernst equation.

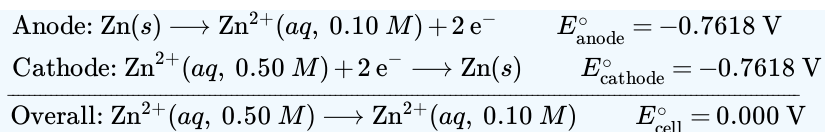
✓ Example 9.4.3: Concentration Cells

What is the cell potential of the concentration cell described by



Solution

From the information given:



The standard cell potential is zero because the anode and cathode involve the same reaction; only the concentration of Zn^{2+} changes. Substituting into the Nernst equation,

$$E_{\text{cell}} = 0.000\text{ V} - \frac{0.0592\text{ V}}{2} \log \frac{0.10}{0.50} = +0.021\text{ V}$$

and the process is spontaneous at these conditions.

Check your answer: In a concentration cell, the standard cell potential will always be zero. To get a positive cell potential (spontaneous process) the reaction quotient Q must be <1 . $Q < 1$ in this case, so the process is spontaneous.

? Exercise 9.4.3

What value of Q for the previous concentration cell would result in a voltage of 0.10 V? If the concentration of zinc ion at the cathode was 0.50 M, what was the concentration at the anode?

Answer

$$Q = 0.00042; [\text{Zn}^{2+}]_{\text{cat}} = 2.1 \times 10^{-4}\text{ M}.$$

Summary

Electrical work (w_{ele}) is the negative of the product of the total charge (Q) and the cell potential (E_{cell}). The total charge can be calculated as the number of moles of electrons (n) times the Faraday constant ($F = 96,485\text{ C/mol e}^{-}$). Electrical work is the maximum work that the system can produce and so is equal to the change in free energy. Thus, anything that can be done with or to a free energy change can also be done to or with a cell potential. The Nernst equation relates the cell potential at nonstandard conditions to the logarithm of the reaction quotient. Concentration cells exploit this relationship and produce a positive cell potential using half-cells that differ only in the concentration of their solutes.

9.4.1: Key Equations

- $E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln K$
- $E_{\text{cell}}^{\circ} = \frac{0.0257\text{ V}}{n} \ln K = \frac{0.0592\text{ V}}{n} \log K \quad (\text{at } 298.15\text{ K})$
- $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{RT}{nF} \ln Q \quad (\text{Nernst equation})$
- $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0257\text{ V}}{n} \ln Q = E_{\text{cell}}^{\circ} - \frac{0.0592\text{ V}}{n} \log Q \quad (\text{at } 298.15\text{ K})$
- $\Delta G = -nFE_{\text{cell}}$
- $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$
- $w_{\text{ele}} = w_{\text{max}} = -nFE_{\text{cell}}$

Glossary

concentration cell

galvanic cell in which the two half-cells are the same except for the concentration of the solutes; spontaneous when the overall reaction is the dilution of the solute

electrical work (w_{ele})

negative of total charge times the cell potential; equal to w_{max} for the system, and so equals the free energy change (ΔG)

Faraday's constant (F)

charge on 1 mol of electrons; $F = 96,485\text{ C/mol e}^{-}$

Nernst equation

equation that relates the logarithm of the reaction quotient (Q) to nonstandard cell potentials; can be used to relate equilibrium constants to standard cell potentials

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