

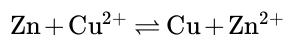
17.14: Cells at Non-Standard Conditions

As shown in the [section on cell notation](#), a [galvanic cell](#) in shorthand form can be written:



The parenthetical notes of (1 M) are frequently omitted because 1 M is at the standard state. However, cells can be created which use concentrations other than 1 M. In such a case, one must always indicate the concentrations as shown above. In fact, as the reaction for the cell written above takes place (that is, as the cell provides electric current), Cu^{2+} will be used up while Zn^{2+} will be generated. The reactant concentrations will decrease and the product concentrations will increase until the solution has reached a [state of equilibrium](#). These equilibrium concentrations are not likely to be at the standard 1 M solutions indicated above.

The voltage of a cell at non-standard state is modified by the relative concentrations of the reactants and products. That is, the cell emf depends on the reaction quotient, Q . The equation for the reaction in the cell is



We can determine the reaction quotient, Q , as follows. (Note that when denoting actual concentrations, which may or may not be equilibrium concentrations, curly brackets are used.)

$$Q = \frac{\{\text{Zn}^{2+}\}}{\{\text{Cu}^{2+}\}}$$

Notice that only the aqueous states are included in the reaction quotient. Using an equation from [Galvanic Cells and Free Energy](#), we can see that the electromotive force is related to ΔG° (at standard states). (Recall that z is the number of electrons transferred and F is the Faraday constant.) This holds true even when the cell is not at standard conditions.

$$\Delta G^\circ = -zFE^\circ \quad \text{and} \quad \Delta G = -zFE$$

We will not derive it here, but there is a relationship for ΔG for non-standard conditions:

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

Combining these equations gives a single equation for the Electromotive force of a non-standard galvanic cell: **The Nernst Equation**.

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{RT}{zF} \ln Q$$

For ease of calculation, we can change the base of the logarithm to base 10 (although most standard calculators have a natural logarithm button), the simple formula below is another commonly used form of the Nernst Equation:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{2.303RT}{zF} \log Q$$

As most of the Galvanic cells in use will be at room temperature ($T = 25^\circ\text{C}$), we can substitute all of the constant values ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and $F = 96,485 \text{ J V}^{-1} \text{ mol}^{-1}$), yielding an even simpler formula:

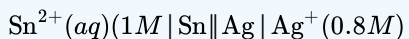
$$E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0592\text{V}}{z} \log Q \quad (T = 298 \text{ K})$$

If you calculate Q for the standard-state concentration of 1 M (or pressure of 1 bar), note how the second term on the right-hand-side disappears and you recover $E_{\text{cell}} = E_{\text{cell}}^\circ$.

Although the Nernst equation is useful to predict the actual voltage of a cell under non-standard conditions, it is frequently more useful to use the measured voltage to *detect* the concentration of one of the species. For instance, if we use a standard H_2/Pt half-cell, the detected voltage of that half reaction coupled with an unknown concentration of Fe^{2+} can be used to determine the concentration of Fe^{2+} .

✓ Example 17.14.1 : Voltage of a Galvanic Cell

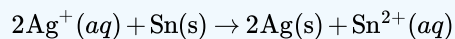
Determine the voltage measured for this galvanic cell. You may need to use the Table of Standard Reduction Potentials.



Solution:

The strategy for solving these problems is to first find the standard electromotive force, as shown in [another section](#), and then write the balanced chemical equation, from which you can derive Q and z .

$$E_{\text{cell}}^{\circ} = 0.7991 \text{ V} - (-0.1375) \text{ V} = 0.9366 \text{ V}$$



The expression for Q can be derived only from the balanced chemical equation. Thus, using the Nernst Equation, we have,

$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^{\circ} - \frac{0.0592 \text{ V}}{z} \log Q \\ &= 0.9366 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{\{\text{Sn}^{2+}(aq)\}}{\{\text{Ag}^+(aq)\}^2} \\ &= 0.9366 \text{ V} - \frac{0.0592 \text{ V}}{2} \log \frac{(1 \text{ M})}{(0.8 \text{ M})^2} \\ E_{\text{cell}} &= 0.9308 \text{ V} \end{aligned}$$

This page titled [17.14: Cells at Non-Standard Conditions](#) is shared under a [CC BY-NC-SA 4.0](#) license and was authored, remixed, and/or curated by [Ed Vitz](#), [John W. Moore](#), [Justin Shorb](#), [Xavier Prat-Resina](#), [Tim Wendorff](#), & [Adam Hahn](#).