17.14: Cells at Non-Standard Conditions

As shown in the section on cell notation, a galvanic cell in shorthand form can be written:

$$\text{Zn} \,|\, \text{Zn}^{2+}\,(1M) \,\|\, \text{Cu}^{2+}\,(1M) \,|\, \text{Cu}$$

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

$$\text{Zn} + \text{Cu}^{2+} \rightleftharpoons \text{Cu} + \text{Zn}^{2+}$$
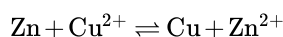
We can determine the reaction quotient, Q, as follows. (Note that when denoting actual concentrations, which may or may not be equilibrium concentrations, curly brackets are used.)

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

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 $\Delta G°$ (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.

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

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

$$\Delta G = \Delta G° + RT \ln Q$$

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

$$E_{\text{cell}} = E°_{\text{cell}} - \frac{RT}{zF} \ln Q$$

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:

$$E_{\text{cell}} = E°_{\text{cell}} - \frac{2.303RT}{zF} \log Q$$

As most of the Galvanic cells in use will be at room temperature ($T = 25$ °C), we can substitute all of the constant values ($R = 8.314$ J mol^{-1} K^{-1} and $F = 96{,}485$ J V^{-1} mol^{-1}), yielding an even simpler formula:
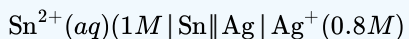
$$E_{\text{cell}} = E°_{\text{cell}} - \frac{0.0592\text{V}}{z} \log Q \qquad (T = 298 \text{ K})$$

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 $E_{\text{cell}} = E°_{\text{cell}}$.

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
>
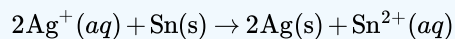> Determine the voltage measured for this galvanic cell. You may need to use the Table of Standard Reduction Potentials.
>
> $$\text{Sn}^{2+}(aq)(1M\,|\,\text{Sn}\,\|\,\text{Ag}\,|\,\text{Ag}^{+}(0.8M)$$
>
> **Solution:**
>
> The strategy for solving these problems is to first find the standard electromotive force, as shown in another section, and then write the balanced chemical equation, from which you can derive Q and z.
>
> $$E^{\circ}_{\text{cell}} = 0.7991\text{ V} - (-0.1375)\text{ V} = 0.9366\text{ V}$$
>
> $$2\text{Ag}^{+}(aq) + \text{Sn}(s) \rightarrow 2\text{Ag}(s) + \text{Sn}^{2+}(aq)$$
>
> The expression for Q can be derived only from the balanced chemical equation. Thus, using the Nernst Equation, we have,
>
> $$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592\text{ V}}{z}\log Q$$
>
> $$= 0.9366\text{ V} - \frac{0.0592\text{ V}}{2}\log \frac{\left\{\text{Sn}^{2+}(aq)\right\}}{\left\{\text{Ag}^{+}(aq)\right\}^{2}}$$
>
> $$= 0.9366\text{ V} - \frac{0.0592\text{ V}}{2}\log \frac{(1\ M)}{(0.8\ M)^{2}}$$
>
> $$E_{\text{cell}} = 0.9308\text{ V}$$

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