

7.4: Types of Electrochemical Cells

Concentration Cells

A concentration cell is an **electrolytic cell** that is comprised of two half-cells with the same electrodes, but differing in concentrations. A concentration cell acts to dilute the more concentrated solution and concentrate the more dilute solution, creating a voltage as the cell reaches an equilibrium. This is achieved by transferring the electrons from the cell with the lower concentration to the cell with the higher concentration.

The **standard electrode potential**, commonly written as E°_{cell} , of a concentration cell is equal to zero because the electrodes are identical. But, because the ion concentrations are different, there is a potential difference between the two half-cells. One can find this potential difference via the **Nernst Equation**,

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0592}{n} \log Q \quad (7.4.1)$$

at 25°C. The E stands for the voltage that can be measured using a voltmeter (make sure if the voltmeter measures it in millivolts that you convert the number before using it in the equation). Note that the Nernst Equation indicates that cell potential is dependent on concentration, which results directly from the dependence of free energy on concentration. Remember that to find Q you use this equation:

$$aA + bB \rightleftharpoons cC + dD \quad (7.4.2)$$

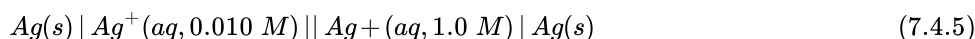
$$Q = \frac{(C)^c * (D)^d}{(A)^a * (B)^b} \quad (7.4.3)$$

When $Q=1$, meaning that the concentrations for the products and reactants are the same, then taking the log of this equals zero. When this occurs, the E_{cell} is equal to the E°_{cell} .

Another way to use the E°_{cell} , or to find it, is using the equation below.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \quad (7.4.4)$$

A voltage can also be generated by constructing an electrochemical cell in which each compartment contains the same redox active solution but at different concentrations. The voltage is produced as the concentrations equilibrate. Suppose, for example, we have a cell with 0.010 M AgNO_3 in one compartment and 1.0 M AgNO_3 in the other. The cell diagram and corresponding half-reactions are as follows:



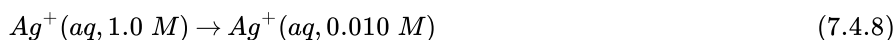
cathode:



anode:



Overall



As the reaction progresses, the concentration of Ag^+ will increase in the left (oxidation) compartment as the silver electrode dissolves, while the Ag^+ concentration in the right (reduction) compartment decreases as the electrode in that compartment gains mass. The total mass of $\text{Ag}(s)$ in the cell will remain constant, however. We can calculate the potential of the cell using the Nernst equation, inserting 0 for E°_{cell} because $E^\circ_{\text{cathode}} = -E^\circ_{\text{anode}}$:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \left(\frac{0.0591 \text{ V}}{n} \right) \log Q = 0 - \left(\frac{0.0591 \text{ V}}{1} \right) \log \left(\frac{0.010}{1.0} \right) = 0.12 \text{ V} \quad (7.4.9)$$

An electrochemical cell of this type, in which the anode and cathode compartments are identical except for the concentration of a reactant, is called a **concentration cell**. As the reaction proceeds, the difference between the concentrations of Ag^+ in the two

compartments will decrease, as will E_{cell} . Finally, when the concentration of Ag^+ is the same in both compartments, equilibrium will have been reached, and the measured potential difference between the two compartments will be zero ($E_{\text{cell}} = 0$).

✓ Example 7.4.2

Calculate the voltage in a galvanic cell that contains a manganese electrode immersed in a 2.0 M solution of MnCl_2 as the cathode, and a manganese electrode immersed in a 5.2×10^{-2} M solution of MnSO_4 as the anode ($T = 25^\circ\text{C}$).

Given: galvanic cell, identities of the electrodes, and solution concentrations

Asked for: voltage

Strategy:

- Write the overall reaction that occurs in the cell.
- Determine the number of electrons transferred. Substitute this value into the Nernst equation to calculate the voltage.

Solution

A This is a concentration cell, in which the electrode compartments contain the same redox active substance but at different concentrations. The anions (Cl^- and SO_4^{2-}) do not participate in the reaction, so their identity is not important. The overall reaction is as follows:



B For the reduction of $\text{Mn}^{2+}(\text{aq})$ to $\text{Mn}(\text{s})$, $n = 2$. We substitute this value and the given Mn^{2+} concentrations into Equation ???:

$$E_{\text{cell}} = E_{\text{cell}}^\circ - \left(\frac{0.0591 \text{ V}}{n} \right) \log Q = 0 \text{ V} - \left(\frac{0.0591 \text{ V}}{2} \right) \log \left(\frac{5.2 \times 10^{-2}}{2.0} \right) = 0.047 \text{ V}$$

Thus manganese will dissolve from the electrode in the compartment that contains the more dilute solution and will be deposited on the electrode in the compartment that contains the more concentrated solution.

? Exercise 7.4.2

Suppose we construct a galvanic cell by placing two identical platinum electrodes in two beakers that are connected by a salt bridge. One beaker contains 1.0 M HCl , and the other a 0.010 M solution of Na_2SO_4 at pH 7.00. Both cells are in contact with the atmosphere, with $P_{\text{O}_2} = 0.20$ atm. If the relevant electrochemical reaction in both compartments is the four-electron reduction of oxygen to water:



What will be the potential when the circuit is closed?

Answer 0.41 V

Fuel Cells

References

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