

CHEM1001 Worksheet 13: Electrochemistry

Model 1: Reduction Potentials

The **standard reduction potential**, E_{red}^0 has units of volts (V) and is a measure of a species' ability to attract electrons. The *more positive* the reduction potential, the *stronger* is the attraction for electrons. Put another way, the *more positive* the reduction potential, the easier the reduction occurs. Some standard reduction potentials are given below.

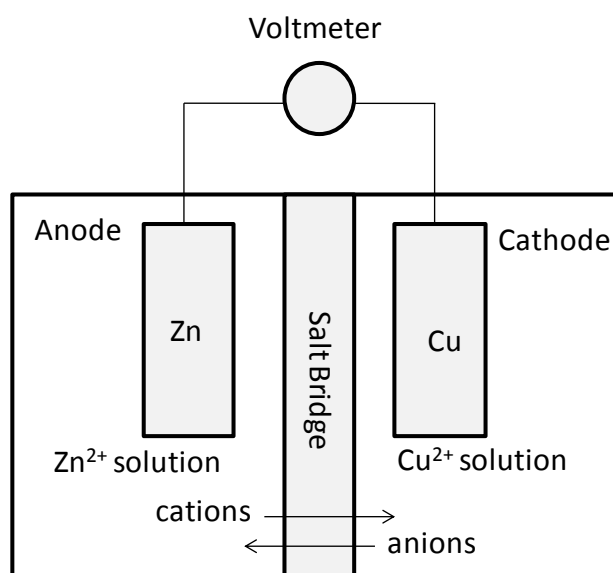
| | Reduction reaction | E_{red}^0 (V) |
|---|----------------------------------------------------------------------------------|------------------------|
| 1 | $\text{Ag}^+(\text{aq}) + \text{e}^- \rightleftharpoons \text{Ag}(\text{s})$ | +0.80 |
| 2 | $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu}(\text{s})$ | +0.34 |
| 3 | $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Ni}(\text{s})$ | -0.25 |
| 4 | $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Zn}(\text{s})$ | -0.76 |

Critical thinking questions

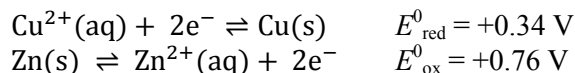
1. Which is a stronger **oxidising** agent: Ag^+ or Cu^{2+} ? Explain how you can tell in terms of the reduction potentials.
2. If reactions 1 and 2 are added together as a redox reaction which do you think will proceed as a reduction and which as an oxidation?(*Hint*:. which one will reverse?)
3. Apply the same logic to reactions 3 and 4. Does it matter that they both have negative reduction potentials?

Model 2: Voltaic Cells

We can harness the electrical energy in a redox reaction, to make a battery, by setting up a **voltaic cell**. To do this, two half reactions are separated into compartments and electrodes are used to facilitate the electron transfer.



The potentials for the two reactions are:



This gives an overall voltmeter reading of:

$$E_{\text{cell}}^0 = E_{\text{ox}}^0 + E_{\text{red}}^0 = +1.10 \text{ V}.$$

This cell is also be described using shorthand notation:



where “||” represents the salt bridge.

Critical thinking questions

1. Explain why the Zn half reaction is proceeding as an oxidation. Why is +0.76 V used as the potential instead of -0.76 V as in the table in Model 1?
2. Which electrode (Zn or Cu) will *erode*, and which one will *gain* mass?

3. Does oxidation or reduction occur at the cathode?
4. Which way do electrons flow through the wire? (*Hint*: are they flowing from the anode to the cathode or vice versa?) Explain why you think this would happen.
5. Electrons flow from the *negative* electrode to the *positive* electrode. Which is positive, the anode or the cathode?
6. The diagram shows anions flowing into the anode compartment, while cations flow into the cathode compartment. Why *must* this happen?
7. If an electrochemical cell with Ag and Cu electrodes was setup, what would be the two half reactions, which would be the cathode and which would be the anode, and what would be the standard cell potential? (*Hint*: use the standard reduction potentials in Model 1.)
8. If an electrochemical cell with Ni and Cu electrodes was setup, what would be two half reactions, which would be the cathode and which would be the anode, and what would be the standard cell potential?
9. If an electrochemical cell with Ni and Zn electrodes was setup, what would be two half reactions, which would be the cathode and which would be the anode, and what would be the standard cell potential?
10. Which combination of these cells would make the highest voltage battery?

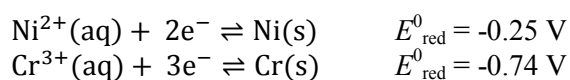
Model 3: Nernst Equation

The *standard* cell potential of the voltaic cell in Model 2 was calculated to be $E_{\text{cell}}^0 = +1.10 \text{ V}$. *Standard* cell potentials correspond to cells where the concentrations of each species are 1M. In batteries, the concentrations of the ions change and the potentials decreases over time. We can calculate this using the Nernst Equation:

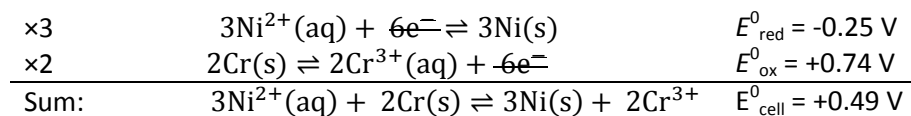
$$E_{\text{cell}} = E_{\text{cell}}^0 - \frac{RT}{nF} \ln Q$$

where E_{cell} is the cell potential, E_{cell}^0 is the standard cell potential, n is the number of electrons that are transferred in the reaction and Q is the reaction quotient. R and F are the gas and Faraday's constant respectively and T is the temperature in Kelvin.

Consider a voltaic cell involving the following half reactions. To calculate the cell potential when $[\text{Ni}^{2+}] = 1.0 \times 10^{-4} \text{ M}$ and $[\text{Cr}^{3+}] = 2.0 \times 10^{-3} \text{ M}$ at $25 \text{ }^\circ\text{C}$, we first need to calculate the standard cell potential by looking up the half cells in a databook:



As the Cr half cell has the *most negative* value, it is reversed and becomes the oxidation. When the half cells are combined, the electrons supplied by the oxidation half cell must balance those used by the reduction half cell. This is achieved by multiplying the half cells as below:



Notice that the half cell equations were multiplied to balance the electrons before they were added. The potentials were *not* multiplied!

From this we can see that 6 electrons are involved so n = 6, We also calculated that E⁰_{cell} = 0.49 V. The reaction quotient, Q, is written down in the normal way; $Q = \frac{[\text{Cr}^{3+}]^2}{[\text{Ni}^{2+}]^3}$.

Lastly, we can put all of this information into the Nernst equation to work out the cell potential when [Ni²⁺] = 1.0 × 10⁻⁴ M and [Cr³⁺] = 2.0 × 10⁻³ M at 25 °C:

$$E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln \frac{[\text{Cr}^{3+}]^2}{[\text{Ni}^{2+}]^3} = (+0.49 \text{ V}) - \frac{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{6 \times 96485 \text{ C mol}^{-1}} \ln \frac{(2.0 \times 10^{-3})^2}{(1.0 \times 10^{-4})^3} = +0.42 \text{ V}$$

Critical thinking questions

1. Apply these steps to the Zn/Cu cell described in Model 2, to work out its cell potential at 298 K when [Cu²⁺] = 0.010 M and [Zn²⁺] = 1.0 M?

2. What happens to a battery when $E_{cell}^0 = \frac{RT}{nF} \ln Q$?

3. What do you do to recharge a battery?

Model 4 Electrolytic cells

An *electrolytic cell* is the opposite of a battery. In a battery, the electrical energy of a chemical reaction between two half cells is harnessed. In an *electrolytic cell* we put in electrical energy to make a reaction go in reverse. This process is called *electrolysis*.

Critical thinking questions

1. Using the voltaic cell in Model 2 as a guide complete the electrolytic cell drawn opposite.

You need to add:

- direction of electron travel
- anode and cathode compartment
- direction in which the cations move
- direction in which the anions move

2. What are the oxidation and reduction half reactions?

3. What is the *minimum* potential needed in the power source to drive this electrolytic cell (*Hint*: what voltage is obtained from this cell when it operates as a battery)

4. Which of the Zn and Cu electrodes will erode and which will gain mass?

We can use *Faraday's Law* to determine the amount of chemical change that occurs during electrolysis.

$$\text{amount of product} = \frac{It}{nF}$$

where the amount of product (mol), I is the current in amps (A), t is the time (s), n is the number of electrons transferred in the reaction and F is Faraday's constant (96485 C mol^{-1}).

5. What unit is A (amps) equivalent to?
6. What *mass* of zinc is deposited on the cathode of an electrolytic cell if a current of 2.00 A is run through the cell for a period of 20.0 min?
7. For an electrolytic cell with the following half reactions, what potential is required to plate silver onto an electrode? And how long will it take to plate 40.0 grams with a current of 5.20 A?

