

Electrochemistry

Review:

Reduction: the gaining of electrons

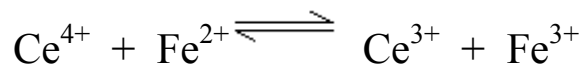
Oxidation: the loss of electrons

Reducing agent (reductant): species that donates electrons to reduce another reagent.

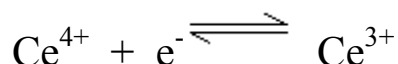
Oxidizing agent (oxidant): species that accepts electrons to oxidize another species.

Oxidation-reduction reaction (redox reaction): a reaction in which electrons are transferred from one reactant to another.

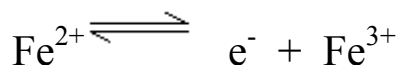
1. For example, the reduction of cerium(IV) by iron(II):



a. The reduction half-reaction is given by...



b. The oxidation half-reaction is given by...



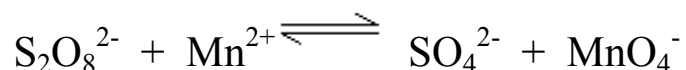
Rules for Balancing Oxidation-Reduction Reactions

A. Write out half-reaction.

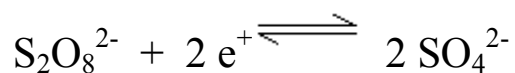
B. Balance the half-reactions by adding H^+ , OH^- or H_2O as needed, maintaining electrical neutrality.

C. Combine the two half-reactions such that the number of electrons transferred in each cancels out when combined.

D. For example, consider the following reaction of the peroxydisulfate ion with manganese ion:

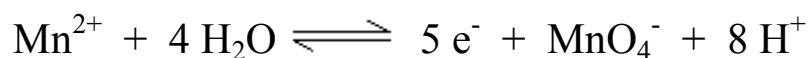


1. The reduction step is...



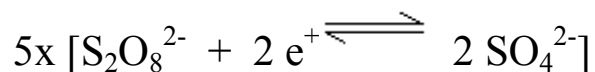
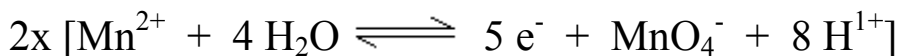
(Each sulfur atom goes from +7 to +6 oxidation state.)

2. The oxidation step is...

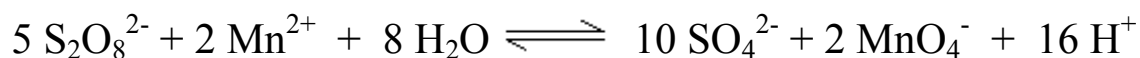


(Manganese(II) loses 5 electrons, going from +2 to +7.)

3. In combining the two equations, the oxidation step must be multiplied by "2," and the reduction step must be multiplied by "5" to cancel out the electrons:



Adding these two equations together...

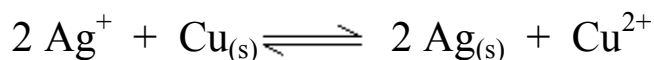


6. Note that the half-reactions are charge-balanced before adding them together.

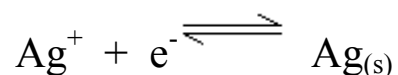
Oxidation-Reduction Reactions in Electrochemical Cells

A. It is possible to separate the half-reactions of an oxidation-reduction reaction in an electrochemical cell.

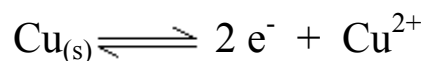
B. Consider the following reaction:



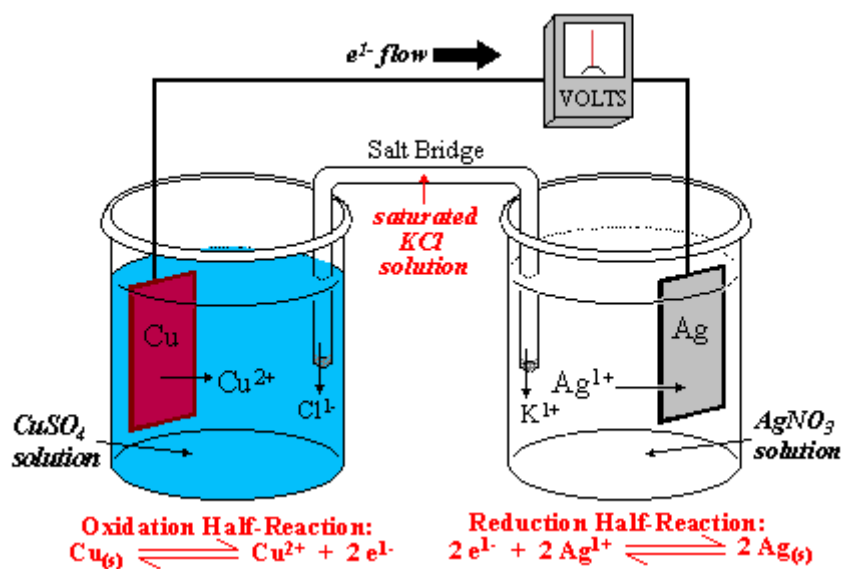
1. The reduction half-reaction is given by...



2. The oxidation half-reaction is given by...



C. These reactions can be "separated" in a galvanic cell (also called a voltaic cell or battery):



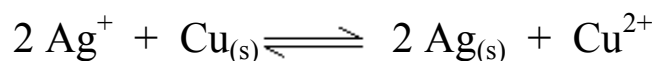
Schematic Representation of Cells

A. The copper(II) sulfate/silver nitrate systems described above would be symbolized...



1. Each vertical line ("|") represents a phase boundary or interface where a potential develops.
2. Each double vertical line ("||") represents two phase boundaries (e.g., the salt bridge).
3. The direction of electron flow is from left to right: Cu--->Ag.

B. The equilibrium expression for this galvanic cell would be...



a. If the battery, initially with 0.0200 M copper ion and 0.0200 M silver ion, is allowed to react to equilibrium, the final concentrations of these ions at equilibrium is determined experimentally to be 0.0300 M copper ion and 2.7×10^{-9} M silver ion.

$$K_{\text{eq}} = \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{2+}]^2} = \frac{.0300}{(2.7 \times 10^{-9})^2} = 4.14 \times 10^{15}$$

Note that the calculation above requires that the cell voltage be zero (i.e., at equilibrium) and that the concentrations be determined by analysis.

Electric charge/Electromotive force

-Electric charge (q) measured in coulombs (C)

- Magnitude of charge of a single electron is 1.602×10^{-19} C

- Mole of electrons has a charge of:

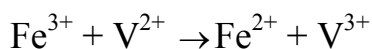
$$(1.602 \times 10^{-19} \text{ C}) \times (6.022 \times 10^{23} \text{ mol}^{-1}) = \underline{9.649 \times 10^4 \text{ C}}$$

$$q = n \cdot F$$

where $n = \#$ moles, $F =$ Faraday constant

Relate (C) to Quantity of Reactions

Ex. If 5.585 g of Fe^{3+} were reduced in the reaction below, how many coulombs of charge must have been transferred from V^{2+} to Fe^{3+} ?



$$0.1000 \text{ mol e}^- \left(9.649 \times 10^4 \frac{\text{C}}{\text{mol e}^-} \right) = 9.649 \times 10^3 \text{ C}$$

Work, Voltage and Free Energy

$$\text{Work (J)} = E \text{ (V)} \cdot q$$

E = diff in electrical potential (potential difference)

Ex. Electrical Work, p. 285

Free Energy, ΔG – Chapter 6 Review*****

$$\Delta G = -nFE$$

(Relation between free energy difference and potential difference)

→ spontaneous reaction: $\Delta G < 0$ and $E > 0$

→ nonspontaneous reaction: $\Delta G > 0$ and $E < 0$

Ohm's Law

$$I = \frac{E}{R}$$

where I = current, R = resistance (Ω)

Power (W)

$$P = \frac{\text{work}}{s} = \frac{E \times q}{s} = E \times \frac{q}{s}$$

$$P = E \cdot I$$

Fig. 14.2 Electric current diagram

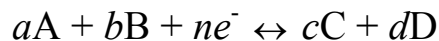
$$I = \frac{E}{R} = \frac{3.0 \text{ V}}{100 \Omega} = 0.030 \text{ A} = 30 \text{ mA}$$

$$P = E \cdot I = (3.0 \text{ V})(0.030 \text{ A}) = 90 \text{ mW}$$

Electrochemical Cell revisited...

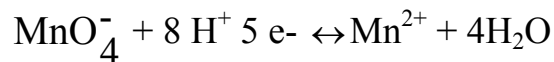
Interpreting Electrode Potentials

- always write half-reactions as reductions (IUPAC)



$$E = E^{\circ} - \frac{0.0592}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Ex. Calculate the electrode potential of a half-cell containing 0.100 M KMnO_4 and 0.0500 M MnCl_2 solution whose pH is 1.000. $E^{\circ}_{\text{MnO}_4/\text{Mn}^{2+}} = 1.51$



$$E = E^{\circ}_{\text{MnO}_4/\text{Mn}^{2+}} - \frac{0.0592}{n} \log \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-][\text{H}^+]^8}$$

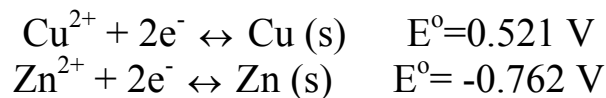
At pH = 1.000,

$$[\text{H}_3\text{O}^+] = 1.00 \times 10^{-1} \text{ M}$$

$$E = 1.51 - \frac{0.0592}{5} \log \frac{0.0500}{(0.100)(1.00 \times 10^{-1})^8} = 1.42 \text{ V}$$

* Advice for Finding Relevant Half-Reactions, 14-4, p. 297

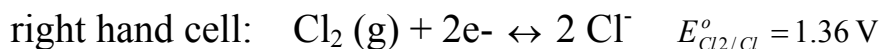
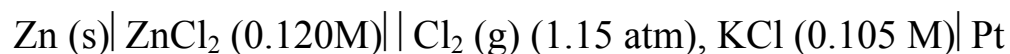
- as the tendency for a half-reaction to proceed in the direction of reduction increases, the electrode potential of the half-cell also increases → determine which substance is better oxidizing agent:



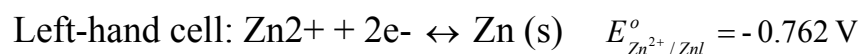
Calculating cell voltage

$$\Delta E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

Ex. Calculate the voltage of the following cell:



$$\begin{aligned} E &= E^{\circ} - \frac{0.0592}{n} \log \frac{[\text{Cl}^-]^2}{P_{\text{Cl}_2}} \\ &= 1.36 - \frac{0.0592}{2} \log \frac{(0.105)^2}{1.15} = 1.42 \text{ V} \end{aligned}$$



$$= E^{\circ} - \frac{0.0592}{n} \log \frac{1}{[\text{Zn}^{2+}]} = -0.762 - \frac{0.0592}{2} \log \frac{1}{0.120} = -0.789 \text{ V}$$

$$\Delta E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

$$= 1.42 - (-0.789) = 2.21 \text{ V}$$

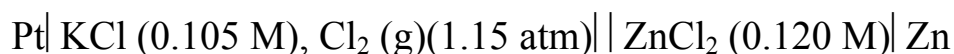
Assumption

-When electrode in cell is not known to be the cathode or right-hand electrode...can assume one electrode is cathode and cell voltage calculated accordingly.

If correct- calculated voltage (+) and the reaction spontaneous

If incorrect – calculated voltage (-) and the spontaneous. Cell reaction will be opposite to the calculated reaction.

Ex. Suppose zinc was the cathode in the cell described above, accordingly made the right-hand electrode:



Calculate the voltage and spontaneous reaction of the cell:

$$E_{\text{zn}} = -0.789 \text{ V}, E_{\text{Pt}} = 1.42 \text{ V}$$

Since zinc is the right-hand electrode:

$$\begin{aligned} \Delta E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= -0.789 - 1.42 = -2.21 \text{ V} \end{aligned}$$

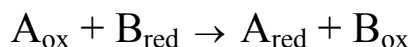
Not spontaneous in the direction written, but rather in the reverse direction

- To establish reaction direction:

Need only to determine which half-cell has the more positive electrode potential

If both electrode potentials are the same, no net driving force (system equilibrium)

Extent of Reaction – The Equilibrium Constant



The voltage of a galvanic cell that would yield this reaction is:

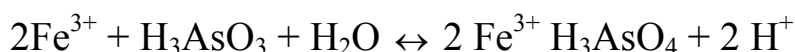
$$\Delta E_{\text{cell}} = E_A - E_B$$

At equilibrium, the cell voltage is zero and $E_A = E_B$

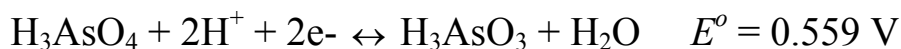
$$\log K_{\text{eq}} = \frac{n(E_A^\circ - E_B^\circ)}{0.0592}$$

*Remember: n is the # of electrons for the two half-reactions and E_A° is the standard electrode potential for the substance being reduced.

Ex. Calculate the equilibrium constant for the reaction:



Half-reactions



$$\log K_{\text{eq}} = \frac{n(E_A^\circ - E_B^\circ)}{0.0592}$$

$$\log K_{\text{eq}} = \frac{2(0.771 - 0.559)}{0.0592} = 7.16$$

$$K_{\text{eq}} = 10^{7.16} = 1.4 \times 10^7$$