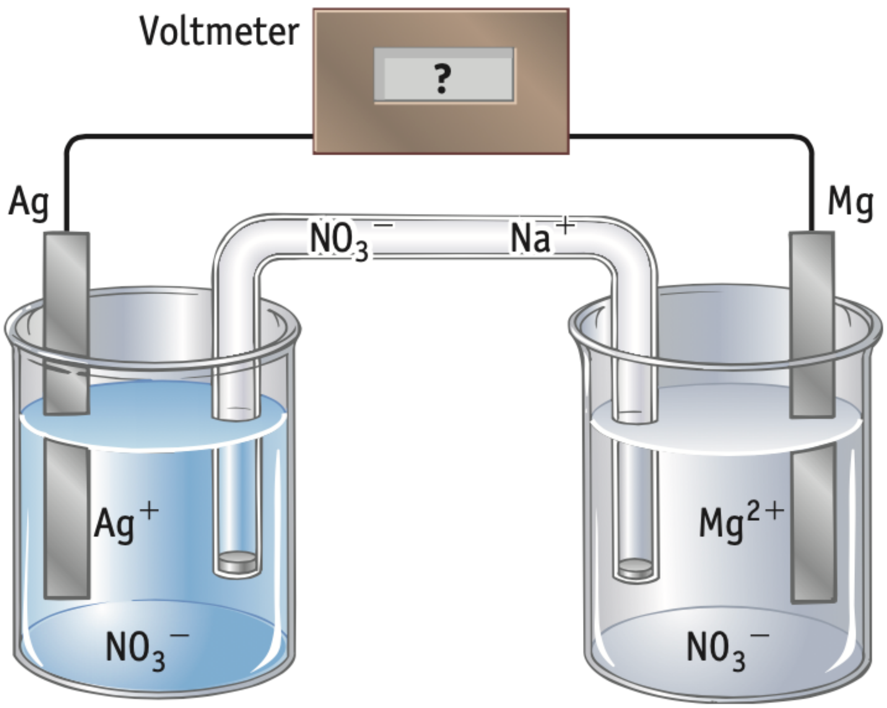
Problems Chapter 19 (Electron Transfer Reactions)

1. Balance the following equations.
   a. Zn (s) + VO^{2+} (aq) → Zn^{2+} (aq) + V^{3+} (aq) (acid solution)
   b. Zn (s) + VO_3^- (aq) → V^{2+} (aq) + Zn^{2+} (aq) (acid solution)
   c. Zn (s) + ClO^- (aq) → $Zn(OH)_2$ (s) + Cl^- (aq) (basic solution)
   d. ClO^- (aq) + $[Cr(OH)_4]^-$ (aq) → Cl^- (aq) + CrO_4^{2-} (aq) (basic solution)
   e. Ag^+ (aq) + C_6H_5CHO (aq) → Ag (s) + C_6H_5COOH (aq) (acid solution)
   f. CH_3CH_2OH (aq) + $Cr_2O_7^{2-}$ (aq) → CH_3COOH (aq) + Cr^{3+} (aq) (acid solution)

2. Magnesium metal is oxidized, and silver ions are reduced in a voltaic cell using Mg^{2+} (aq 1 M)|Mg and Ag^+ (aq, 1 M)|Ag half-cells.



   a. Label each part of the cell.
   b. Write equations for the half-reactions occurring at the anode and the cathode, and write an equation for the net reaction at the cell.
   c. Trace the movement of electrons in the external circuit. Assuming the salt bridge contains $NaNO_3$, trace the movement of the Na^+ and NO_3^- ions in the salt bridge that occurs when a voltaic cell produces current. Why is a salt bridge required in a cell?

3. Which of the following reactions is (are) product-favored?
   a. Zn (s) + I_2 (s) → Zn^{2+} (aq) + 2 I^- (aq)
   b. 2 Cl^- (aq) + I_2 (s) → Cl_2 (g) + 2 I^- (aq)
   c. 2 Na^+ (aq) + 2 Cl^- (aq) → 2 Na (s) + Cl_2 (g)
   d. 2 K (s) + 2 H_2O (l) → 2 K^+ (aq) + H_2 (g) + 2 OH^- (aq)

4. In the table of standard reduction potentials, locate the half-reactions for the reductions for the reductions of the following metal ions to the metal: Sn^{2+} (aq), Au^{+} (aq), Zn^{2+} (aq), Co^{2+} (aq), Ag^{+} (aq), Cu^{2+} (aq). Among the metal ions and metals that make up these half reactions:
    a. Which metal ion is the weakest oxidizing agent?
    b. Which metal ion is the strongest oxidizing agent?
    c. Which metal is the strongest reducing agent?
    d. Which metal is the weakest reducing agent?
    e. Will Sn (s) reduce Cu^{2+} (aq) to Cu (s)?
    f. Will Ag (s) reduce Co^{2+} (aq) to Co (s)?
    g. Which metal ions on the list can be reduced by Sn (s)?
    h. What metals can be oxidized by Ag^{+} (aq)?

5. A cell is constructed using the following half-reactions:

    Ag^{+} (aq) + e^{-} → Ag (s)
    Ag_2SO_4 (s) + 2 e^{-} → 2 Ag (s) + SO_4^{2-} (aq) $E^\circ = 0.653$ V

    a. What reactions should be observed at the anode and cathode?
    b. Calculate the solubility product constant, K_{sp}, for Ag_2SO_4.

6. Electrolysis of molten NaCl is done in cells operating at 7.0 V and 4.0×10^4 A. What mass of Na (s) and Cl_2 (g) can be produced in 1 day in such a cell? What is the energy consumption in kilowatt-hours? (1 kWh = 3.6×10^6 J and 1 J = 1 CV)

7. Write equations for the half-reactions that occur at the anode and cathode in the electrolysis of *molten* KBr, KBr (l). What are the products formed at the anode and cathode in the electrolysis of *aqueous* KBr, KBr (aq)?

8. A voltaic cell set up utilizing the reaction

    Cu (s) + 2 Ag^{+} (aq) → Cu^{2+} (aq) + 2 Ag (s)

    has a cell potential of 0.45 at 298 K. Describe how the potential of this cell will change as the cell is discharged. At what point does the cell potential reach a constant value? Explain your answer?

9. Two Ag^{+} (aq)|Ag half-cells are constructed. The first has $[Ag^{+}]$ = 1.0 M, the second has $[Ag^{+}] = 1.0 \times 10^{-5}$ M. When linked together with a salt bridge and external circuit, a cell potential is observed. (This kind of voltaic cell is referred to as a *concentration cell*.)
    a. Draw a picture of this cell, labeling all components. Indicate the cathode and the anode, and indicate in which direction electrons flow in the external circuit.
    b. Calculate the cell potential at 298 K.

10. Calculate equilibrium constant for the following reactions at 298 K. Indicate whether the equilibrium as written is reactant- or product-favored.
    a. $2\ Cl^{-}\ (aq) + Br_2\ (l) \Leftrightarrow Cl_2\ (aq) + 2\ Br^{-}\ (aq)$
    b. $Fe^{2+}\ (aq) + Ag^{+}\ (aq) \Leftrightarrow Fe^{3+}\ (aq) + Ag\ (s)$

11. Iron (II) ion undergoes a disproportionation reaction to give Fe (s) and the iron (III) ion. That is, iron (II) ion is both oxidized and reduced within the same reaction.

    $3\ Fe^{2+}\ (aq) \Leftrightarrow Fe\ (s) + 2\ Fe^{3+}\ (aq)$

    a. What two half-reactions make up the disproportionation reaction?
    b. Use the values of the standard reduction potentials for the two half-reactions in part (a) to determine whether the disproportionation reaction is product-favored.
    c. What is the equilibrium constant for this reaction at 298 K?

12. Consider the following half-reactions:

    $Pt^{2+}\ (aq) + 2\ e^{-} \rightarrow Pt\ (s)$ $\quad E^{\circ} = 1.118\ V$
    $PtCl_4^{2-}\ (aq) + 2\ e^{-} \rightarrow Pt + 4\ Cl^{-}\ (aq)$ $\quad E^{\circ} = 0.755\ V$
    $NO_3^{-}\ (aq) + 4H^{+}\ (aq) + 3\ e^{-} \rightarrow NO\ (g) + 2\ H_2O\ (l)$ $\quad E^{\circ} = 0.96\ V$

    Explain why platinum metal will dissolve in aqua regia (a mixture of hydrochloric and nitric acids) but not in either concentrated nitric or concentrated hydrochloric acid individually.

13. Consider the standard voltaic cell based on the following half-reactions

    $Cu^{2+}\ (aq) + 2\ e^{-} \rightarrow Cu$
    $Ag^{+}\ (aq) + e^{-} \rightarrow Ag$

    The electrodes in this cell are Ag (s) and Cu (s). Does the cell potential increase, decrease or remain the same when the following changes occur in the standard cell?

    a. $CuSO_4$ (s) is added to the copper half-cell compartment (assuming no volume change).
    b. NH_3 (aq) is added to the copper half-cell compartment. Hint: Cu^{2+} reacts with NH_3 to form $Cu(NH_3)_4^{2+}$.
    c. NaCl (s) is added to the silver half-cell compartment. Hint: Ag^{+} reacts with Cl^{-} to form AgCl (s).
    d. Water is added to both half-cell compartments until the volume of solution is doubled.
    e. The silver electrode is replaced with a platinum electrode.
       $Pt^{2+}\ (aq) + 2\ e^{-} \rightarrow Pt\ (s)$

14. A voltaic cell is constructed based on the following reaction and initial concentrations:

    Fe^{2+} (0.0050 M) + Ag^{+} (2.0 M) ⇔ Fe^{3+} (0.0050 M) + Ag (s)

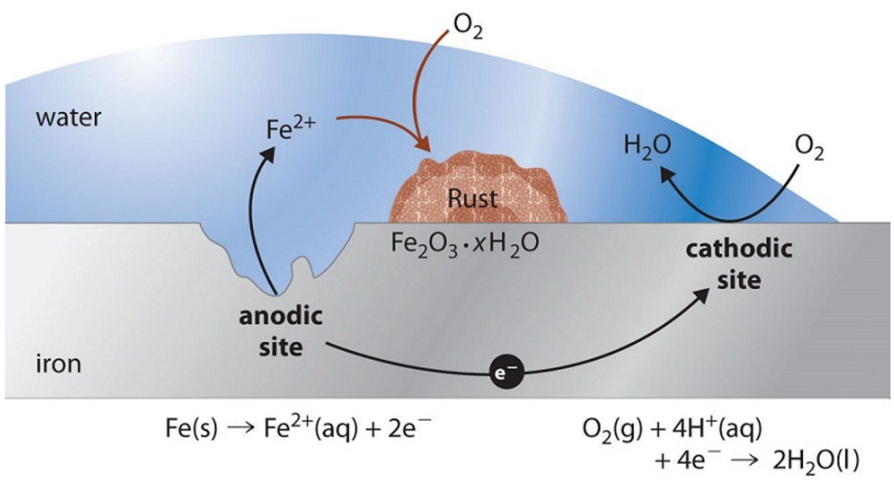
    Calculate [Fe^{2+}] when the cell reaction reaches equilibrium.

15. A battery relies on the oxidation of Mg (s) and the reduction of Cu^{2+} (aq). The initial concentrations of Mg^{2+} and Cu^{2+} are 1.0×10^{-4} M and 1.5 M, respectively, in 1.0-liter half-cells.
    a. What is the initial voltage of the battery?
    b. What is the voltage of the battery after delivering 5.0 A for 8.0 h?
    c. How long can the battery deliver 5.0 A before going dead?

16. The molar mass of a metal (m) is 50.9 g/mol; it forms a chloride of unknown composition. Electrolysis of a sample of the molten chloride with a current of 6.42 A for 23.6 minutes produces 1.20 g of M at the cathode. Determine the empirical formula of the chloride.

Joan Berkowitz: the first female president of the Electrochemical Society

Metals are used extensively in our everyday lives and have an extremely broad range of applications in manufacturing and industry. The integrity of metallic structures can be compromised through oxidation reactions. Through such reactions, metal atoms are converted to metal cations (through electron loss), resulting in loss of the material's desirable metallic properties (e.g., material strength, electrical conductivity, magnetic properties). Vehicles and equipment designed for space exploration should be constructed from materials that can resist oxidation as they are exposed to high temperatures that accelerate these harmful processes.



Joan Berkowitz is a pioneer electrochemist who developed materials for NASA that are stable against high-temperature oxidation and can be used in spacecraft construction. She loved science since young age and studied chemistry at Swarthmore College. While her high school boyfriend and Swarthmore classmate Arthur Mattuck went to graduate school at Princeton University, Berkowitz could not follow him there because Princeton at that time (1952) did not accept women for graduate studies in chemistry. Instead, she obtained her PhD in chemistry at the University of Illinois – Urbana-Champaign (the same institution that awarded the doctoral degree in chemistry to St. Elmo Brady, the first African American recipient of this degree in USA). During her research that she did for the space program as part of the Arthur D. Little management consulting company, she discovered that molybdenum disilicide and tungsten disilicide ($MoSi_2$ and WSi_2) have remarkable resistance against high temperature oxidation, which made these materials suitable for building spacecrafts. Berkowitz was also highly involved in studying issues concerning the environment and investigated ways to reduce pollution from particulate emission by coal-burning plants. Berkowitz served as the first female president of The Electrochemical Society (international professional association that promotes research in the field of electrochemistry) in 1979–1980.

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