Fundamentals of Analytical Chemistry

Chapter 18
Introduction to Electrochemistry

Problems

- 1, 4, 7, 9, 13a-c, 16, 18, 20, 22

## Oxidation/Reduction

- Oxidation
  - Gain of oxygen atoms
  - Loss of hydrogen atoms
  - LOSS OF ELECTRONS!
- Reduction
  - Loss of oxygen atoms
  - Gain of hydrogen atoms
  - GAIN OF ELECTRONS

Oxidation/Reduction

- Must have both oxidation and reduction processes for a reaction to occur
  - Electrons are transferred, not 'lost' or 'gained'
- Oxidizing agent (oxidant)
  - Causes another species to be oxidized
  - Reduced!
- Reducing agent (reductant)
  - Causes another species to be reduced
  - Oxidized!


Balancing Redox Equations

- Half-reaction Method
  - Identify species undergoing change in oxidation state
  - Write individual ½ reactions for species involved in a change in oxidation state
  - Mass balance and charge balance the ½ reactions
  - CHECK FOR REDOX!
  - Balance the electron exchange
  - Recombine, cancelling 'common' species

$MnO_4^- + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2$
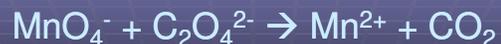
- Identify species undergoing change in oxidation state
  - Manganese and carbon
- Write individual ½ reactions for species involved in a change in oxidation state
  - $MnO_4^- \rightarrow Mn^{2+}$
  - $C_2O_4^{2-} \rightarrow CO_2$

$MnO_4^- + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2$

- Mass balance and charge balance the ½ reactions
  - For manganese ½ reaction – mass balance
  - $MnO_4^- \rightarrow Mn^{2+}$
    - Manganese is balanced
    - We need 4 oxygens in the products (add H_2O)
      - $MnO_4^- \rightarrow Mn^{2+} + 4H_2O$
    - We need 8 hydrogens on the reactants side (add H^+)
      - $8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$
  - Charge Balance
    - Add electrons to equalize the charge on each side
    - $5e^- + 8H^+ + MnO_4^- \rightarrow Mn^{2+} + 4H_2O$

$MnO_4^- + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2$
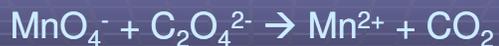
- Mass balance and charge balance ½ reactions
  - For oxalate ½ reaction – mass balance
    - $C_2O_4^{2-} \rightarrow 2CO_2$
  - Charge balance
    - $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$
- Insure both oxidation and reduction!
- Balance the electron exchange
  - $10e^- + 16H^+ + 2MnO_4^- \rightarrow 2Mn^{2+} + 8H_2O$
  - $5C_2O_4^{2-} \rightarrow 10CO_2 + 10e^-$
- Recombine (leaving off common species)
  - $16H^+ + 2MnO_4^- + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10\ CO_2 + 8H_2O$

Balancing Redox Reactions

- Basic solution
  - Balance as previous, then 'neutralize' H^+ with OH^-
  - Cancel common species (again!)
  - $(16H^+ + 16OH^-) + 2MnO_4^- + 5C_2O_4^{2-} \rightarrow$ $2Mn^{2+} + 10\ CO_2 + 8H_2O + 16OH^-$
    - $16H^+ + 16OH^- = 16H_2O$
    - Then cancel 8 H_2O
  - $8\ H_2O + 2MnO_4^- + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10\ CO_2 + 16OH^-$


Terminology

- Electrochemical Cell
  - Same as 'system' in thermodynamics
  - Transfer of electrons
  - Voltaic (or galvanic)
    - Spontaneous chemical reaction leads to current flow
    - Oxidized species must be physically isolated from reduced species
  - Electrolytic
    - Current flow forces a non-spontaneous process to occur

Electrochemical Cell

- Electrodes
  - Interface between charge transport by electrons and charge transport by ions
    - Reduction – Cathode
    - Oxidation – Anode
    - Electrodes may or may not be directly involved in the ½ reaction
      - Inert (redox) electrode only provides a surface for a reaction
      - May be an anode or a cathode (or both)
      - Typically Pt
  - Salt Bridge
    - 3-5% KCl in Agar
    - Allows charge transport w/o mixing of redox species

Electrochemical Cell

- Typical voltaic cell
  - Copper is the cathode
  - Zinc is the anode
- Half reactions
  - $Cu^{2+} + 2e^- \rightarrow Cu$
  - $Zn \rightarrow Zn^{2+} + 2e^-$
- Overall reaction
  - $Cu^{2+} + Zn \rightarrow Cu + Zn^{2+}$
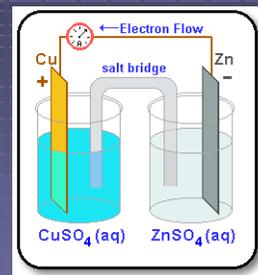
Electrochemical Cells

- Cell Shorthand
  - Zn | Zn^{2+} (conc) || Cu^{2+} (conc) | Cu
    - Start at the anode
    - List all electroactive species (ignoring counter ions)
    - The symbol | indicates a phase change
    - || indicates two phase changes, typically associated with a salt bridge
- Reversible Cells
  - Can 'recharge' with an external potential greater than the cell potential (car battery)

Electrode Potentials

- Current flow indicates a difference in cell potential
  - From thermodynamics, $\Delta G = -nFE$
  - Cell potential is related to free energy
  - Sign for cell potential is opposite that for free energy
    - Negative free energy – spontaneous reaction
    - Positive cell potential – spontaneous reaction

Half-Cell Potentials

- Cannot be measured independently
  - Cannot have a ½ reaction occur independently!
- Cannot determine from *ab initio* calculations
- Must be determined in comparison to other ½ reactions
  - Relative values

Half-Cell Potentials

- Standard Hydrogen Electrode (SHE)
  - $2H^+ + 2e^- \rightarrow H_2(g)$
  - When all species are present <u>under standard conditions</u>, the ½ cell potential for this electrode is BY DEFINITION 0V.
  - All other ½ cell potentials are relative to the SHE
    - The cell of interest is by definition the cathode, the SHE is the anode ($H_2 \rightarrow 2H^+ + 2e^-$)

Standard Cell Potential

- $E^O_{cell} = E^O_{cathode} - E^O_{anode}$
  - Values for $E^O_{½}$ are in Appendix 5
  - Values are 'standard reduction potentials'
    - Determined with the given cell under standard conditions acting as the cathode.
- For the reaction $2Ag^+ + Cu \rightarrow 2Ag + Cu^{2+}$
  - $E^O_{cathode} = 0.799$ V
  - $E^O_{anode} = 0.337$ V
  - $E^O_{cell} = 0.799 - 0.337 = 0.462V$

Standard Electrode Potential

- Relative quantity
- ALWAYS a reduction value
- Everything at unit activity
- Independent of stoichiometry of reaction
- Positive value means spontaneous relative to the SHE
- Temperature dependent

Electrode Potential Under Non-Standard Conditions

- Very few cells are standard cells
- Nernst Equation

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

- R = ideal gas constant (8.314 J/mol·K)
- T = temperature in K
- n = moles of electrons exchanged
- F = Faraday's Constant (96,487 J/V)
- Q = Mass action quotient

Electrode Potential Under Non-Standard Conditions

- 'Working' Nernst equation
  - Substitute in all constants
  - Assume 298K
  - Convert from ln to log by multiplying by ln10

$$E_{cell} = E_{cell}^{o} - \frac{0.05916}{n} \log Q$$

Electrode Potential Under Non-Standard Conditions

- Can be applied to ½ cells as well
  - General equation: $E_{cell} = E_{cathode} - E_{anode}$
  - Nernst equation for ½ cell

$$E_{1/2} = E_{1/2}^{o} - \frac{0.05916}{n} \log Q$$

  - n = number of electrons in the ½ reaction
    - Independent of the number of electrons exchanged!

Limitations

- Use of concentrations
  - Should use activities
- Effect of other equilibria
  - Ions may interact with other species (i.e. iron with chloride)

- Formal Potentials
  - Unless otherwise specified, Q=1 (using concentrations rather than activities) and other conditions specified