

# Electrochemistry

- Topics Covered
  - Spontaneity of redox reactions
  - Effect of concentration on cell emf
- Homework
  - Read 20.7-20.8
  - Exercises 39, 43, 49, 51, 57

## Spontaneity of Redox Reactions

- Any reaction that can occur in a voltaic cell to produce a positive emf must be spontaneous
- In general, we can write:
  - $E^\circ = E^\circ_{\text{red}}(\text{reduction process}) - E^\circ_{\text{red}}(\text{oxidation process})$
- A positive value of E indicates a spontaneous process and a negative value of E indicates a nonspontaneous one

## Sample Problems

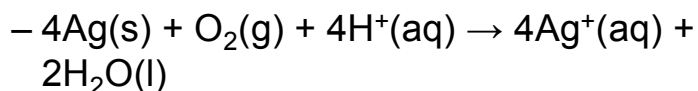
- Determine whether or not the following reactions are spontaneous under standard conditions
  - $\text{Cu(s)} + 2\text{H}^+(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{H}_2(\text{g})$ 
    - Answer: Nonspontaneous
  - $\text{Cl}_2(\text{g}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{Cl}^-(\text{aq}) + \text{I}_2(\text{s})$ 
    - Answer: Spontaneous

## EMF and Free Energy Change

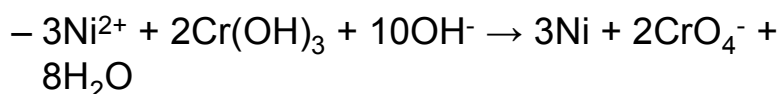
- Gibbs free energy and emf of a redox reaction are related in the following way:
  - $\Delta G = -nFE$  or  $\Delta G^\circ = -nFE^\circ$  (at standard conditions)
  - $n$  is a positive number that represents the number of electrons transferred in the reaction
  - $F$  is called Faraday's constant and is the quantity of charge on 1 mol of electrons
    - $1 F = 96,500 \text{ C/mol} = 96,500 \text{ J/V-mol}$
  - A positive value of  $E$  and a negative value of  $\Delta G$  both indicate that a reaction is spontaneous

## Sample Problems

- Calculate  $\Delta G^\circ$  for the following reactions using standard reduction potentials.



- Answer: -170 kJ/mol



- Answer: 87 kJ/mol

## Effect of Concentration on Cell EMF

- As a voltaic cell discharges, reactants are consumed and products are generated, so the concentrations of these substances change
- The emf progressively drops until  $E = 0$ , at which point the cell is “dead”
- At that point the concentrations of reactants and products are in equilibrium

## The Nernst Equation

- To find the emf of a cell under nonstandard conditions we can use the Nernst equation:

$$E_{cell} = E_{cell}^{\circ} - \frac{RT}{nF} \ln Q \quad \text{or} \quad E_{cell} = E_{cell}^{\circ} - \frac{0.0592}{n} \log Q @ 298 K$$

- Q is the reaction quotient

## Sample Problems

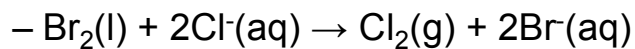
- Given the following reaction:
  - $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{I}^-(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{I}_2(\text{s}) + 7\text{H}_2\text{O}(\text{l})$
- Calculate the emf at 298 K when  $[\text{Cr}_2\text{O}_7^{2-}] = 2.0 \text{ M}$ ,  $[\text{H}^+] = 1.0 \text{ M}$ ,  $[\text{I}^-] = 1.0 \text{ M}$ , and  $[\text{Cr}^{3+}] = 1.0 \times 10^{-5} \text{ M}$ .
  - Answer: 0.89 V
- If the voltage of a Zn-H<sup>+</sup> cell is 0.45 V at 25°C when  $[\text{Zn}^{2+}] = 1.0 \text{ M}$  and  $P_{\text{H}_2} = 1.0 \text{ atm}$ , what is the concentration of H<sup>+</sup>?
  - Answer:  $5.8 \times 10^{-6} \text{ M}$

## Sample Problems

- Using standard reduction potentials, calculate the equilibrium constant for the oxidation of  $\text{Fe}^{2+}$  by  $\text{O}_2$  in acidic solution

- Answer:  $1 \times 10^{31}$

- Calculate the equilibrium constant for the following reaction:



- Answer:  $1.2 \times 10^{-10}$