

Chemistry 475

Redox Reactions and Electrochemistry

Redox Reactions

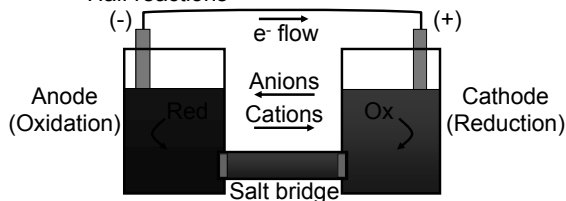
- Family of Reactions in which only Electron Transfer occurs
 - Reduction: gain of electrons
 - Oxidation: loss of electrons
- Other Redox Reactions
 - Atom transfer
 - Radical abstraction/recombination
 - Oxidative addition/reductive elimination

Describing Redox Reactions

- Oxidation Numbers
 - Track gain/loss of electrons relative to elemental state
 - Rules for assigning from chemical formula
 - Rules for assigning from Lewis dot structure
 - Ionic model of electron counting (contrast with formal charge which is pure covalent)
- Used to Balance Redox Reactions
 - Half-reaction method

Describing Redox Reactions

- Standard Cell Potentials (E^0)
 - Relative to SHE at 1.00 m, 1.00 bar, 25.00 °C
 - Direction of spontaneous change
 - Half reactions



Describing Redox Reactions

- Shorthand Notation for Cells
 - | indicates phase boundary
 - || indicates salt bridge ($E_{\text{junction}} = 0$)
 - “Electrode, species” indicates species present on electrode surface
 - Oxidation on left, reduction on right (assumed spontaneous)
- $\text{Zn (s)} + 2 \text{HCl (aq)} \longrightarrow \text{ZnCl}_2 \text{ (aq)} + \text{H}_2 \text{ (g)}$
 $\text{Zn (s)} \mid \text{ZnCl}_2 \text{ (aq)} \parallel \text{HCl (aq)} \mid \text{H}_2 \text{ (g)}, \text{Pt (s)}$

Describing Redox Reactions

- Cell Potentials can be written in Terms of Standard Reduction Potentials (E^0)
 - Rules for using E^0
 - When can you not add two E^0 ?
- Relationship to ΔG^0 for Reaction

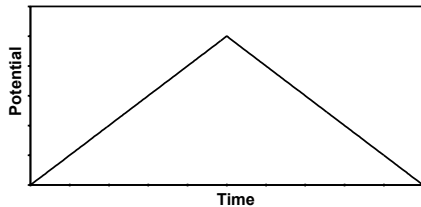
$$\Delta G = -n \cdot \mathcal{F} \cdot E$$

- Nernst Equation gives $E(T, \text{activity})$

$$E = E^0 - \frac{RT}{n\mathcal{F}} \ln(Q)$$

Cyclic Voltammetry

- Primary Method to measure E^0
 - Three electrode method
 - Apply linear ramp of V , measure I (proportional to concentration)



Cyclic Voltammetry

- Each Couple shows two Waves in CV
 - One wave is for reduction (up), one wave for oxidation (down)
 - Determination of oxidation state
 - Average of waves peak potentials is E^0
 - Difference in peaks is $59/n$ mV for a reversible process
- Varying Scan Speed gives Kinetics
- Primary Standard

Cyclic Voltammetry

