

Reading guide and suggested problems for Chapter 12

Chapter 12: Coordination Chemistry: Reactions and Mechanisms. Chapter 12 discusses ligand substitution and oxidation/reduction reactions in coordination complexes.

Learning goals:

- 1) Understand a reaction coordinate diagram, the meaning of ΔG and $\Delta G^\ddagger$, and how these two things relate to the thermodynamics and kinetics of a reaction.
- 2) Identify kinetically inert and labile metal complexes for ligand substitution based on their d electron configuration.
- 3) Know the general mechanisms for dissociative and associative ligand substitution in octahedral and square planar complexes, interpret experimental data and determine if a reaction is dissociative or associative, relate reaction intermediates to the products that form in these reactions.
- 4) Understand the trans effect in substitution reactions for square planar Pt(II) complexes.

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Suggested reading

12.1: Background on reaction coordinate diagrams and how ΔG and $\Delta G^\ddagger$ relate to the reaction's equilibrium constant and rate constant.

12.2, 12.2.1: Defines "labile" and "inert" metal complexes for ligand substitution

12.2.2, 12.3, 12.3.1, 12.3.3: Mechanisms of substitution. These sections describe the dissociative and associative mechanisms of ligand substitution and go a little bit into the rate law equations for these reactions. I do not expect you to know the rate law equations, however you should understand the steps involved in each reaction mechanism and be able to identify the rate determining step in each.

12.4, 12.4.1: Evidence for a reaction going through a dissociative mechanism: This section describes the concept of "Ligand Field Activation Energy" and goes point by point through the different factors that can affect reaction rates in a dissociative mechanism. Get to know these factors!

12.4.3 : Evidence for reactions going through an associative mechanism: The main factor that indicates that an associative type pathway is used is that reaction rate is largely dependent on the identity of the incoming ligand.

12.4.5: The kinetic chelate effect. Chelating ligands undergo ligand substitution reactions at a slower rate than analogous monodentate ligands (for example, ethylene diamine complexes are slower to undergo ligand substitution than amine complexes).

12.5, 12.5.1, 12.5.2. Stereochemistry of reactions. Depending on the starting material and the intermediate that forms, products with different stereochemistries can form. You should be able to predict the structures of products based on whether a square pyramidal or trigonal bipyramidal intermediate forms, or be able to identify the structure of the intermediate based on the structures of the products and reactants.

12.6, 12.6.1, 12.6.2. Substitution in square planar complexes. These sections discuss the mechanism of ligand substitution in square planar complexes (an associative mechanism),

which results in the rates of these reactions being largely dependent on the nature of the incoming ligand.

12.7, 12.7.1 The trans effect. This describes a phenomenon known as the trans effect that occurs in square planar Pt(II) complexes. Based on the ordering of trans effect ligands, you should be able to predict the products formed in ligand substitution reactions. You will have to memorize the trans effect series, briefly:

CO/CN⁻ > PR₃ > SCN⁻ > I⁻ > Br⁻ > Cl⁻ > NH₃ ~ OH⁻ > H₂O

12.8, 12.8.2: Oxidation/reduction reactions. These sections give a general overview of redox reactions and go over factors that can influence the reduction potential of metal complexes. Section 12.8.1 goes into great details about inner sphere vs. outer sphere reactions, this is not a focus of the class.

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Relevant homework problems:

12.1, 12.2, 12.3, 12.4, 12.5, 12.8

12.15, 12.16, 12.17a