5.03 In-Class Exam 4

Christopher C. Cummins

April 30, 2010

Instructions

Clearly write your name at the top of this front page, but otherwise do not write on this front page as it will be used for scoring. This exam is closed-book and no calculators or electronic devices may be employed. There are five sections so please read over the exam before you begin and expect to take on average ten minutes per section. Read all questions carefully before writing down any answers. Enjoy the material!

Section	Points	Possible Points
1		20
2		20
3		20
4		20
5		20
Total:		100

1 Werner's Coordination Theory

The questions for this section are worth 4 points each.

1. Why did Werner's ability to prepare two and only two geometric isomers of $[CoA_4B_2]$ complexes *not* constitute a proof of his coordination theory?
2. What property of $[Co(en)_2(NO_2)_2]Cl$ would have been very useful to Werner had he discovered it? Note: en is the abbreviation for 1,2-ethylenediamine ($H_2NCH_2CH_2NH_2$).
3. The cation in the isomer of $[Co(en)_2(NO_2)_2]Cl$ exhibiting the property of interest belongs to what point group?
4. Use the simple notation of Mohamadou to represent in 2D the isomers that are possible for a complex of the type $[MABC_4]$.
5. Is a complex with three bidentate ligands such as $[Co(en)_3]^{3+}$ chiral?

2 The Trans Effect and Cisplatin

The questions for this section are worth 4 points each.

1. What is a distinguishing feature of the reaction coordinate for ligand substitution at square planar platinum in the case of ethylene as the ligand that is trans to the leaving group?

2. Draw the structure of the yellow compound obtained upon addition of ammonia to $K_2[PtI_4]$.

3. When DNA becomes platinated upon reaction with the antitumor drug cisplatin, what are the ligands (other than DNA bases) that remain on the platinum?

4. In the case of ligand substitution at square planar platinum(II), which is the stronger trans effect ligand: chloride, or iodide?

5. Describe briefly the nature of the chemical interaction between cisplatin and DNA.

3 Ligand Substitution and Water Exchange

The questions for this section are worth 4 points each.

1. True or false: a water molecule stays on average in the first coordination sphere of $[Ir(OH_2)_6]^{3+}$ nearly 300 years before being replaced by another one coming from bulk solvent water.

2. What is the mechanistic classification given to a ligand substitution reaction in which there is evidence in support of an intermediate having a lower coordination number?

3. Measuring water exchange kinetics as a function of what parameter has been most informative as to mechanism?

4. When a ligand substitution reaction has $\Delta V^{\ddagger}$ close to zero, what does this say about the structure of the activated complex (synonym for transition state)?

5. What two factors should be maximized in the design of an effective magnetic resonance imaging (MRI) agent?

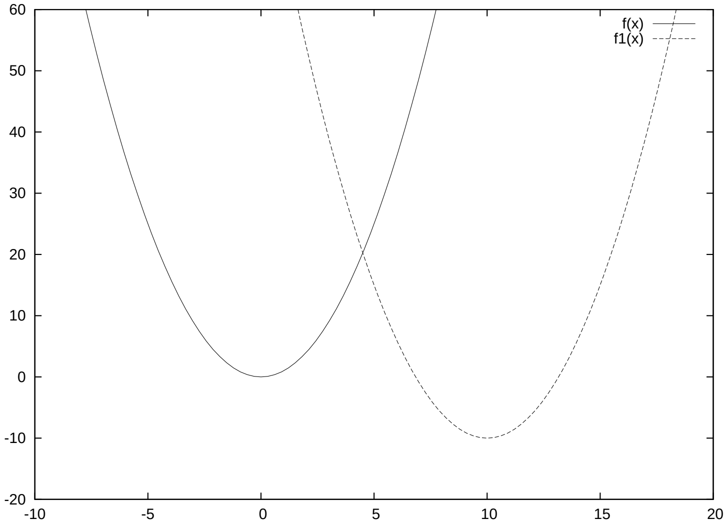
4 Electron Transfer

The questions for this section are worth 4 points each.

1. Draw the structure including all ligands of the successor complex formed in the reduction of $[CoCl(NH_3)_5]^{2+}$ by aqueous chromium(II).

2. True or false: the reaction of the preceding problem is not only an electron transfer reaction but also an atom transfer reaction.

3. Looking at the outer-sphere case diagrammed below, would it be true to say that $-\Delta G^\circ$ is greater than λ?



4. What is the approximate value of λ (arbitrary units) in the case of the above diagram?

5. In the degenerate outer-sphere electron transfer reaction between aqueous iron(II) and iron(III), what can you say about the Fe—O bond distances for the two iron atoms of the activated complex?

5 Mixed Valence Complexes and Mössbauer Spectroscopy

The questions for this section are worth 4 points each.

1. An intervalence charge transfer (IVCT) band that is *not* sensitive to changes in solvent polarity is characteristic for which Robin and Day class of mixed-valence complexes?

2. Briefly, why is it that $[(H_3N)_5Ru(4,4'\text{-bipyridine})Ru(NH_3)_5]^{5+}$ is a class II system whereas $[(H_3N)_5Ru(\text{pyrazine})Ru(NH_3)_5]^{5+}$ can be described as class II/III?

3. What does it mean if in a cyclic voltammogram (electrochemical experiment) only a single oxidation event is observed for a biferrocene molecule with a particular spacer between the two ferrocene units?

4. In the situation where the Mössbauer spectrum of a mixed-valence diiron complex exhibits a pair of quadrupole doublets, is the corresponding IVCT band expected to be sensitive to changes in solvent polarity?

5. In the box below, sketch out the Mössbauer spectrum of a class III biferrocenium ion for which $\delta = 0.4$ and $\Delta E_Q = 1.0$.

-2 -1 0 1 2