Chm 451   Fall 2013   Exam 3   December 4, 2013   Name:

Show your work. Box your answers as appropriate. Explanations limited to 20 words.

1. In class we set up microstate tables in order to determine the term symbols for the free ions d^2 and d^3. Time doesn't allow us to complete this process for d^4 on the exam, but we could at least determine the size of the grid we would need.

   1A. (3 pts) Across the top we would have listed all M_S values. How many columns would you plan for and what is the value of S? (2 answers)

   1B. (3 pts) Similarly, we would display all M_L values as rows. How many rows would you plan for and what is the value of L? (2 answers)

   1C. (2 pts) What is the ground state term symbol for d^4?

2. In an octahedral field of ligands, the d^4 configuration splits.

   2A. (4 pts) Considering only high spin possibilities, sketch an energy diagram (or Tanabe-Sugano diagram) showing this split and sketch an example microstate for each.

   2B. (2 pts) What is the ground state term symbol for an octahedral d^4 metal ion?

   2C. (2 pts) What is the term symbol of the excited state?

   2D. (1 pt) Indicate Δ_o on your diagram.

3. (2 pts each) These questions continue on with the octahedral d^4 example from the previous questions. Again consider high-spin complexes only.

   3A. How many spin-allowed d-d electronic transitions would you predict to be observed in the uv-vis spectrum?

   3B. In addition to what you predicted in 3A, there is a large absorbance in the uv with a molar absorptivity much greater than that for d-d absorbances. What is the cause of this?

   3C. Would the absorbance(s) shift to longer or shorter wavelengths if the metal ion Cr^{+2} (d^4) were replaced by Mn^{+3}, also d^4?

4. (4 pts) Suppose you had only the Tanabe-Sugano diagrams for octahedral complexes available, and were interested in assigning the electronic spectrum for $CoCl_4^{-2}$, tetrahedral d^7. Which octahedral Tanabe-Sugano diagram would you use? Explain why.

5. (6 pts) Tetrahedral complexes are also affected by Jahn-Teller distortions. Predict whether distortions are expected for each of the electron configurations, $d^0 - d^5$. (Need not predict elongation vs. contraction.)

6. (4 pts) A solution of $[Fe(OH_2)_6](NO_3)_3$ has only a pale color, but one of $K_3[Fe(CN)_6]$ is bright red. Why is this so?

7. (3 pts) $K[Fe(S_2CNR_2)_3]$ is an octahedral complex with dithiocarbamato ligands, $^-S_2CNR_2$, where R = an alkyl, such as methyl. At room temperature, solutions of this complex exhibit a large absorbance in the visible spectrum, but when the solution is cooled, the solution turns a light canary yellow. Explain.

8. (4 pts) Consider the substitution reaction involving ethylenediamine, en, $NH_2CH_2CH_2NH_2$:

   $$[Ru(NH_3)_6]^{+3} + en \rightarrow [Ru(NH_3)_4en]^{+3} + 2\ NH_3$$

   Would you expect the equilibrium constant for this reaction to be <1, ≈1, >1? Explain in terms of thermodynamics.

9. (4 pts) Consider the substitution reaction:

   $$[M(H_2O)_6]^{+n} + H_2^{18}O \rightarrow [M(H_2O)_5(H_2^{18}O)]^{+n} + H_2O$$

   The rate of this exchange varies over magnitudes depending on the metal ion. Would you expect Cr^{+3} or high spin Fe^{+3} to have the faster exchange rate? Explain.

10. Consider the substitution reaction and data:

$$[Co(NH_3)_5X]^{2+} + H_2O \rightarrow [Co(NH_3)_5H_2O]^{3+} + X^-$$

X^-	k_{fwd}	$K_{eq} = k_{fwd}/k_{rev}$
F^-	8.6×10^{-8}	0.04
Cl^-	1.7×10^{-6}	0.9
Br^-	6.5×10^{-6}	2.9

10A. (6 pts) Propose the mechanism (we discussed in class) for this reaction and identify the slow step.

10B. (2 pt) Write the rate law for the mechanism.

10C. (2 pts) Would you expect either k or K to change if a better entering group, such as NH_3 were available instead of H_2O?
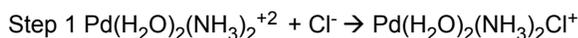
k should: **decrease   stay the same   increase**

K should: **decrease   stay the same   increase**

11. (4 pts) Consider the substitution reactions:

$$[Ru(NH_3)_6]^{+3} + Cl^- \rightarrow [Ru(NH_3)_5Cl]^{+2} + NH_3$$
$$[Ru(en)_2(NH_3)_2]^{+3} + Cl^- \rightarrow [Ru(en)_2(NH_3)(Cl)]^{+2} + NH_3$$
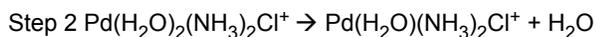
The rate of this exchange varies over magnitudes. Would you expect first or second reaction to have the larger (faster) rate constant? Explain.

12. (4 pts) Square planar complexes often undergo substitution via an associative mechanism as shown in this example. Indicate the signs of ΔH and ΔS for each step by adding <, =, or > (for example, ΔH < 0)

Step 1 $Pd(H_2O)_2(NH_3)_2^{+2} + Cl^- \rightarrow Pd(H_2O)_2(NH_3)_2Cl^+$

ΔH   0; ΔS   0

Step 2 $Pd(H_2O)_2(NH_3)_2Cl^+ \rightarrow Pd(H_2O)(NH_3)_2Cl^+ + H_2O$

ΔH   0; ΔS   0

13. Nitrogen monoxide (commonly called nitric oxide) is a ligand in inorganaic and organometallic chemistry. As a ligand it is called nitrosyl.

13A. (3 pts) Sketch the Lewis dot structure of nitrogen monoxide. In order to get any partial credit for this problem, your Lewis dot structure must be correct! Check: Has no atom exceeded the octet? Have you conserved electrons?

13B. (3 pts) Show how $(OC)_5MnNO$ obeys the 18-electron rule.

13C. (2 pts) What is the predicted Mn-N-O bond angle?

14. In addition to being a 1-electron donor as addressed in Question 13, the nitrosyl ligand can also function as a 3-electron donor: one can imagine that the ligand simply transferred one electron to the metal, making it NO^+ and then bonded in such a way as to donate two more e^-.
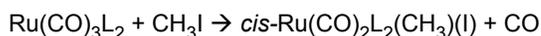
14A. (3 pts) Sketch the Lewis dot structure for NO^+.

14B. (2 pt) What other ligand does this remind you of?

14C. (2 pt) Is NO^+ a π-back-bonding ligand?

14D. (2 pts) What is the Co-N-O bond angle in $Co(CO)_3(NO)$?

15. $Ru(CO)_3L_2$, where L = PPh_3 reacts with CH_3I as shown. The product features CH_3I oxidatively added *cis* (C and I have very similar electronegativities). The reaction mechanism involves two-steps.
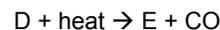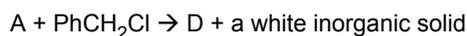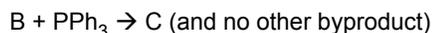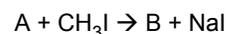
$$Ru(CO)_3L_2 + CH_3I \rightarrow \textit{cis}\text{-}Ru(CO)_2L_2(CH_3)(I) + CO$$
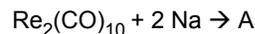
15A. (2 pts) After counting the electrons in $Ru(CO)_3L_2$, what is the first step in the mechanism?

15B. (2 pts) What is the second step?

15B. (2 pts) Sketch the transition state in the second step. You can use [Ru] to represent the intermediate from Step 1.

16. (8 pts) Dimeric metal carbonyls such as $(OC)_5Re\text{-}Re(CO)_5$, have a chemistry that can be compared to that of a halogen (example: I_2). Predict the products of the following sequence in a non-reactive solvent. Identify A – D. Identify E for a 2 pt bonus!

$$Re_2(CO)_{10} + 2\ Na \rightarrow A$$
$$A + CH_3I \rightarrow B + NaI$$
$$B + PPh_3 \rightarrow C \text{ (and no other byproduct)}$$
$$A + PhCH_2Cl \rightarrow D + \text{a white inorganic solid}$$
$$D + heat \rightarrow E + CO$$

A	B	C
D	E	
	(bonus)	

17. (3 pts) Continuing with the previous problem, does A have a stronger or weaker CO bond stretching energy than $Re_2(CO)_{10}$? Explain in terms of π-back-bonding.
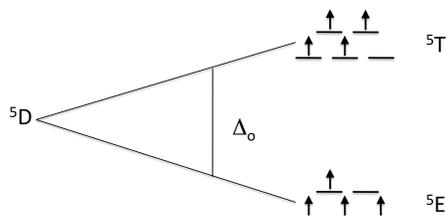
Answers:

1A. five columns (M_S = 2, 1, 0, -1, -2), S = 2

1B. 13 rows (M_L = 6 … -6), L = 6

1C. ^5D

2A.

2B. ^5E

2C. ^5T

3A. one

3B. L→MCT

3C. shorter wavelengths

4. octahedral d^3 (or d^8)

5. No: d^0 d^2 d^5
Yes: d^1 d^3 d^4

6. A solution of $[Fe(OH_2)_6](NO_3)_3$ is high-spin d^5 (no spin-allowed transitions) and $K_3[Fe(CN)_6]$ is low-spin d^5.

7. This compound is d^6. At room temperature it is high-spin with spin-allowed transitions. At low temp it is low-spin diamagnetic, with no spin-allowed transitions (light canary yellow.)

8. $\Delta H \approx 0$ because the ligands are similar (N-based), $\Delta S > 0$ and so $\Delta G < 0$, therefore K > 1.

9. $[Fe(H_2O)_6]^{+3}$ is high spin d^5 and exchanges ligands rapidly due to CFSE = 0. $[Cr(H_2O)_6]^{+3}$ is d^3 and is slow to exchange due to relatively large CFSE = 1.2 Δ_o.

10A.
$$[Co(NH_3)_5X]^{2+} \rightarrow [Co(NH_3)_5]^{3+} + X^- \text{ slow}$$
$$[Co(NH_3)_5]^{3+} + H_2O \rightarrow [Co(NH_3)_5H_2O]^{3+}$$

10B. rate = $k_1[[Co(NH_3)_5X]^{2+}]^1$

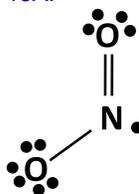10C. k should: **stay the same;** K should: **increase**

11. The first one is faster because the first step (dissociation) has a larger entropy factor.

12. (4 pts) Square planar complexes often undergo substitution via an associative mechanism as shown in this example. Indicate the signs of ΔH and ΔS for each step by adding <, =, or > (for example, $\Delta H < 0$)

Step 1 **$\Delta H < 0$; $\Delta S < 0$**

Step 2 **$\Delta H > 0$; $\Delta S > 0$**

13A.

13B. $(OC)_5MnNO$ has 5 CO = 10 e + Mn(0) is 7e + one electron for the Mn-N σ-bond.

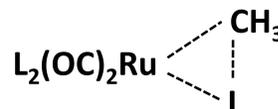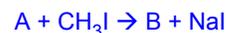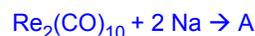13C. The predicted Mn-N-O bond angle is slightly less than 120º.

14A.

14B. CO

14C. Yes

14D. 180º.

15. Step 1. $Ru(CO)_3L_2 \rightarrow Ru(CO)_2L_2 + CO$
Step 2. $Ru(CO)_2L_2 + CH_3I \rightarrow cis\text{-}Ru(CO)_2L_2(CH_3)(I)$

16. (8 pts) Dimeric metal carbonyls such as $(OC)_5Re\text{-}Re(CO)_5$, have a chemistry that can be compared to that of a halogen (example: I_2). Predict the products of the following sequence in a non-reactive solvent. Identify A – D. Identify E for a 2 pt bonus!

$$Re_2(CO)_{10} + 2\ Na \rightarrow A$$
$$A + CH_3I \rightarrow B + NaI$$
$$B + PPh_3 \rightarrow C \text{ (and no other byproduct)}$$
$$A + PhCH_2Cl \rightarrow D + \text{a white inorganic solid}$$
$$D + \text{heat} \rightarrow E + CO$$

A. $Na[Re(CO)_5]$
B. $Re(CO)_5CH_3$
C. $cis\text{-}Re(CO)_4(COCH_3)(PPh_3)$
D. $Re(CO)_5CH_2C_6H_5$
E. $\eta^3\text{-}(OC)_4ReCH_2C_6H_5$

17. There is more π-back-bonding causing a weaker CO bond stretching energy.