Sample final exam answers

1. For both these compounds, the formal oxidation state is Mn(II), which is d⁵. Since NCS⁻ is a weak-field, high-spin ligand (from the spectrochemical series), the electron configuration for the octahedral complex will be (t₂g)³(e₉)², and it will have 5 unpaired electrons. The tetrahedral complex, which is also high-spin, will have electron configuration (e)²(t₂)³ and it will also have 5 unpaired electrons. Since the magnetic susceptibility is a function of the number of unpaired electrons, you can’t tell these compounds apart in this way.

2. (a) The Cu(I) complex is d¹⁰ and colorless; the Cu(II) complex is d⁹ and blue. The colors are a result of d-d electronic transitions; none of these are possible in the d¹⁰ case, since there are no empty orbitals into which an electron can go. However, for the d⁹ case, such an excitation is possible.
(b) For ¹FeBr₆³⁻, this is Fe(III), d⁵. Since Br⁻ is a weak-field ligand, this is a high-spin complex with electron configuration (t₂g)³(e₉)² and 5 unpaired electrons. It is paramagnetic and has CFSE = 3(–2/5Δ₀) + 2(3/5Δ₀) = 0.
For ²[FeCl₄]²⁻, this is Fe(II), d⁶. Since the complex is tetrahedral, it is high-spin, with electron configuration (e)³(t₂)³ and 4 unpaired electrons. It is paramagnetic and has CFSE = 3(–3/5Δₜ) + 3(2/5Δₜ) = –3/5Δₜ.

3. The required Born-Haber cycle is sketched below.
From this cycle, $\Delta H_f^\circ(MgO) = \Delta H_{\text{sublimation}}(Mg) + 1/2D(O-O) + IE_1(Mg) + IE_2(Mg) + EA(O) + EA(O^-) + U_{\text{lattice}}(MgO)$

Plugging in the numbers provided you get:

$-601.7 \text{ kJ/mol} = 147.7 \text{ kJ/mol} + 1/2(498.3) \text{ kJ/mol} + 737.7 \text{ kJ/mol} + 1451 \text{ kJ/mol}$

$-141.1 \text{ kJ/mol} + EA(O^-) -3963 \text{ kJ/mol}$

solve for $EA(O^-) = 917 \text{ kJ/mol}$

4. (a) For the particle in a box, with quantum number $n$,

$E_n = n^2 \hbar^2 / 8mL^2$, and the energy separation between 2 quantum states is

$\Delta E = (2n+1)\hbar^2 / 8mL^2$

The wavelength of light absorbed during excitation from the ground state to the excited state is given by

$\Delta E = \hbar c/\lambda$

so $\lambda = \hbar c/\Delta E = \hbar c/(2n+1)h^2/8mL^2 = 8hcmL^2/(2n+1)h^2$

$\lambda = 8cmL^2/(2n+1)h$

For this problem, plug in $n=N/2$, but $N=2$ for ethylene, so $n=1$, and $L = 1.32\text{Å}$

$\lambda = 8(3\times10^8 \text{ m/s})(9.11\times10^{-31}\text{kg})(1.32\text{Å} \times 10^{-10}\text{m/Å})^2 / 3(6.626\times10^{-34}\text{Js})$

$\lambda = 1.92\times10^{-8}\text{m} \times 10^9\text{nm/m} = 19.2 \text{ nm}$
(b) From part (a) \( \lambda = \frac{8cmL^2}{(2n+1)h} \)

or, since \( n=\frac{N}{2} \),
\[ \lambda = \frac{8cmL^2}{(N+1)h} \]

Since \( L \) is proportional to \( N \), then

**\( \lambda \text{ is proportional to } \frac{N^2}{N} = N \)**

Therefore, the wavelength will increase as \( N \) increases.

5. As in sample exam 1,

Arrhenius equation: \( k=Ae^{-\frac{E_a}{RT}} \)

for the catalyzed reaction, \( k'=Ae^{-\frac{E_a'}{RT}} \)

Divide these to get:
\[ \frac{k}{k'} = e^{-\frac{\Delta E_a}{RT}} \text{ where } \Delta E_a = E_a - E_a' \]

\[ \ln(\frac{k}{k'}) = -\frac{\Delta E_a}{RT} \]

\[ \ln(\frac{1}{100})(8.31\text{J/molK})(298\text{K}) = -\Delta E_a \]

\( \Delta E_a = 11.4 \text{ kJ/mol} \)

Since the activation energy in the presence of the catalyst is given to be 10 kJ/mol, **the activation energy without catalyst must be 21.4 kJ/mol.**

Using this information,

\( k_1=Ae^{-\frac{E_a}{RT_1}} \text{ for the reaction at } T_1 = 25^\circ C \)

\( k_2=Ae^{-\frac{E_a}{RT_2}} \text{ for the reaction at } T_2 = ? \)

Divide these to get
\[ \frac{k_1}{k_2} = e^{-\frac{E_a}{R}(\frac{1}{T_1} - \frac{1}{T_2})} \]

\[ \ln \left( \frac{k_1}{k_2} \right) = -\frac{E_a}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]

Plug in \( \frac{k_1}{k_2} = 1/100, E_a = 21.4 \text{ kJ/mol}, \text{ and } T_1 = 25^\circ C = 298K, \text{ to get} \)

\[ \ln(1/100) = \left( -21.4 \times 10^3 \text{J/mol} \right)/\left( 8.31 \text{J/molK} \left( \frac{1}{298K} - \frac{1}{T_2} \right) \right) \]

\( T_2 = 638K = 365^\circ C \)
6. The electron configurations for these molecules are as follows:

NO has 11 valence electrons: \((\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2px}, \pi_{2py})^4 (\sigma_{2pz})^2 (\pi^*_{2px}, \pi^*_{2py})^1\)

C\(_2\) has 8 valence electrons: \((\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2px}, \pi_{2py})^4\)

N\(_2\) has 10 valence electrons: \((\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2px}, \pi_{2py})^4 (\sigma_{2pz})^2\)

An electron added to NO will end up in the \(\pi^*\) antibonding MO, increasing the energy of the system, but removing an electron from NO is favorable energetically since an antibonding electron is removed.

Adding an electron to \(C\(_2\)\) gives an additional bonding electron in the \(\sigma_{2pz}\) MO, which will stabilize the system, while removing one is bad since a bonding \(\pi\) electron is lost.

Adding an electron to \(N\(_2\)\) is unfavorable since it will be added to the antibonding \(\pi^*\) MO, and removing one will also be bad since a bonding \(\pi\) electron is taken away.

Summary: Removing an electron stabilizes NO, and adding an electron stabilizes \(C\(_2\)\). Neither one stabilizes \(N\(_2\)\).

7. This is the photoelectric effect applied to an ion instead of a metal surface.

First find the ionization energy of ground-state \(Li^{2+}\) using the Bohr model:

\[
\Delta E = -2.18 \times 10^{-18} J Z^2 \left( \frac{1}{n_i^2} - \frac{1}{n_f^2} \right)
\]

Plug in \(Z = 3\), \(n_i = 1\) and \(n_f = \infty\) to get the ionization energy of \(Li^{2+}\)

\[= 1.96 \times 10^{-17} J\]

Now \(E = h \nu = \frac{hc}{\lambda} = IE + \frac{1}{2}mv^2\) for the photoelectric effect.

Plug in the wavelength and the IE to get

\[
\left( \frac{1}{2}mv^2 \right) = \left( 6.626 \times 10^{-34} Js \right) \left( 3 \times 10^8 m/s \right) / \left( 5 \text{ nm} \right) / \left( 1 m / 10^9 \text{ nm} \right) - 1.96 \times 10^{-17} J
\]

\[= 3.98 \times 10^{-17} J - 1.96 \times 10^{-17} J = 2.02 \times 10^{-17} J\]

solve for \(v\) by plugging in the electron mass of \(9.11 \times 10^{-31} \text{ kg}\)

\(v = 6.66 \times 10^6 \text{m/s}\) (satanic?)
8. (a) CH₂ is bent, based on trigonal planar coordination with an ideal HCH bond angle of 120°. It will be less than 120° because of the lone pair on C. The C hybridization is sp².

(b) NCN²⁻ is linear. No deviations expected. sp at C

(c) XeO₃ is pyramidal, with ideal OXeO angle of 109.5°. The presence of a lone pair on Xe will distort this to reduce this angle (<109.5°) sp³ at Xe.

(d) SCl₃⁺ is pyramidal, with ideal CISCI angle of 109.5°. The presence of a lone pair on S will distort this to reduce this angle (<109.5°) sp³ at S.

(e) PF₆⁻ is octahedral, no deviations, d²sp³ at P.

9. (a) true The intermolecular forces (London dispersion forces, in this case) acting on these atoms increase with size and polarizability, in the order given.

(b) false From the argument of part (a) above, you might expect AsH₃ to have a higher boiling point than NH₃. However, N is more electronegative than is As, so hydrogen bonding is important in NH₃ but not in AsH₃. The resulting stronger intermolecular forces in NH₃ explain the higher boiling point.

(c) true Uₐₗₜₐₜₐ is proportional to –MZ⁺Z⁻/d₀. Here M is the same, d₀ is comparable, and the products of the charges differ by a factor of 4. Thus MgO has larger lattice energy than NaF, and therefore a higher melting point.

10. (a) (iii) (d) (i) and (ii)

(b) (i) (e) (iv)

(c) (i) and (iii)