Chem 6 Sample exam 3 (final) brief answers

1. Because \( E = \frac{hc}{\lambda} \), shortest wavelength means biggest energy. This must correspond to a transition from \( n = \infty \) to the unknown quantum number \( n \). The energy of this transition is given by
\[
\Delta E = -2.18 \times 10^{-18} \text{ J} Z^2 \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right)
\]
Plug in \( Z = 1 \) for hydrogen, \( n_i = n \), \( n_i = \infty \) and solve for \( n \)
\[
\Delta E = \frac{hc}{\lambda} = (-2.18 \times 10^{-18} \text{ J} (1/n_i^2))I
\]
So \((6.626 \times 10^{-34} \text{ J})(3 \times 10^8 \text{ m/s})/(3280 \text{ nm} \times 1 \text{ m}/10^9 \text{ nm})/2.18 \times 10^{-18} \text{ J} = 1/n_i^2 \)
And \( n_i = 6 \).
Now we can find the wavelength for line B. The far-right line (largest wavelength) must be the smallest energy transition, from \( n = 7 \) to \( n = 6 \). So, line B must be due to the transition from \( n = 8 \) to \( n = 6 \). Plug-n-chug:
\[
\Delta E = -2.18 \times 10^{-18} \text{ J} (1/8^2 - 1/6^2) = -2.65 \times 10^{-20} \text{ J}
\]
Convert to wavelength
\[
I\Delta E = \frac{hc}{\lambda} \text{ or } \lambda = \frac{hc}{I\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J})(3 \times 10^8 \text{ m/s})}{2.65 \times 10^{-20} \text{ J}}
\]
= 7.5 \times 10^{-6} \text{ m} \times 10^9 \text{ nm/m} = 7500 \text{ nm}

2. Rate = \( k[A^+] \)
Steady-state: \( \frac{d}{dt}[A^+] = k_1[A]^2 - k_{-1}[A^*][A] - k_2[A^+] = 0 \)
Solve for \( [A^+] \)
\[
k_{-1}[A^*][A] + k_2[A^+] = k_1[A]^2
\]
\[
(k_{-1}[A] + k_2)[A^*] = k_1[A]^2
\]
\[
[A^*] = \frac{k_1[A]^2}{(k_{-1}[A] + k_2)}
\]
Plug in to the rate expression
\[
\text{Rate} = \frac{k_2 k_1 [A]^2}{(k_{-1}[A] + k_2)}
\]
There are two possible extremes with the magnitude of the terms in the denominator. If \( k_{-1}[A] \gg k_2 \), then the denominator \( \sim k_{-1}[A] \). Then the rate = \( k_2 k_1 [A]^2/(k_{-1}[A]) = k_2 k_1 [A]/(k_{-1}) \) or \( k_2 K_{eq}[A] \) which is first-order in \( [A] \). Physically, this means that the rate of the second step is very slow, in comparison to the faster first step. Note that if this 2\textsuperscript{nd} step is slow (rate-determining), then overall rate = rate of 2\textsuperscript{nd} step = \( k_2[A^+] \)
but \( [A^+] \) from the fast 1\textsuperscript{st} equilibrium step is given by \( [A^*][A]/[A]^2 = K_{eq} \) or \( K_{eq}[A] = [A^*] \). Plug this in to the rate expression to get
rate = \( k_2 K_{eq}[A] \), same as the result above from the steady-state approach.

For the other extreme, at low pressure (i.e. low \( [A] \)), then \( k_{-1}[A] \ll k_2 \), so that the denominator \( \sim k_2 \). Then the rate = \( k_2 k_1 [A]^2/(k_2) = k_1[A]^2 \) which is second-order in \( [A] \).
Physical significance: the slow, rate-determining, step is now the first step, bimolecular formation of \( A^* \), and its decomposition (step 2) is fast in comparison.
Again writing the overall rate as equal to the rate of the first, slow step:
Rate = \( k_1[A]^2 \) which, as it should, matches the steady-state result.
3a. Here’s the MO energy level scheme for HF. As described in class, the F 2s is too different in energy from the H 1s for these orbitals to form MOs; the F 2p, and 2p, AOs have the wrong symmetry to combine with the H 1s. Therefore these orbitals are nonbonding (same as they started, unchanged F AOs). The F 2p and the H 1s AOs combine to form sigma-bonding and sigma-antibonding MOs.

![MO energy level scheme for HF](image)

The **HOMO is the degenerate set of the 2p nonbonding MOs**; these are just unchanged F 2p atomic orbitals (2px and 2py, since the 2pz is used to make the sigma and sigma* MOs). So, they look like unchanged F p-orbitals; I've sketched one above.

3b. **Ionization of HF will occur from** the highest-energy MO, i.e. the HOMO above. But this is just an unchanged F 2p atomic orbital (which is the same orbital from which you'd remove an electron to ionize F). So, the ionization energies of F and HF should be the same.

**Note:** many students incorrectly tried to use the MO energy level scheme for heteronuclear diatomics like CO (see question 7). This is inappropriate because the H p-orbitals are too high in energy to contribute to MOs in its compounds; only the H 1s orbital is available. We tried to give partial credit in this case, where possible.

4. Here’s the completed structure. There are 2 possible resonance structures differing in the double bond pattern in the ring, but just drawing one was fine.

![Completed structure](image)

<table>
<thead>
<tr>
<th>hybridization</th>
<th>C atom numbers (don’t forget to include N and O too)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp</td>
<td>2,3</td>
</tr>
<tr>
<td>sp²</td>
<td>4,5,6,7,8,9, N, O</td>
</tr>
<tr>
<td>sp³</td>
<td>1</td>
</tr>
<tr>
<td>dsp³</td>
<td>none</td>
</tr>
</tbody>
</table>
Carbon Bond Angles

<table>
<thead>
<tr>
<th>carbon</th>
<th>Bond Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>109.5°</td>
</tr>
<tr>
<td>2</td>
<td>180°</td>
</tr>
<tr>
<td>4</td>
<td>120°</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>bond</th>
<th>orbitals used to make bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2-C3</td>
<td>Sigma: sp hybrid on each</td>
</tr>
<tr>
<td></td>
<td>Pi: 2 p-orbitals</td>
</tr>
<tr>
<td>C9-O</td>
<td>Sigma: sp² hybrid on each</td>
</tr>
<tr>
<td></td>
<td>Pi: 1 p-orbital</td>
</tr>
</tbody>
</table>

For C2-C3, you need to make 2 π-bonds. One p-orbital per C was used up to make the sp hybrids on C2 and C3 (which are used to make the sigma bonds), leaving 2 p-orbitals on each one to make the 2 orthogonal π-bonds. For sp²-hybridized C9 and O, 2 p-orbitals on each C were used to make the hybrids (these make the sigma bonds), leaving one p-orbital on each C to make the π-bond.

5a. The lattice energy U (for MX, like NaCl) depends on the charges of the ions and the distance between them:

\[ U \sim MZ^+Z^-/d \]

Where M is the Madelung constant.

For MX₂, assuming a similar idea, the charges Z⁺ and Z⁻ don't change; they're always M²⁺ and X⁻. So it must be the distances that change. As you go across a row in the transition metals, adding d-electrons, you are increasing Z, while the added valence d-electrons are not efficient at shielding each other, so Zeff increases and the ions become smaller. This means the distance d between M ions and X ions is smaller too and the lattice energy is bigger.

5a continued. Same idea, but more familiar; the halides get bigger in the sequence F...I as you are adding electrons to shells of greater n; so again the distance d between M and X increases and lattice energy drops in this order.

5b. The extra stabilization is due to the crystal field stabilization energy (characteristic of metal ions with octahedral coordination), which is zero for the special cases of zero d-electrons (Ca(II)), 10 d-electrons (Zn(II)), and 5 d-electrons in the high-spin case (Mn(III)).

6a. CS₂ is bigger, has more electrons, and is more polarizable than CO₂, so it experiences greater London forces, has stronger intermolecular interactions, and has a higher boiling point than CO₂. It turns out the bp is low enough for it to be a liquid under standard conditions.

6b. All three have roughly similar London forces and dipoles. The increased boiling points track the increase in strength of intermolecular interactions. Hydrogen bonding involving the OH and C=O groups in 2 and 3 give these higher boiling points than 1, and the replacement of H by Cl in 3 vs 2 should increase both London forces (more
electrons) and dipole-dipole interactions (a new, sizable, bond dipole has been introduced) in \( \text{3 vs 2} \), resulting in a higher boiling point.

6c. The meniscus shapes reflect the relative magnitudes of adhesive (glass-liquid) and cohesive (liquid-liquid) interactions. Water and the silica glass are attracted strongly (hydrogen bonding and dipole-dipole interactions) so water tries to climb up the glass walls and the meniscus curves up. Mercury in contrast has weaker interactions with the glass than with itself, so it avoids the glass and the meniscus curves down.

7a. CO has 10 valence electrons so the electron configuration is \((\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p})^4(\sigma_{2p})^2\). The next orbital up in energy \((\pi^*_{2p})\), which is unoccupied, is the LUMO. This is a degenerate set of \(\pi\)-symmetry antibonding MOs made from \(p_x\) and \(p_y\) atomic orbitals. Since C and O atomic orbitals have different energies (O's are lower since it has higher \(Z_{\text{eff}}\)), the MOs are polarized (they have different relative contributions of the atomic orbitals to the MOs). The LUMO will have a greater contribution from the higher-energy AOs on carbon. So it looks like this (I have just drawn one of the degenerate set). It could be formed from either \(p_x\) or \(p_y\) orbitals.

7b. Combine with a \(d_{xz}\) orbital. I have chosen to show my LUMO as formed from the \(p_x\) orbital so the paper will be the \(xz\) plane. Note the \(\pi\)-symmetry of the M-C bonding interaction. If you used the \(p_y\) orbitals to make your LUMO, you should choose the metal \(d_{yz}\) MO; the picture will look the same, just the axes will be a little different.
8. The appropriate Born-Haber cycle is sketched below.

From the Born-Haber cycle,
\[ \Delta H_f^o (\text{HeCl}) = \Delta H_f^o (\text{Cl}(g)) + \text{IE(He)} + \text{EA(Cl)} + U(\text{HeCl}) \]
\[ = 122 \text{ kJ/mol} + 2377 \text{ kJ/mol} -355 \text{ kJ/mol} + U(\text{HeCl}) \]
To make this thermodynamically favorable, \( \Delta H_f^o (\text{HeCl}) \) must be <0.
This means that
\[ 0 > 2144 \text{ kJ/mol} + U (\text{HeCl}) \]
The lattice energy U must be a large negative number, bigger in magnitude than –2144 kJ/mol. To make this happen, use the equation given for the lattice energy and plug in all the numbers.

\[ \text{lattice energy} = \frac{M_N A Q_1 Q_2}{4\pi\varepsilon_0 d} \]

\[ -2144 \text{ kJ/mol} = \frac{[(1.75)(6.02x10^{23}/\text{mol})(-1.60x10^{-19}\text{C})(1.60x10^{-19}\text{C})]/4\pi(8.854x10^{-12}\text{C}^2\text{J}^{-1}\text{m}^{-1})(1000\text{J/kJ})(d)} \]
Solve for d to get
\[ d = 1.13x10^{-10} \text{m} = 1.13\text{Å} \]
So d would have to be this length, or shorter. A ballpark number for a chemical bond length is on the order of an angstrom, so that seems plausible. However, since Cl is a pretty big atom (ionic radius of 1.81 Å), this seems too short. Thus, either of these answers was OK, as long as you justified it. Many students through math errors (often involving unit conversions) got physically unreasonable distances, and correctly realized this.

9. Both are Fe(III), d^5. From the spectrochemical series, the CN^- complex is low-spin and the bromide one is high-spin. Their electron configurations are thus \( (t_{2g})^5 \) and \( (t_{2g})^3(e_g)^2 \) respectively, with 5 and 1 unpaired electrons. This gives the magnetic moments from the formula \( \mu = [(n)(n+2)]^{1/2} \) where \( n \) is the number of unpaired electrons, so 5.92 and 1.73 BM respectively. Thus magnetic measurements could certainly be used to distinguish the compounds.
The absorption spectrum (color) depends on the magnitude of the orbital splitting \( \Delta_0 \). By definition this is bigger for the low-spin cyanide compound. So you’d expect peaks at higher energy (since it’s a larger \( \Delta E \) for the transition) for this one in comparison to the bromide complex.
However, since it's high-spin $d^6$ there are no allowed transitions, so you'd expect the color to be very weak -- the sample would be essentially colorless.

10a. (ii)
10b. (iv)
10c. (i)
10d. (iii)
10e. (iii)

10a. XeF$_2$ is linear; XeF$_3^+$ is like ClF$_3$, so it's T-shaped; XeF$_4$ is square planar, and ethylene is a planar molecule with trigonal planar C atoms, so only XeF$_3^+$ has a dipole moment.

10b. The bond orders are 1 (H$_2$), 2.5 (CN), 2 (O$_2$), and 0.5 (He$_2^+$).

10c. From the demo (or the MO scheme), O$_2$ is paramagnetic and N$_2$ is not. WCl$_6$ is W(VI), d$^0$, so it must be diamagnetic. Cr(CO)$_6$ is Cr(0), d$^6$, low-spin because of the CO ligands, so it's (t$_{2g}$)$^6$ and diamagnetic too.

10d. All are true except for (iii), see the text bottom of page 797...ice's melting point actually decreases with increasing pressure.

10e. The maximum uncertainty ($\Delta x$) in the particle's position is $L$. Since $\Delta P\Delta x \geq \hbar/2$ (Heisenberg's uncertainty principle), then the minimum uncertainty in momentum ($\Delta P$) is $\hbar/2L$. Then the minimum uncertainty in the energy (which is all kinetic energy, or $(1/2)mv^2$ or $p^2/2m$) must be $\Delta p^2/2m = (\hbar/2L)^2/2m = (\h/4\pi L)^2/2m = h^2/16\pi^2 L^2/2m = h^2/32\pi^2 mL^2$. 