

## Sample final exam answers

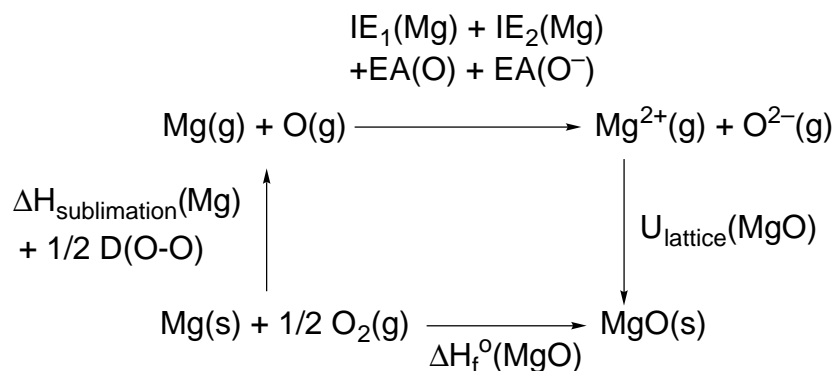
1. For both these compounds, the formal oxidation state is Mn(II), which is  $d^5$ . Since  $\text{NCS}^-$  is a weak-field, high-spin ligand (from the spectrochemical series), the electron configuration for the octahedral complex will be  $(t_{2g})^3(e_g)^2$ , and it will have 5 unpaired electrons. The tetrahedral complex, which is also high-spin, will have electron configuration  $(e)^2(t_2)^3$  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  $d^{10}$  and colorless; the Cu(II) complex is  $d^9$  and blue. The colors are a result of d-d electronic transitions; none of these are possible in the  $d^{10}$  case, since there are no empty orbitals into which an electron can go. However, for the  $d^9$  case, such an excitation is possible.

(b) For **1**  $\text{FeBr}_6^{3-}$ , this is Fe(III),  $d^5$ . Since  $\text{Br}^-$  is a weak-field ligand, this is a high-spin complex with electron configuration  $(t_{2g})^3(e_g)^2$  and **5 unpaired electrons**. It is **paramagnetic** and has  **$\text{CFSE} = 3(-2/5\Delta_o) + 2(3/5\Delta_o) = 0$** .

For **2**  $[\text{FeCl}_4^{2-}]$ , this is Fe(II),  $d^6$ . Since the complex is tetrahedral, it is high-spin, with electron configuration  $(e)^3(t_2)^3$  and **4 unpaired electrons**. It is **paramagnetic** and has  **$\text{CFSE} = 3(-3/5\Delta_t) + 3(2/5\Delta_t) = -3/5\Delta_t$** .

3. The required Born-Haber cycle is sketched below.



From this cycle,  $\Delta H_f^\circ(\text{MgO}) = \Delta H_{\text{sublimation}}(\text{Mg}) + 1/2D(\text{O}-\text{O}) + \text{IE}_1(\text{Mg}) + \text{IE}_2(\text{Mg}) + \text{EA}(\text{O}) + \text{EA}(\text{O}^-) + U_{\text{lattice}}(\text{MgO})$

Plugging in the numbers provided you get:

$$\begin{aligned}
 -601.7 \text{ kJ/mol} &= 147.7 \text{ kJ/mol} + 1/2(498.3) \text{ kJ/mol} + 737.7 \text{ kJ/mol} + 1451 \text{ kJ/mol} \\
 &-141.1 \text{ kJ/mol} + \text{EA}(\text{O}^-) -3963 \text{ kJ/mol}
 \end{aligned}$$

solve for **EA(O<sup>-</sup>) = 917 kJ/mol**

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

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

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

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

$$\Delta E = hc/\lambda$$

$$\text{so } \lambda = hc/\Delta E = hc/(2n+1)h^2/8mL^2 = 8hcmL^2/(2n+1)h^2$$

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

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

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

$$\lambda = 1.92 \times 10^{-8} \text{ m} \times 10^9 \text{ nm/m} = 19.2 \text{ nm}$$

(b) From part (a)  $\lambda = 8cmL^2/(2n+1)h$

or, since  $n=N/2$ ,

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

Since L is proportional to N, then

**$\lambda$  is proportional to  $N^2/N = N$**

**Therefore, the wavelength will increase as N increases.**

5. As in sample exam 1,

Arrhenius equation:  $k=Ae^{-E_a/RT}$

for the catalyzed reaction,  $k'=Ae^{-E_a'/RT}$

Divide these to get:

$$k/k' = e^{-\Delta E_a/RT} \text{ where } \Delta E_a = E_a - E_a'$$

$$\ln(k/k') = -\Delta E_a/RT$$

$$\ln(1/100)(8.31J/molK)(298K) = -\Delta E_a$$

$$\Delta E_a = 11.4 \text{ kJ/mol}$$

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,

$$k_1=Ae^{-E_a/RT_1} \text{ for the reaction at } T_1 = 25^\circ\text{C}$$

$$k_2=Ae^{-E_a/RT_2} \text{ for the reaction at } T_2 = ?$$

Divide these to get

$$k_1/k_2 = e^{-E_a/R(1/T_1 - 1/T_2)}$$

$$\ln(k_1/k_2) = -E_a/R(1/T_1 - 1/T_2)$$

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

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

$$\mathbf{T_2 = 638\text{K} = 365^\circ\text{C}}$$

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<sub>2</sub> has 8 valence electrons:  $(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2px}, \pi_{2py})^4$

N<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub>. Neither one stabilizes N<sub>2</sub>.**

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

First find the ionization energy of ground-state Li<sup>2+</sup> using the Bohr model:

$$\Delta E = -2.18 \times 10^{-18} \text{J} Z^2 (1/n_f^2 - 1/n_i^2)$$

Plug in  $Z = 3$ ,  $n_i = 1$  and  $n_f = \text{infinity}$  to get the ionization energy of Li<sup>2+</sup>

$$= 1.96 \times 10^{-17} \text{J}$$

now  $E = h\nu = hc/\lambda = IE + (1/2)mv^2$  for the photoelectric effect.

Plug in the wavelength and the IE to get

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

$$= 3.98 \times 10^{-17} \text{J} - 1.96 \times 10^{-17} \text{J} = 2.02 \times 10^{-17} \text{J}$$

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

$$\mathbf{v = 6.66 \times 10^6 \text{m/s}} \text{ (satanic?)}$$

8. (a)  $\text{CH}_2$  is **bent**, based on trigonal planar coordination with an ideal HCH bond angle of  $120^\circ$ . It will be **less than  $120^\circ$**  because of the lone pair on C. The C hybridization is  **$\text{sp}^2$** .

(b)  $\text{NCN}^{2-}$  is **linear. No deviations expected.  $\text{sp}$  at C**

(c)  $\text{XeO}_3$  is **pyramidal**, with ideal OXeO angle of  $109.5^\circ$ . The presence of a lone pair on Xe will distort this to reduce this angle ( **$<109.5^\circ$** )  **$\text{sp}^3$**  at Xe.

(d)  $\text{SCl}_3^+$  is **pyramidal**, with ideal ClSCL angle of  $109.5^\circ$ . The presence of a lone pair on S will distort this to reduce this angle ( **$<109.5^\circ$** )  **$\text{sp}^3$**  at S.

(e)  $\text{PF}_6^-$  is **octahedral, no deviations,  $\text{d}^2\text{sp}^3$  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  $\text{AsH}_3$  to have a higher boiling point than  $\text{NH}_3$ . However, N is more electronegative than is As, so hydrogen bonding is important in  $\text{NH}_3$  but not in  $\text{AsH}_3$ . The resulting stronger intermolecular forces in  $\text{NH}_3$  explain the higher boiling point.

(c) **true**  $U_{\text{lattice}}$  is proportional to  $-\text{MZ}^+\text{Z}^-/d_0$ . Here M is the same,  $d_0$  is comparable, and the products of the charges differ by a factor of 4. Thus  $\text{MgO}$  has larger lattice energy than  $\text{NaF}$ , and therefore a higher melting point.

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

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

(c) **(i) and (iii)**