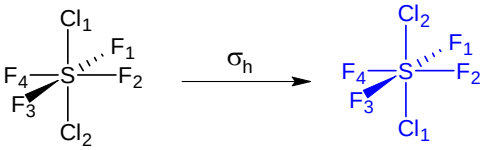
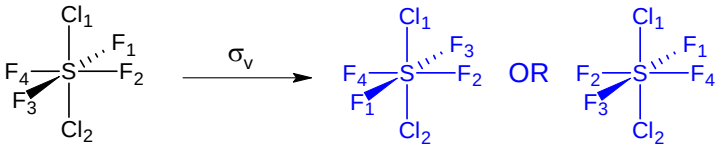
MIDTERM SOLUTIONS --- CHEM 2351 (W11)

Question 1 (a) Perform the symmetry operations. (5 points)

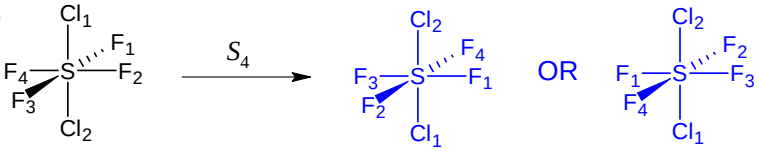
(i)



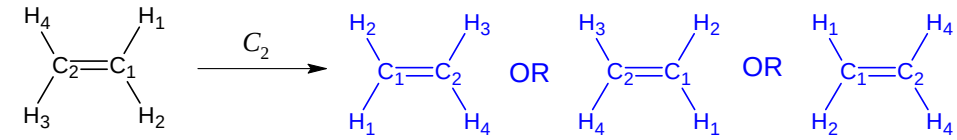
(ii)



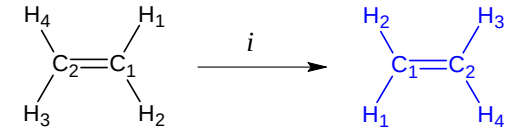
(iii)



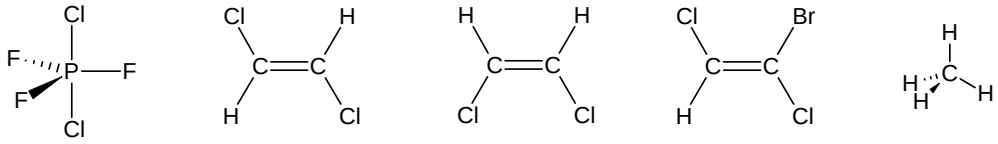
(iv)



(v)



(b) Give the point groups for **4 of the following 5** molecules (4 points)



(i) D_{3h} (ii) C_{2h} (iii) C_{2v} (iv) C_s (v) T_d

Question 2 (a) Using the Born-Meyer Equation, calculate the theoretical lattice enthalpy (ΔH_L^o) for MgO, which has the rock salt structure (ccp packing of anion, cation fills all the octahedral holes). Note: $r_{Mg^{2+}}$ = 0.86 Å, $r_{O^{2-}}$ = 1.26 Å. (2 points)

Filling the values in as follows will give you the correct units:

$$\Delta H_L = \frac{(6.022\times10^{23})(+2)(-2)(1.6022\times10^{-19})^2}{4\pi(8.8542\times10^{12})(2.12\times10^{-10})}\left(1-\frac{0.345}{2.12}\right)(1.74756) = 3840\text{kJ / mol}$$

where 2.12 Å is the sum of the two ionic radii 0.86 + 1.26.

(b) Determine the actual (experimental) lattice enthalpy (ΔH_L) using the following data (all values in kJ/mol): (3 points)

ΔH_f° = -601	ΔH_{vap} (Mg) = 146	$\Delta H_{O=O}$ ($O_2 \rightarrow 2\ O^\bullet$) = 494
	ΔH_{IE} ($Mg \rightarrow Mg^{2+}$) = 2189	ΔH_{IE} ($O^{2-} \rightarrow O^\bullet$) = -603

Remember that the goal is to determine ΔH_L, defined as

$$Mg^{2+}\ (g)\ +\ O^{2-}\ (g)\ \rightarrow\ MgO\ (s)$$

The following series of equations will give you the above reaction:

$Mg\ (s)\ +\ ½\ O_2\ (g)\ \rightarrow\ MgO\ (s)$	ΔH_f° = -601
$Mg\ (g)\ \rightarrow\ Mg\ (s)$	$-\Delta H_{vap}$ = -146
$Mg^{2+}\ (g)\ +\ 2\ e^-\ \rightarrow\ Mg\ (g)$	$-\Delta H_{IE(Mg)}$ = -2189
$O^\bullet\ (g)\ \rightarrow\ ½\ O_2\ (g)$	$-½\Delta H_{O=O}$ = -247
$O^{2-}\ (g)\ \rightarrow\ O^\bullet\ (g)$	$-\Delta H_{IE(O)}$ = -603
	ΔH_L = -3786 kJ/mol

(c) What does the energy match (or lack thereof) say about the nature of the MgO lattice? Note: these are crude calculations, so an error of up to ±20% is not significant. (1 point)

These numbers are very close together, therefore the assumptions made in the Born-Meyer equation (*e.g.*, that the lattice is made up of hard charged spheres) are valid. What this means in "real life" is that MgO is best described as an ionic structure (a covalent structure would not have packed spheres, which would throw off the Born-Meyer estimate).

Question 3 Answer **6 of the following 9** in the space provided (2 points each, 12 points total)

(a) Rationalise the following observation: KCl packs in the rock-salt structure (ccp with all octahedral holes are filled) whereas ZnS occurs in the sphalerite structure (ccp with one half the tetrahedral holes filled).

Octahedral holes are bigger, therefore the relative sizes of K^+ and Cl^- are closer than the relative sizes of Zn^{2+} and S^{2-}. (the Zn^{2+} must be smaller relative to the S^{2-} to fit into the smaller tetrahedral holes).

(b) Calculate the potential generated in this redox reaction under the conditions given:
All concentrations = 0.1 *M*, 1 atm pressure of all gasses, T = 500 K

$$3\ Fe^{3+}\ (aq)\ +\ V\ (s)\ \leftrightharpoons\ V^{3+}\ (aq)\ +\ 3\ Fe^{2+}\ (aq) \qquad E^\circ = 1.61\ V$$

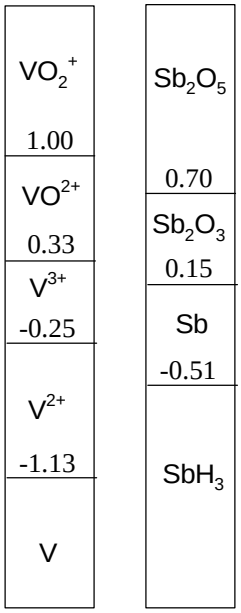
noting that the activity of a solid ≡ 1,

$$\Delta E = 1.61 - \frac{(8.315)(500)}{3(96485)} \ln \frac{(0.1)(0.1)^3}{(1)(0.1)^3} = -1.64$$

The units are J/C, which = A.

(c) Calculate the standard reduction potential for the following reaction (see Question 3 (d) for stepwise potentials):

$$V\,(s) \rightleftharpoons VO_2^+\,(aq)$$



$\Delta E° = [(2)(-1.13) + (1)(-0.25) + (1)(0.33) + (1)(1.00)] / 5 = -0.236$ V

(d) Using the predominance diagrams at right, predict a pair of stable products for the reaction of vanadium metal with antimony(V) oxide. Give the standard potential $\Delta E°$ for your reaction.

$$V\,(s) + Sb_2O_5\,(s) \rightarrow ?$$

Some potential solutions to this problem:

$30\ H^+ + 3\ Sb_2O_5 + 10\ V \rightarrow 6\ Sb + 10\ V^{3+} + 15\ H_2O$ $\quad \Delta E° = 0.837 + 0.37 = 0.907$ V

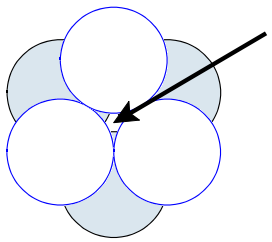
$12\ H^+ + 3\ Sb_2O_5 + 4\ V \rightarrow 3\ Sb_2O_3 + 4\ V^{3+} + 6\ H_2O$ $\quad \Delta E° = 0.837 + 0.70 = 1.537$ V

(e) Briefly describe two different types of alloys.

We covered 3 types, any 2 of these will do:
- interstitial, where a metal is close packed and the second metal goes into the holes (octahedral or tetrahedral)
- substitutional, where metals of similar size and electronegativity, so the close-packed layers are randomly distributed A and B metals
- intermetallic, where there is some sort of bonding between the metals (to form a specific new bimetallic metal)

(f) Describe an octahedral hole in a close-packed lattice.

In a close-packed lattice, the junction of 6 close-packed spheres, three in the upper layer and three in the lower layer.



(g) Describe the trend (called the "Lanthanide Contraction") in atomic size as you move left to right across the periodic table, and explain why it occurs

Electrons in the same shell do not shield each other, therefore as you go left-to-right, the effective nuclear charge increases (Z_{eff}) because the number of protons in the nucleus increases, but the number of shielding electrons stays the same (at whatever the previous noble gas number was). As a result, all the valence electrons see an increaseing Z_{eff} and are consquently pulled toward the nucleus, resulting in a "contraction" of atomic size

(h) Describe the Inert Pair Effect and explain why it occurs.

s-orbitals of all types have a larger wavefunction near the nucleus (electrons in the orbital have a larger penetration) than *p*- or *d*-orbitals. Thus, electrons in *s*-orbitals are better able to sense the actual charge on the nucleus. When a nucleus gets very large (very high positive charge), all electrons move faster, but the *s*-electrons are most effected, being drawn closer to the nucleus. The mass increase due to relativistic effects further causes the electrons to become lower in energy (decreasing in *E* much faster than *p*-electrons). Thus, they become more difficult to remove, and therefore form an "inert" pair of electrons.

(i) Many exceptions to the Aufbau Principle (order of filling electrons into orbitals) occur. Explain a situation where such an exception might occur and why.

Many orbitals in different subshells are close in energy. Often times, the difference in energy between two adjacent orbitals is similar to the pairing energy. Thus, it may be energetically favourable to have, say, 6 unpaired electrons in Cr ($1s^2 2s^2 2p^6 3s^2 3d^5 4s^1$) than to have 2 electrons paired in the lower-energy 4*s* orbital (*i.e.*, $1s^2 2s^2 2p^6 3s^2 3d^4 4s^2$). (the latter would be the preferred Aufbau filling order)