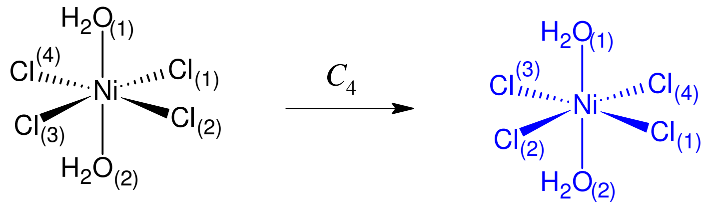
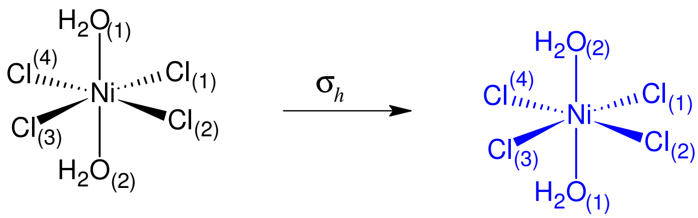
Question 1 (a) Perform the given symmetry operations. (5 points)

(i)

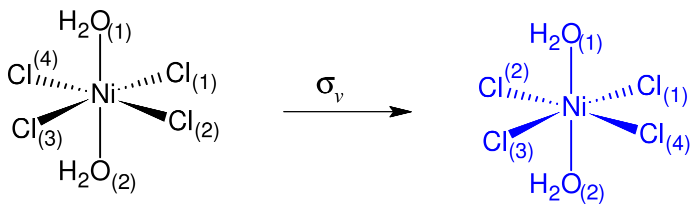


(or rotate the other way)

(ii)

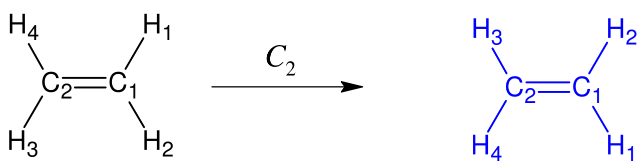


(iii)



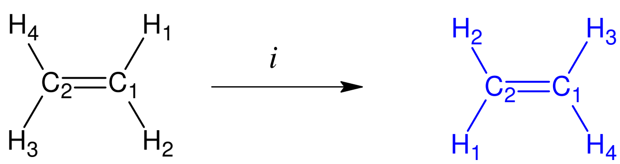
(there are several other choices as well)

(iv)

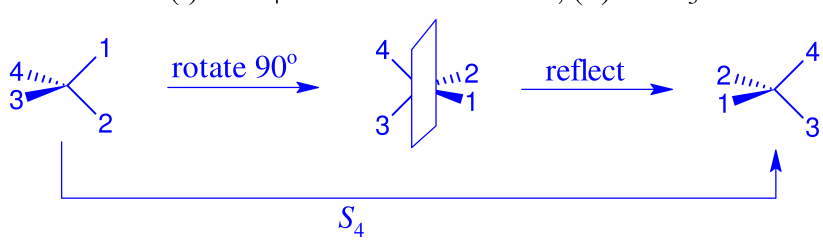


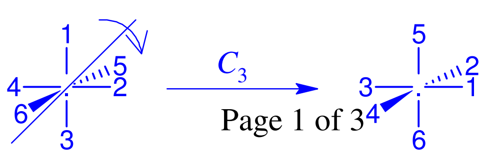
(there are two other choices as well)

(v)



(b) Demonstrate: (i) the S_4 axis on a tetrahedron, (ii) the C_3 axis on an octahedron. (2 points)





<u>Question 2</u> (a) Find the experimental lattice enthalpy (ΔH_L) of MgO. The following might be useful (values in kJ/mol): (2.5 points)

$\Delta H_f° = -601$	ΔH_{vap} (Mg(*s*) → Mg(*g*)) = 146	$\Delta H_{O=O}$ (O_2(*g*) → 2 $O^{\bullet}$(*g*)) = 494
ΔH_{IE} (Mg(*g*) → Mg^{2+}(*g*)) = 2189	ΔH_{IE} (O^{2-} (*g*) → $O^{\bullet}$(*g*)) = -603	

we want: Mg^{2+} (*g*) + O^{2-} (*g*) → MgO (*s*)

Mg^{2+} (*g*) → Mg (*g*)	$-\Delta H_{IE} = -2189$
Mg (*g*) → Mg (*s*)	$-\Delta H_{vap} = -146$
Mg (*s*) + ½ O_2 (*g*) → MgO (*s*)	$\Delta H_f° = -601$
O^{2-} (*g*) → $O^{\bullet}$ (*g*)	$\Delta H_{IE} = -603$
½ [2 $O^{\bullet}$ (*g*) → O_2 (*g*)]	<u>$-½ \Delta H_{O=O} = -247$</u>
	$\Delta H_L = -3786$

(b) Calculate the theoretical lattice enthalpy ($\Delta H_L°$) for MgO which adopts the rock salt structure (fcc anions with Mg^{2+} in the octahedral holes). Note: $r_{Mg2+} = 0.86$ Å, $r_{O2-} = 1.26$ Å. (1.5 points)

Using the Kapustinkii equation:

$$\Delta H_L^{\circ} = \frac{n z_A z_B}{r_A + r_{B0}}\left(1 - \frac{d^*}{r_A + r_B}\right)\mathcal{K} = \frac{2(2)(-2)}{0.86 + 1.26}\left(1 - \frac{0.345}{0.86 + 1.26}\right)(1.21) = -3.823\text{MJ/mol}$$

$$= 3823 \text{ kJ/mol}$$

Using the Born-Meyer equation:

$$\Delta H_L^{\circ} = \frac{N_A z_A z_B e^2}{4\pi\varepsilon_0 d}\left(1 - \frac{d^*}{d}\right)\mathcal{A} = \frac{(6.02\times10^{23})(2)(-2)(1.6022\times10^{-19})^2}{4\pi(8.8542\times10^{-12})(2.12\times10^{-10})}\left(1 - \frac{0.345}{2.12}\right)(1.74756)$$

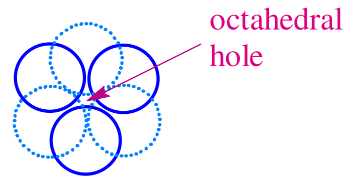
$$= 3835 \text{ kJ/mol}$$

(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 (the theoretical value *vs.* the experimental value) are very close, which means that the model used to create the Kapustinskii or Born-Meyer equation is valid. In other words, the MgO lattice acts has hard spheres to give a purely ionic solid.

(d) Describe (with a drawing, if you like) an octahedral hole. (1 point)

With close-packed spheres, there is a location in the lattice (such as that shown) where there is vacant space surrounded by 6 close-packed spheres. This space is therefore bordered on and defined by six points, which makes it an octahedral space.



Question 3 (a) Briefly describe two (2) types of alloys (2 points)

Any two of the following:

(i) Where two atoms are of similar sizes, structure, and electronegativity, they will form a mixture with atoms of the two types occupying random lattice positions (substitutional)

(ii) Where one atom is much smaller, and occupies holes in the lattice created by the other atom (interstitial)

(iii) Where the atoms have covalent or other more complex bonding, the alloy has very different properties from either of the components, and a specific structure/composition (intermetallic)

(b) Explain the relative values of the first ionization energies for the following elements: Ca (590), Sr (550), and Ba (503 kJ/mol). (2 points)

First ionization energy decreases as you go down a group. The larger the value of n (principle quantum number), the further it is from the nucleus, therefore the easier it is to remove from the atom.

(c) Tin chloride can exist as either $SnCl_2$ or $SnCl_4$, while the only lead analogue that's stable is $PbCl_2$. Explain. (2 points)

Cl is a strong enough oxidizing agent to remove electrons to either the Sn^{2+} or Sn^{4+} oxidation states. However, because of the inert pair effect (where the 6*s* electrons are stabilized faster than the 6*p* electrons due to the large Z_{eff} on very heavy elements), chlorine can only oxidize lead to the Pb^{2+} oxidation state.

(d) Gadolinium (Gd) is an exception to the Aufbau principle. Explain why. (2 points)
Expected (Aufbau) electron configuration: [Xe] $4f^{8}\ 6s^{2}$
Actual configuration: [Xe] $4f^{7}\ 5d^{1}\ 6s^{2}$

There are seven 4*f* orbitals, therefore the $4f^{8}$ configuration has one orbital with paired electrons. Therefore, since the 4*f* and 5*d* levels are so close, promoting one electron to 5*d* to remove the pairing energy is favorable.

(e) Briefly describe two types of defect that could occur in an ionic lattice. (2 points)

Any two of the following:

(i) a missing formula unit (Schottky defect)

(ii) exchanging sites (usually of atoms), where two spheres switch between their normal places

(iii) an ion moves to a different site (*e.g.* from O-hole to T-hole) (Frenkel defect)

(iv) an anion missing, replaced by an electron (F-centre)

(v) an extended defect (*e.g.* two crystals growing together, looks like a fault line)