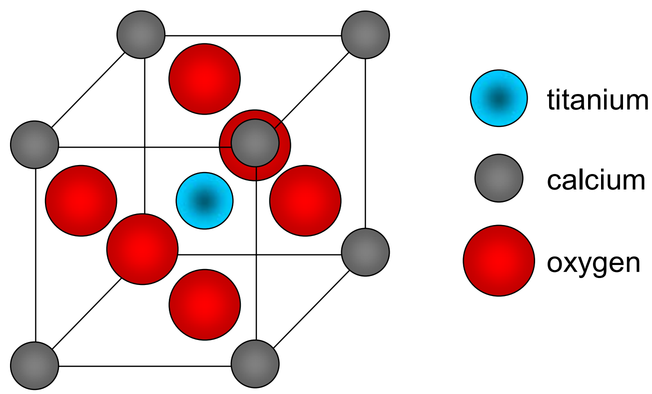
CHEM 121
Spring 2006
Quiz 7

Name: ____



1. Perovskite is a mineral containing calcium, titanium and oxygen. The diagram shown above represents perovskite's unit cell where the titanium is in the center of the cell, there are calciums on the corners of the cell and oxygens on the face of the cubic cell. Note that in this depiction one calcium is hidden behind an oxygen.

a. (5 Points) What is the formula of perovskite?

8 calcium on corners, counting 1/8 each = 1

6 oxygen on faces, counting 1/2 each = 3

1 titanium in center, counting as 1 = 1

The chemical formula of perovskite is $CaTiO_3$.

b. (2 Points) The number of formula units in the unit cell is **1**.

c. (3 Points) What are the oxidation numbers of each element in perovskite?

Ti **4+**

Ca **2+**

O **2-**

d. (1 Point) The coordination number of the Ti is **6**.

e. (1 Point) The coordination number of the Ca is **12**.

f. (4 Points) Could a Fe^{3+} derivative of perovskite be made without modifying the lattice?

Whether we replaced the Ti^{4+} with Fe^{3+} or replaced any of the Ca^{2+} with Fe^{3+}, we would always have an imbalance of charge that would require addition or removal of ions to balance out. As changing the number of ions constitutes a modification of the lattice, it is not possible to make a Fe^{3+} derivative of perovskite without changing the lattice.

2. Consider the following energy changes.

	ΔE (kJ/mole)
$Mg (g) \rightarrow Mg^{+} (g) + e^{-}$	+735
$Mg^{+} (g) \rightarrow Mg^{2+} (g) + e^{-}$	+1445
$O (g) + e^{-} \rightarrow O^{-} (g)$	-141
$O^{-} (g) + e^{-} \rightarrow O^{2-} (g)$	+878

a. (4 Points) Explain why magnesium oxide exists as $Mg^{2+}O^{2-}$ and not as $Mg^{+}O^{-}$. Note that no calculation is required.

For $Mg^{2+}O^{2-}$ the lattice energy will be at least four times greater than the lattice energy of $Mg^{+}O^{-}$. This will be accentuated by the smaller size of the Mg^{2+} relative to both O^{2-} and Mg^{+}. Even though it will take more energy to make Mg^{2+} and O^{2-} than to make Mg^{+} and O^{-}, the energy released when Mg^{2+} and O^{2-} come together provides the necessary energy.

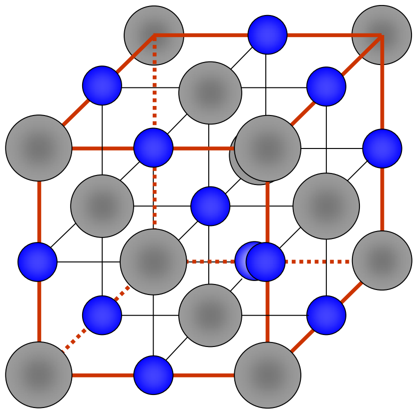
Note this is similar to what we seen before where coupling an unfavorable reaction to a favorable one can make the unfavorable one occur (remember Le Châtelier's Principle). What happens here is similar, the very favorable lattice energy provides the energy required to make the unfavorable ionizations occur.

b. (4 Points) What experiment could be done to confirm that magnesium oxide does not exist as $Mg^{+}O^{-}$? Explain how it would differentiate between the two formulations.

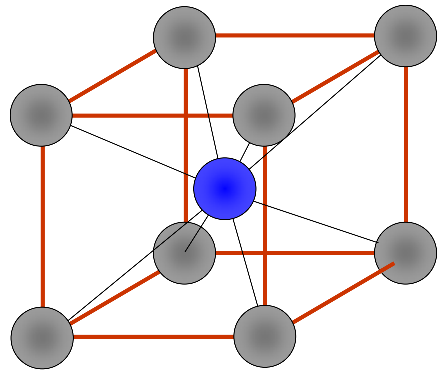
The electronic configuration of Mg^{+} is [Ne] $3s^1$ and that of O^{-} is [He] $2s^2$ $2p^5$, while both Mg^{2+} and O^{2-} have the [He] $2s^2$ $2p^6$ electronic configuration. We would expect $Mg^{2+}O^{2-}$ to be diamagnetic, while $Mg^{+}O^{-}$ should be paramagnetic.

Note that in reality $Mg^{+}O^{-}$ would exhibit complicated magnetism that would depend on temperature (we haven't discussed why), but it would not be diamagnetic.

3. (4 Points) CsF has the same structure as NaCl (a cubic close pack lattice of Cs^+ with F^- in all the octahedral holes). However, the structure of CsBr, CsI and CsCl is a cubic lattice of anions with the Cs^+ in the center of the cell. Why the difference?



CsF Structure



CsCl/CsBr/CsI Structure

The F^- ion is much smaller than Cs^+ or the other halides (Cl^-, Br^-, I^-). Remember that size increases down a group and decreases across a period. The holes in a cubic close pack lattice of Cs^+ ions must be large enough to accommodate F^-, but are too small for any other halide. To have holes that are large enough to accommodate the larger halides, the Cs^+ ions pack differently.

4. (10 Points) Problem 5-124 to this quiz.

Let x = mass of C_3H_8 and y = mass of C_6H_{14}.

The reactions that occur are

$$C_3H_8\,(g) + 5\,O_2\,(g) \rightarrow 3\,CO_2\,(g) + 4\,H_2O\,(g)$$

$$C_6H_{14}\,(g) + 19/2\,O_2\,(g) \rightarrow 6\,CO_2\,(g) + 7\,H_2O\,(g)$$

The amount of CO_2 that forms is

$$0.8339\text{ g }CO_2\left(\frac{1\text{ mole }CO_2}{44.09\text{ g}}\right) = 0.01894_8\text{ mole }CO_2$$

The amount of CO_2 formed in each reaction is

$$x\text{ g }C_3H_8\left(\frac{1\text{ mole }C_3H_8}{44.096\text{ g}}\right)\left(\frac{3\text{ mole }CO_2}{1\text{ mole }C_3H_8}\right) = (0.06803_3)(x)\text{ mole }CO_2$$

$$y\text{ g }C_6H_{14}\left(\frac{1\text{ mole }C_6H_{14}}{86.176_6\text{ g }C_6H_{14}}\right)\left(\frac{6\text{ mole }CO_2}{1\text{ mole }C_6H_{14}}\right) = (0.069624)(y)\text{ mole }CO_2$$

The total number of moles of CO_2 is thus

$$(0.06803_3)(x)\,\text{mole CO}_2 + (0.069624)(y)\,\text{mole CO}_2 = 0.01894_8\ \text{mole CO}_2$$

$$(0.06803_3)(x) + (0.069624)(y) = 0.01894_8$$

$$(x) + \left(\frac{0.069624}{0.06803_3}\right)(y) = \left(\frac{0.01894_8}{0.06803_3}\right)$$

$$(x) + (1.023_3)(y) = 0.2785_1$$

The mass of C_3H_8 and the mass of C_6H_{14} are related as follows.

$$x + y = 0.2759\ \text{g}$$

Solving for y gives y = 0.11 g C_6H_{14}.

Find % by mass of C_6H_{14} in the sample.

$$\%\ \text{C}_6\text{H}_{14}\ \text{by mass} = \frac{0.11_2\ \text{g}}{0.2759\ \text{g}} \times 100 = 41.\%$$

The % by mass of C_3H_8 is thus 59.% by difference.

The % by mass of C_3H_8 in the sample is 59.% and the % by mass of C_6H_{14} in the sample is 41.%