

Inorganic Chemistry with Doc M.

Day 10. Ionic Thrills, Part 1.

Topics:

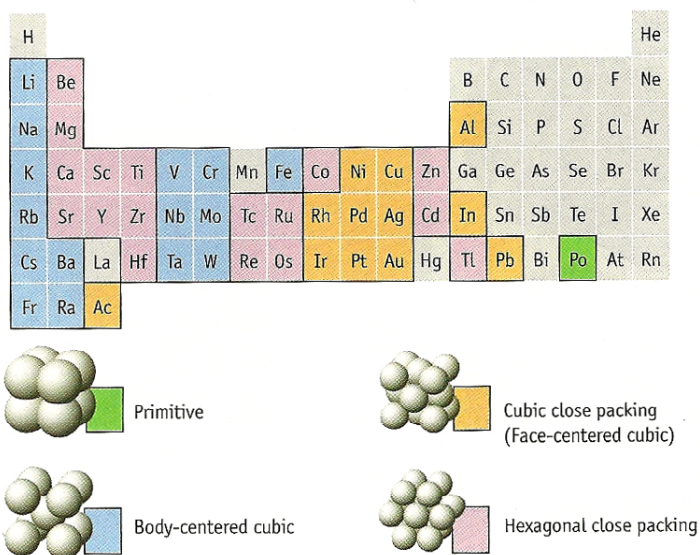
1. Properties of ionic substances
2. Cubic lattices and the periodic table
3. Simple cubic unit cell
4. Face-centered unit cell
5. Body-centered unit cell
6. Sodium chloride lattice
7. Octahedral and tetrahedral holes
8. The cesium chloride lattice
9. The fluorite lattice
10. The zinc blende lattice
11. Diamond

1. Properties of Ionic Substances

- (a) List properties of ionic compounds.

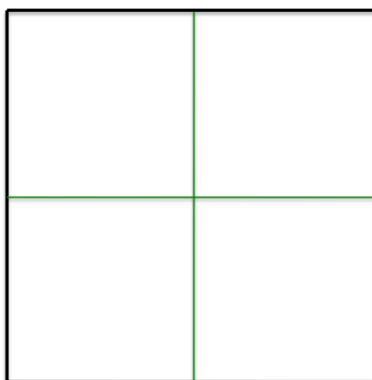
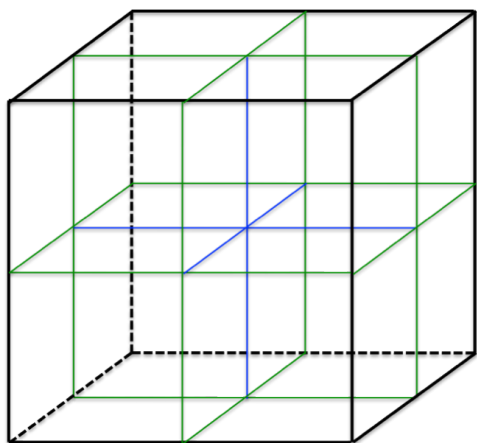
- (b) How would one identify a compound as either ionic or covalent?

2. Cubic lattice structures and the periodic table. A number of metals exist in one of the cubic lattice types. The three cubic lattices are simple cubic, face-centered cubic and body-centered cubic.



3. The simple cubic unit cell.

(a) Sketch in the atoms for a **simple cube**. Example: polonium



(b) Where do the atoms come into contact with one another? Show this on the front view (above right).



(c) How many atoms are present per unit cell? Show work.



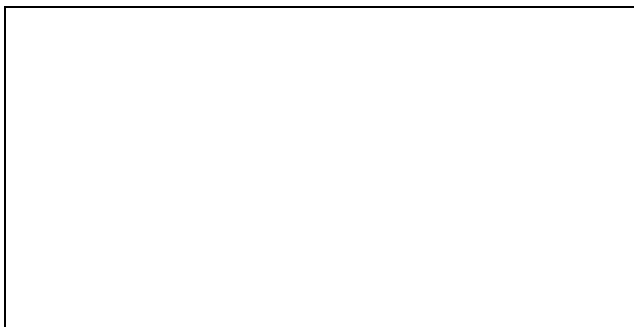
(d) How does the atomic radius, r , compare to the unit cell edge length, e ? Solve for e .



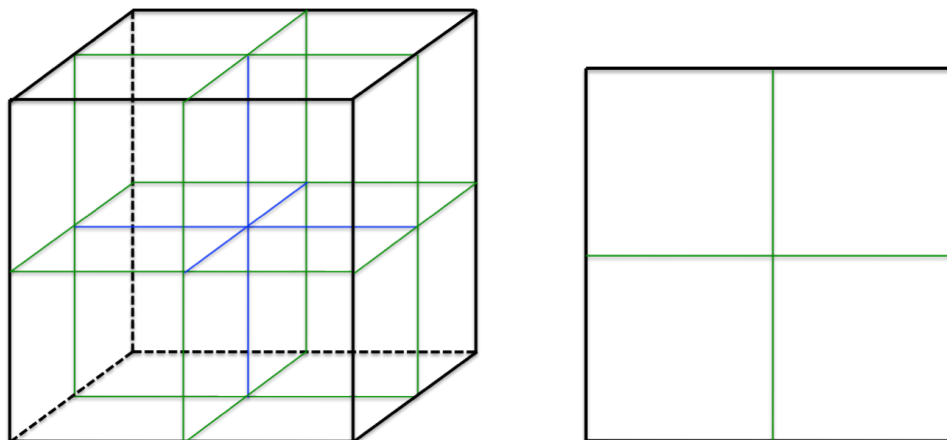
(e) What is the formula for volume in terms of r ?



(f) What percent of the space in the unit cell is occupied? Report this as a number.



4. The face-centered cube (examples: Al, Ca, Ni, Cu, Ge, Sr, Rh, Pd, Ag)



(a) The **fcc** lattice allows atoms to be close-packed (as densely packed as possible — more on this later.) The atoms of the **fcc** structure make contact along the face-diagonals as shown above right. Sketch in the atoms for a face-centered cube on the cubic unit cell templates above – use small circles in the figure at left so that the locations can be seen and large space-filling circles in the front view (above right) to show where the atoms come into contact with one another.

(b) How many atoms are present per unit cell? Show work.

(c) How does the atomic radius, r , compare to the unit cell edge length, e ? Solve for e .

(d) What is the formula for volume in terms of r ?

(e) What percent of the space in the unit cell is occupied? Report this as a number.

(f) Calcium exists in the fcc lattice. Given that the atomic radius of metallic calcium is 197 pm, calculate the volume of a unit cell of calcium in cm^3 .

- (g) Determine the density of calcium and compare your results with the known density, 1.54 g/cm^3 .



- (h) Determine the density of calcium erroneously assuming it exhibited a simple cube lattice and compare your results with the known density, 1.54 g/cm^3 .



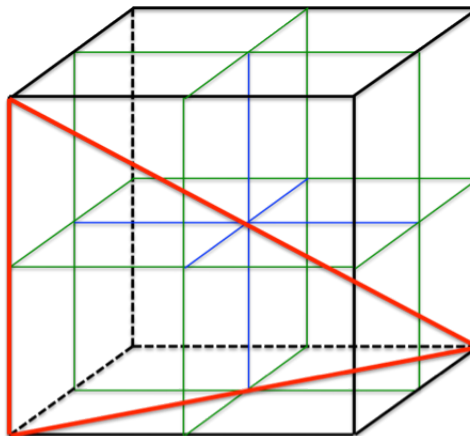
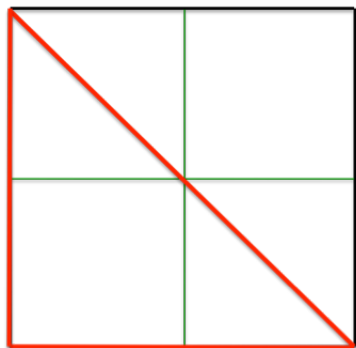
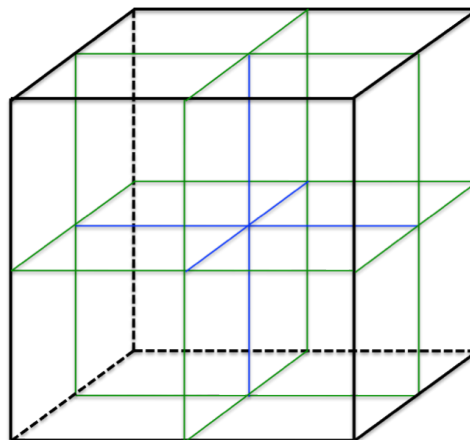
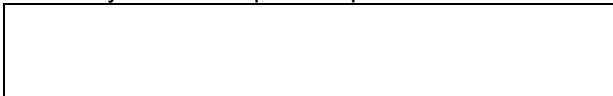
5. The body-centered Cube

- (a) Sketch in the atoms for a **body-centered cube**
(examples: All Group I, Ba, V, Cr, Mn, Fe, Nb, Mo, W)

- (b) Where do the atoms come into contact with one another?



- (c) How many atoms are present per unit cell? Show work.



(d) How does the atomic radius, r , compare to the unit cell edge length, e ? Solve for e .

(e) What is the formula for volume in terms of r ?

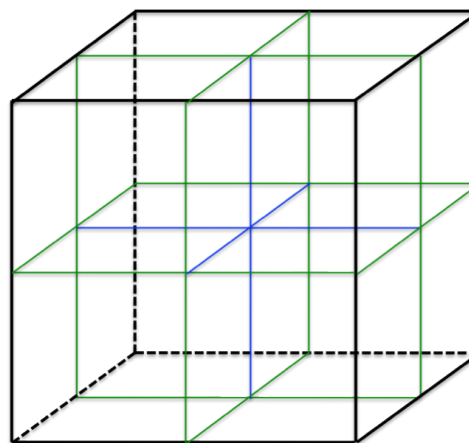
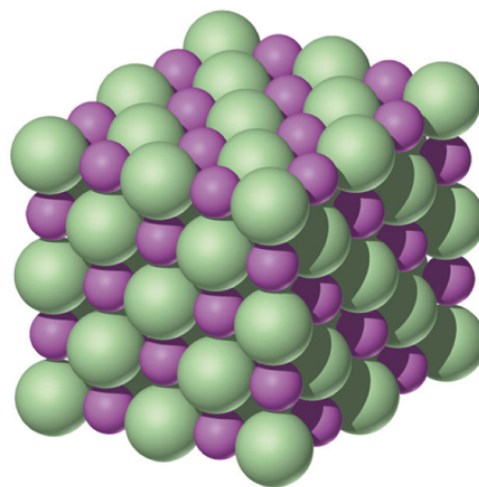
(f) What percent of the space in the unit cell is occupied? Report this as a number.

6. The sodium chloride lattice. (MANY ionic compounds have this structure including all of the alkaline earth oxides, e.g. MgO , SrO). (a) In the case of NaCl , which ions are the large spheres and which are the small ones?

(b) The anions and cations each form a lattice of their own called a **sub-lattice**. What is the sub-lattice of anions?

(c) Sketch the NaCl lattice on the template (right) placing the anions so that they are on the corners of the cube.

(d) Locations within all unit cells have names, most of which you already know, such as corner, face-center, body center. Another position is the edge-center. From its name, you should be able to describe the location of the edge-center positions. How many edge-centered positions are there in the fcc unit cell?



(e) Edge-centered positions are only partially inside each a particular unit cell. What fraction of each edge-centered position is in any given unit cell? Multiply by the number of edge-centered positions determined above and you have the total maximum occupancy for ions using edge-centered positions. What is this number?

(f) In the case of NaCl, the unit cell is thought of in terms of the sub-lattice chloride ions, perhaps because they are largest. From that perspective, most of the Na^+ cations occupy the edge-centers of the unit cell. There is one more sodium cation that is not on an edge-centered position. Where is it?

(g) Summarize what we have learned so far by completing the rest of the table.

	Corner positions $8 \times \frac{1}{8} = 1$	Face-centered positions $6 \times \frac{1}{2} = 3$	Body-centered positions $1 \times 1 = 1$	Edge-centered positions $12 \times \frac{1}{4} = 3$
Simple cube	Yes		No	
Face-centered cube				
Body-centered cube	Yes		Yes	
NaCl lattice		Chlorides		Sodium cations

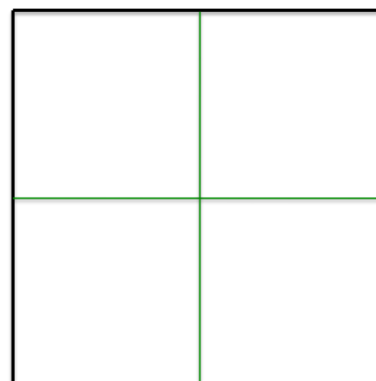
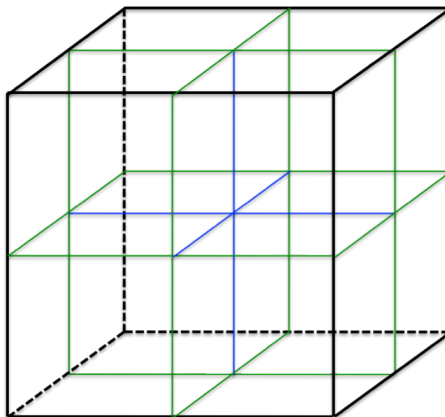
(h) What is the ratio of Cl^- to Na^+ in the unit cell? How does this compare to its formula?

(i) The Na^+ ion has a radius of 116 pm and the Cl^- ion has a radius of 167 pm. Determine the length of the edge, e , and the volume, V , of the unit cell (in cm^3).

(j) Predict the density of NaCl and compare it to the actual value, 2.165 g/cm^3 .

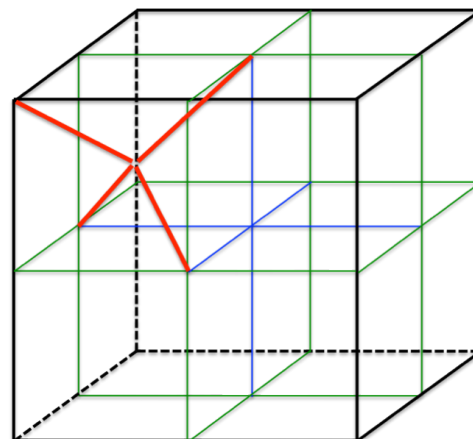
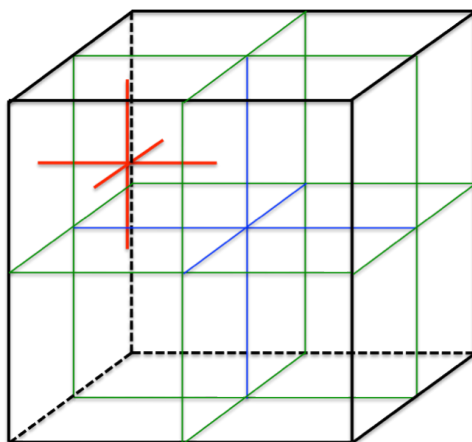
7. Octahedral and tetrahedral holes.

Close-packed unit cells include the **fcc** and the hexagonal close-packed (**hcp**) unit cells — we have not yet discussed the **hcp** unit cell. Both fcc and hcp have the large ions (or neutral atoms) arranged in a close-packed arrangement (there is no more efficient way to pack these



spheres.) Yet, between the spheres, there are open spaces. Upon closer inspection, these “holes” are one of only two types. There are larger holes defined as the space created by six of the large spheres all equally distant from the center of the hole — these are called **octahedral holes**. Copy your work from the top of page 3 here and identify the octahedral holes by marking them with “O”. All together, you should find 13 locations for octahedral holes.

There are smaller holes defined as the space created by the space created by four of the large spheres all equally distant from the center of the hole — called **tetrahedral holes**. The location

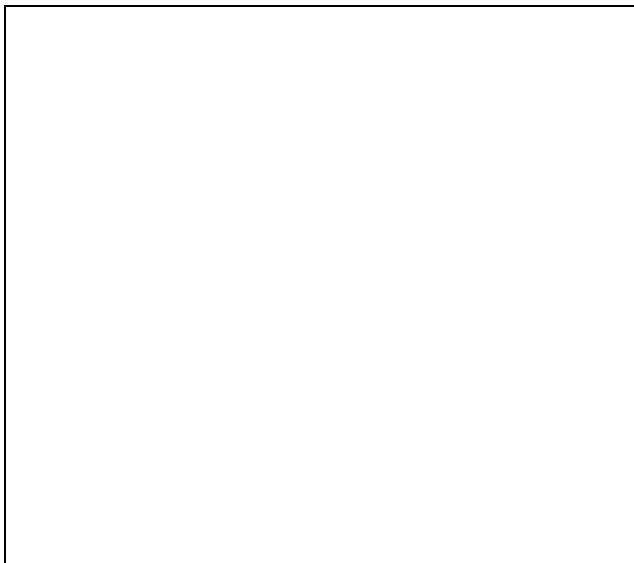


of one of these holes is shown two different ways in the figures below. The Cartesian coordinates shown in the figure on the left only indicate the center of the tetrahedral hole. How many tetrahedral holes are present within a fcc unit cell?

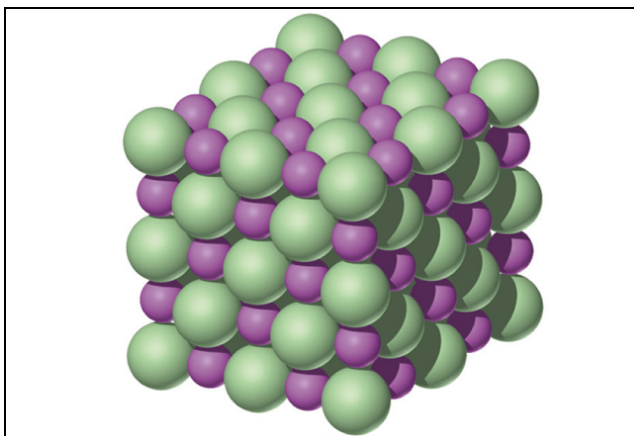
(b) Determine the ratio of spheres : octahedral holes : tetrahedral holes fully contained within the fcc unit cell.

- (c) Using four spheres, place three of them in mutual contact — a plane of three spheres that make an equilateral triangle shape — the C_3 face of a tetrahedron.

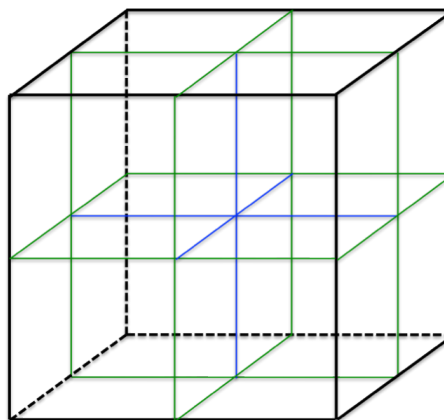
Sketch this below. Place the fourth sphere on a second layer above the first three and resting in the divot of the three touching spheres. Imagine a much smaller sphere in the tiny 4-sided, 3-dimensional hole created by the four spheres. You have created a tetrahedral hole.



- (d). Let's return to the NaCl lattice. Each sodium cation is in an octahedral hole. What are the closest neighbors of each sodium cation? How many nearest neighbors does each ion in NaCl have?



8. The cesium chloride lattice. The CsCl lattice is usually encountered when we have cations that are similar in radius to the anions. Both anion and cation sub-lattices form a simple cube, however one sub-lattice is offset by one-half the edge distance in all three dimensions (that is to say that the cation sub-lattice occupies the body-centered positions of the anion sub-lattice (or visa versa).



- (a) Sketch the CsCl lattice on this template placing the anions so that they are on the corners of the cube.
- (b) Complete the following table for NaCl and CsCl. Write either Na^+ (or Cs^+) or Cl^- .

	Corner	Face-center	Body-center	Edge-center
NaCl				
CsCl				

(c) What sub-lattices does Cl^- have in the CsCl structure?

(d) What is the ratio of Cs^+ to Cl^- in the unit cell?
How does this compare to its formula?

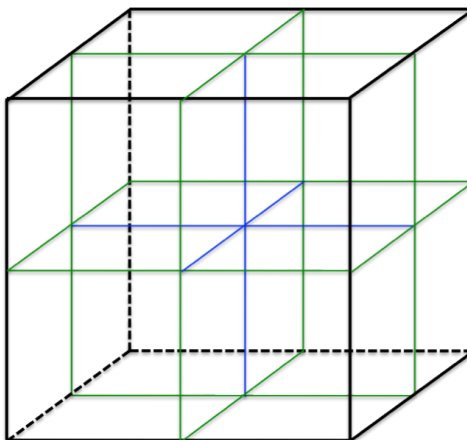
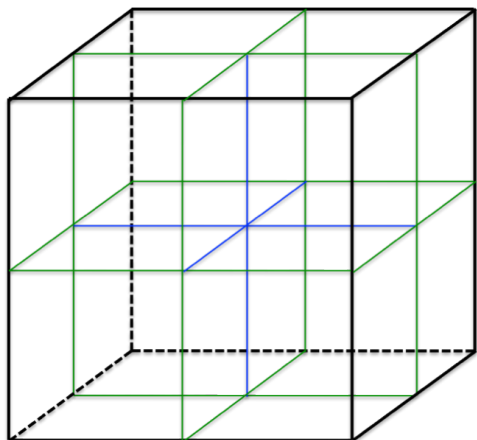
(e) What is the coordination number for Cs^+ and Cl^- in the CsCl structure? What is the coordination number for Na^+ and Cl^- in the NaCl structure?

(f) The density of CsCl is 3.988 g/cm^3 . Knowing that density = mass/volume, determine the volume of the CsCl unit cell and use that value to determine the length of an edge, e , in units of pm.

(g) Continuing on, use the value for the edge, e , to determine the diagonal length from one corner to the opposite corner of the cube. This distance equals $2 \times r_{\text{Cs}^+} + 2 \times r_{\text{Cl}^-}$.
Given the ionic radius for Cs^+ ion is 188 pm, calculate the r_{Cl^-} in pm.

9. The fluorite lattice. Fluorite is CaF_2 . There are two equivalent ways to think about the fluorite structure.

- (a) The fluorides form a simple cubic lattice. Sketch eight unit cells worth of fluorides on the template provided at left, below



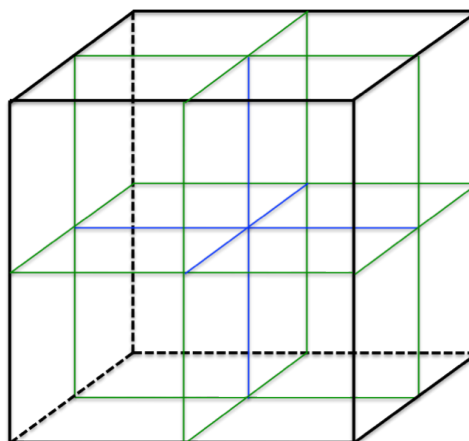
- (b) The calcium cations exist in alternating body-center positions. Sketch them in.
 (c) What is the coordination number (number of nearest neighbors of opposite charge) for each ion?

- (d) The other way to think about the fluorite structure is to think of a fcc of calcium ions (Ca^{+2} has slightly larger radius than F^-) with the fluorides in all of the tetrahedral holes. Sketch this on the right template, above.

- (e) What is the coordination number for each ion?

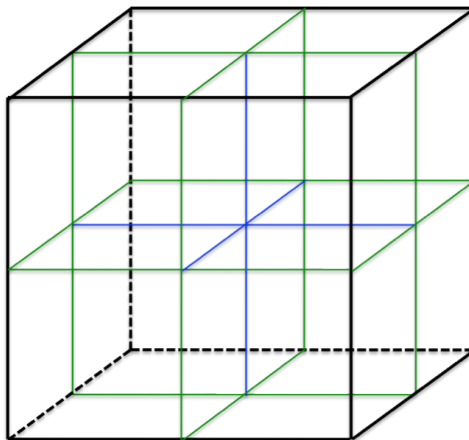
10. The zinc blende lattice. The ZnS is “zinc blende.” The lattice consists of a **fcc** sulfide sub-lattice with Zn^{+2} cations occupying half (alternate) of the tetrahedral holes.

- (a) Sketch the ZnS lattice on this template.
 (b) What is the coordination number (number of nearest neighbors of opposite charge) for each ion?



(c) How many S^{2-} anions are there per unit cell? Explain.

11. Diamond. Diamond has the same structure as zinc blende except that all of the occupied positions are taken by carbons (both the zinc cation and the sulfide anion positions). Sketch diamond here and connect every carbon to its four nearest neighbors. Do you see the tetrahedral angle?



Review for the ACS Final Exam: Solid State

1. What is the empirical formula of a compound that crystallizes with anions in a fcc array sublattice with cations in half of the octahedral holes?

- A. MX B. MX_2 C. MX_4
D. M_2X E. M_2X_4

2. Calcium silicate crystallizes with oxygen ions in a fcc sublattice. The calcium ions occupy octahedral holes and the silicon atoms are in tetrahedral holes. What fraction of each type of hole is occupied?

	Octahedral	Tetrahedral
A.	1/4	1/8
B.	1/2	1/2
C.	1/4	1/2
D.	1/2	1/8
E.	1/8	1/4

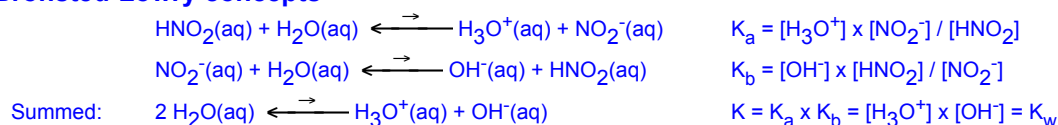
3. Which of the following compounds would be most likely to exhibit the sodium chloride lattice?

- (a) MgO (b) K_2S (c) $CsCl$
(d) BeI_2 (e) RbI

Answers: B, D, A

Answers to Day 9.

1. Bronsted-Lowry concepts



(b) Complete this table of acid/base conjugate pairs.

Acid	K_a	Base	K_b
chromic acid, H_2CrO_4	1.8×10^{-1}	HCrO_4^-	5.6×10^{-14}
hydrofluoric acid, HF	3.5×10^{-4}	F^-	2.9×10^{-11}
phosphoric acid, H_3PO_4	7.5×10^{-3}	H_2PO_4^-	1.3×10^{-12}
dihydrogen phosphate, H_2PO_4^-	6.2×10^{-8}	HPO_4^{2-}	1.6×10^{-7}
hydrogen phosphate, HPO_4^{2-}	4.8×10^{-13}	PO_4^{3-}	2.1×10^{-2}
$\text{Pb}(\text{OH})(\text{OH}_2)^+$	1.0×10^{-11}	lead(II) hydroxide, $\text{Pb}(\text{OH})_2$	9.6×10^{-4}
NH_4^+	5.6×10^{-10}	ammonia, NH_3	1.8×10^{-5}
CH_3NH_3^+	2.7×10^{-11}	methyl amine, CH_3NH_2	3.7×10^{-4}

2. Lewis acid and base concepts

Lewis acids: BF_3 , Al^{3+} , CPh_3^+ ($\text{Ph} = \text{C}_6\text{H}_5$), Fe^{+2} , AlCl_3 ; Lewis bases: NH_3 , H_2O , F^- , Cl^- ; Neither: CH_4

3. Oxyacids

Ranked strongest acid to weakest acid:

HIO_4 , HIO_3 , HIO_2 , HIO

NaHSO_4 , NaHSO_3 ,

4. Polyprotic acids

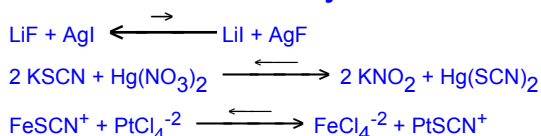
$K_a = 10^{-12} - 10^{-13}$ for the second proton lost for germanic acid, and $\text{p}K_a = \sim 12 - 13$

5. pH of salts

LiCl , pH neutral; KBr , pH neutral; NH_4NO_3 , pH acidic; RbNO_2 , pH basic; CsF , pH basic; $\text{Fe}(\text{ClO}_4)_2$, pH

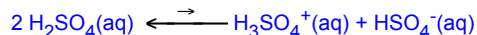
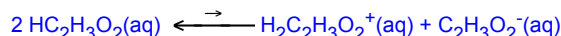
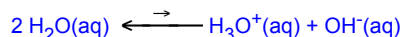
acidic; NaHSO_4 , pH acidic; Na_2SO_4 , pH basic; $\text{NaC}_2\text{H}_3\text{O}_2$, pH basic

6. Hard-soft acid-bases chemistry.

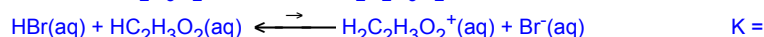
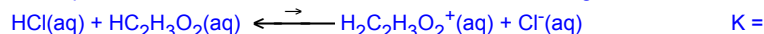


7. Non-aqueous solvents.

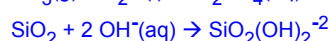
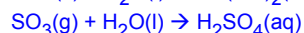
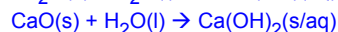
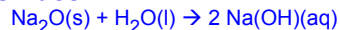
The 6 strong acids: $\text{HCl}(\text{aq})$, $\text{HBr}(\text{aq})$, $\text{HI}(\text{aq})$, $\text{HBO}_3(\text{aq})$, $\text{HClO}_4(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$



The equilibrium that occurs when HCl and HBr are added to glacial acetic acid:



8. Oxides.



Amphoteric oxides. Some oxides are amphoteric. That is, they react with both acids and bases. Amphoteric oxides include BeO , Al_2O_3 , Ga_2O_3 , SnO_2 , and PbO_2 . Indicate them on the periodic table.

