Inorganic 09348 2001

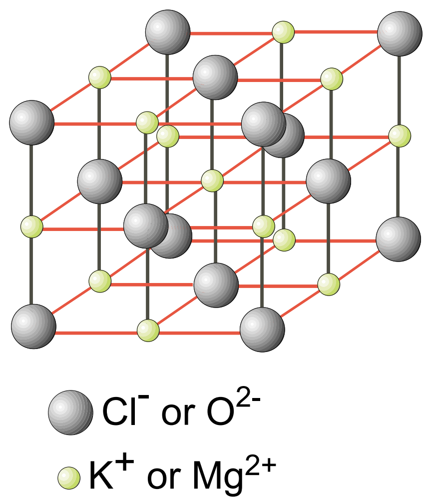
Friday "Take-Home" Quiz 2

October 12, 2001

Question 1 – Which salt is the most dense MgO or KCl?

Ion	Radius
Mg^{2+}	0.066 nm
O^{2-}	0.132 nm
K^{+}	0.133 nm
Cl^{-}	0.181 nm

Both MgO and KCl crystallize in the “NaCl” structure, as shown in the picture bellow.



One want to calculate the density,

$$d = \frac{M}{V},$$

where M is the mass of the unit cell and V is the volume of the unit cell.

From the picture, one can see that this kind of cubic lattice has a side, a, given by

$$a = 2r_{\text{cat}} + 2r_{\text{anion}}$$

The volume, V, is then

$$V = a^3$$

To determine the mass of a unit cell, one must calculate the number of each atom per unit cell and then multiply this number by the corresponding mass of the atom.

<u>MgO</u>

$$a_{\text{MgO}} = 2r_{\text{Mg}^{2+}} + 2r_{\text{O}^{2-}} \quad \Rightarrow \quad a_{\text{MgO}} = 2\times 0.066\times 10^{-9} + 2\times 0.132\times 10^{-9} \quad \Leftrightarrow \quad \boxed{a_{\text{MgO}} = 3.96\times 10^{-10}\ \text{m}}$$

$$V_{\text{MgO}} = a_{\text{MgO}}{}^{3} \quad \Rightarrow \quad \boxed{V_{\text{MgO}} = 6.21\times 10^{-29}\ \text{m}^3}$$

$$\# \text{ of } = Mg^{2+} \quad (1\times1)+\left(12\times\frac{1}{4}\right)=4$$

$$\# \text{ of } = O^{2-} \left(6\times\frac{1}{2}\right)+\left(8\times\frac{1}{8}\right)=4$$

$$M_{MgO} = 4\times M_{Mg^{2+}} + 4\times M_{O^{2-}} \Rightarrow \quad M_{MgO} = 4\times24.3\times10^{-3} + 4\times16\times10^{-3} \Leftrightarrow M_{MgO} = 0.1612\,\text{kg.mol}^{-1}$$

$\Rightarrow$ if one divide by the Avogadro constant $\Rightarrow$ $\boxed{M_{MgO} = 2.68\times10^{-25}\text{ kg}}$

$$d_{MgO} = \frac{M_{MgO}}{V_{MgO}} \Rightarrow d_{MgO} = \frac{2.68\times10^{-28}}{6.21\times10^{-29}} \Leftrightarrow \boxed{d_{MgO} = 4.32\times10^{3}\text{ kg.m}^{-3}} \Leftrightarrow \boxed{d_{MgO} = 4.32\,\text{g.cm}^{-3}}$$

<u>KCl</u>

$$a_{KCl} = 2r_{K^+} + 2r_{Cl^-} \Rightarrow a_{KCl} = 2\times0.133\times10^{-9} + 2\times0.181\times10^{-9} \Leftrightarrow \boxed{a_{KCl} = 6.28\times10^{-10}\text{ m}}$$

$$V_{KCl} = a_{KCl}{}^{3} \Rightarrow \boxed{V_{MgO} = 2.48\times10^{-28}\text{ m}^3}$$

Because the unit cell is the same we have

$$\# \text{ of } = K^{+} \; (1\times1)+\left(12\times\frac{1}{4}\right)=4$$

$$\# \text{ of } = Cl^{-} \left(6\times\frac{1}{2}\right)+\left(8\times\frac{1}{8}\right)=4$$

$$M_{KCl} = 4\times M_{K^+} + 4\times M_{Cl^-} \Rightarrow M_{KCl} = 4\times39.1\times10^{-3} + 4\times35.5\times10^{-3} \Leftrightarrow M_{KCl} = 0.2984\,\text{g.mol}^{-1} \Rightarrow$$

$\Rightarrow$ if one divide by the Avogadro constant $\Rightarrow$ $\boxed{M_{KCl} = 4.81\times10^{-25}\text{ kg}}$

$$d_{KCl} = \frac{M_{KCl}}{V_{KCl}} \Rightarrow d_{KCL} = \frac{4.81\times10^{-25}}{2.48\times10^{-28}} \Leftrightarrow \boxed{d_{KCl} = 1.94\times10^{3}\text{ kg.m}^{-3}} \Leftrightarrow \boxed{d_{KCl} = 1.94\,\text{g.cm}^{-3}}$$

One can see that $d_{MgO} > d_{KCL}$, which means that MgO is more dense that KCl.

Question 2 – Assign names to the 21 models shown in class.

No.	Names
1.	B
2.	C (diamond)
3.	$CrCl_3$
4.	GaAs
5.	ZnS (Zincblende)
6.	CaF_2 (Fluorite)
7.	Mg_2SiO_4 (olive)
8.	Calcite (CaO_3)
9.	NaCl (halide)
10.	CsCl
11.	TiO_2 (Rutile)
12.	ZnS (Wurtzite)
13.	SiO_2 (α quartz)
14.	Si (p type)
15.	Si (n type)
16.	Si (npn)
17.	$H_2O(s)$ (ice)
18.	Al
19.	P (white)
20.	Sn (grey)
21.	Sn (White)

Question 3 – Suggest two structures for the 1:1 electrolyte formed in the reaction of IF_7 with KF. Deduce the number of IR and Raman bands expected for each of these structures.

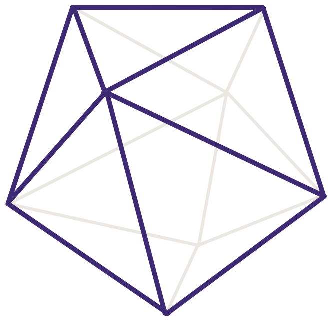
$$IF_7 + KF \rightarrow K^+ + IF_8^-$$

The structure of IF_8^- has many possible theoretical possibilities such as:

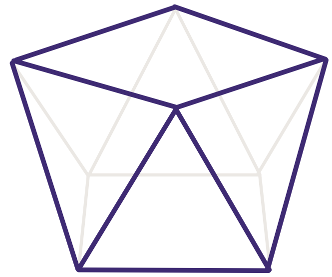
1. Cubic structure (O_h)
2. Square anti-prism (D_{4d})
3. Trigonal Dodecahedron (C_{2v})
4. Bi-capped trigonal prism (C_{2v})
5. Hexagonal by-pyramid (D_{6h})
6. Planar octagonal (D_{8h})

In reality the most stable structures are 2 and 3. These are the structures that will be studied below.

Trigonal Dodecahedron



Square anti-prism



D_{4d}	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C_2'$	$4\sigma_d$		
A_1	1	1	1	1	1	1	1		$x^2+y^2,\ z^2$
A_2	1	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	1	1	-1		
B_2	1	-1	1	-1	1	-1	1	z	
E_1	2	$\sqrt{2}$	0	$-\sqrt{2}$	-2	0	0	(x,y)	
E_2	2	0	-2	0	2	0	0		(x^2-y^2, xy)
E_3	2	$-\sqrt{2}$	0	$\sqrt{2}$	-2	0	0	(R_x, R_y)	(xz, yz)

D_{4d}	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C_2'$	$4\sigma_d$
Γ_r	8	0	0	0	0	0	2

Order = h = 1 + 2 + 2 + 2 + 1 + 4 + 4 = 16

$$\# A_1 = \frac{1}{16}[(1\times1\times8)+(1\times2\times0)+(1\times2\times0)+(1\times2\times0)+(1\times1\times0)+(1\times4\times0)+(1\times4\times2)] = 1$$

$$\# A_2 = \frac{1}{16}[(1\times1\times8)+(1\times2\times0)+(1\times2\times0)+(1\times2\times0)+(1\times1\times0)+(-1\times4\times0)+(-1\times4\times2)] = 0$$

$$\# B_1 = \frac{1}{16}[(1\times1\times8)+(-1\times2\times0)+(1\times2\times0)+(-1\times2\times0)+(1\times1\times0)+(1\times4\times0)+(-1\times4\times2)] = 0$$

$$\# B_2 = \frac{1}{16}[(1\times1\times8)+(-1\times2\times0)+(1\times2\times0)+(-1\times2\times0)+(1\times1\times0)+(-1\times4\times0)+(1\times4\times2)] = 1$$

$$\# E_1 = \frac{1}{16}[(2\times1\times8)+(\sqrt{2}\times2\times0)+(0\times2\times0)+(-\sqrt{2}\times2\times0)+(-2\times1\times0)+(0\times4\times0)+(0\times4\times2)] = 1$$

$$\# E_2 = \frac{1}{16}[(2\times1\times8)+(0\times2\times0)+(-2\times2\times0)+(0\times2\times0)+(2\times1\times0)+(0\times4\times0)+(0\times4\times2)] = 1$$

$$\# E_3 = \frac{1}{16}[(2\times1\times8)+(-\sqrt{2}\times2\times0)+(0\times2\times0)+(\sqrt{2}\times2\times0)+(-2\times1\times0)+(0\times4\times0)+(0\times4\times2)] = 1$$

$$\boxed{\Gamma_r = A_1 + B_2 + E_1 + E_2 + E_3}$$

	Origin				
	A_1	B_2	E_1	E_2	E_3
Infra Red		One line	One line		
Raman	One line			One line	One line

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
Γ_r	8	0	4	4

Order = h = 1 + 1 + 1 + 1= 4

$$\# A_1 = \frac{1}{4}[(1\times1\times8)+(1\times1\times0)+(1\times1\times4)+(1\times1\times4)] = 4$$

$$\# A_2 = \frac{1}{4}[(1\times1\times8)+(1\times1\times0)+(-1\times1\times4)+(-1\times1\times4)] = 0$$

$$\# B_1 = \frac{1}{4}[(1\times1\times8)+(-1\times1\times0)+(1\times1\times4)+(-1\times1\times4)] = 2$$

$$\# B_2 = \frac{1}{4}[(1\times1\times8)+(-1\times1\times0)+(-1\times1\times4)+(1\times1\times4)] = 2$$

$$\boxed{\Gamma_r = 4A_1 + 2B_1 + 2B_2}$$

	Origin		
	A_1	B_1	B_2
Infra Red	four lines	two lines	two lines
Raman	four lines	two lines	two lines