Chapter 16 Problems

18) Predict which substance in each of the following pairs would have the stronger intermolecular forces.

a. CO_2 or OCS Permanent Dipole present in selected compound, but not the other. Draw the VSEPR structures and it becomes more obvious.
b. PF_3 or PF_5 Same as a.
c. SF_2 or SF_6 Same as a.
d. SO_3 or SO_2 Same as a.

20) In each of the following groups of substances, pick the one that has the given property. Justify your answer.

a. Highest boiling point: HCl, Ar, or F_2
HCl is the only polar molecule here and will have the strongest intermolecular forces.
b. Highest freezing point: H_2O, NaCl, or HF
NaCl has ion-ion interactions which are stronger than the hydrogen bonding present in the other two compounds.
c. Lowest vapor pressure at 25 ^{o}C: Cl_2, Br_2, I_2
I_2 is the largest and most polarizable of the three compounds so the dispersion forces will be greatest in I_2.
d. Lowest freezing point: N_2, CO, or CO_2
N_2 is the smallest and least polarizable so it will have the weakest dispersion forces.
e. Greatest Viscosity: H_2S, HF, or H_2O_2
H_2O_2 has the most/strongest hydrogen bonding ability so it has the highest intermolecular forces.
f. Greatest heat of vaporization: CH_3OCH_3, CH_3CH_2OH, or $CH_3CH_2CH_3$
CH_3CH_2OH is the only one of these three with hydrogen bonding ability so it will have the greatest heat of vaporization.

24) Consider the following melting point data:

Compound	**NaCl**	**$MgCl_2$**	**$AlCl_3$**	**$SiCl_4$**	**PCl_3**	**SCl_2**	**Cl_2**
mp (^{o}C)	801	708	190	-70	-91	-78	-101
Compound	**NaF**	**MgF_2**	**AlF_3**	**SiF_4**	**PF_5**	**SF_6**	**F_2**
mp (^{o}C)	997	1396	1040	-90	-94	-56	-220

Account for the trnds in melting points for the two series of compounds in terms of interparticle forces.

The ionic compounds (NaCl, $MgCl_2$, NaF, MgF_2, and AlF_3) all have very high melting points as we would expect from their very strong intermolecular forces.

The molecular compounds ($SiCl_4$, PCl_3, SCl_2, Cl_2, SiF_4, PF_5, SF_6 and F_2) all have much lower melting points because the intermolecular forces here are mostly dispersion forces with the occasional dipole moment thrown in (PCl_3 and SCl_2 are polar).

$AlCl_3$ doesn't fit into either category very well because it is a compound that straddles the line between ionic and molecular.

34) Carbon diselenide, CSe_2, is a liquid at room temperature. The normal boiling point is 125 ^oC, and the melting point is -45.5 ^oC. Carbon disulfide, CS_2, is also a liquid at room temperature, with normal boiling and melting points of 46.5 ^oC and -111.6 ^oC, respectively. How do the strengths of the intermolecular forces vary from CO_2 to CS_2, to CSe_2? Explain your answer.

We know from experience that CO_2 is NOT a liquid at room temperature, so without looking up its normal boiling point (nbp), we still know that for the three compounds nbp will increase in the order of $CO_2 < CS_2 < CSe_2$. Since the nbp's increase in that order, so do the strengths of the intermolecular forces, dispersion forces in this case. O, S, and Se are all in the same family and increase in size and polarizability as you go down the family in the periodic table. As you increase in size and polarizability, the strength of dispersion forces increases.

44) Irridium (Ir) has a face-centered cubic unit cell with an edge length of 383.3 pm. Calculate the density of solid iridium.

Face-centered cubic cells have four atoms per unit cell (½ atom on each face and 1/8 atom on each corner), so we can figure the mass of the unit cell according to the following calculation:

$$\frac{192.2\text{ g}}{\text{mol}}\left(\frac{1\text{ mol}}{6.022 \times 10^{23}\text{ atoms}}\right)\left(\frac{4\text{ atoms}}{\text{unit cell}}\right) = 1.277 \times 10^{-21}\text{ g/unit cell}$$

The volume of the unit cell is simply the cube of the length of an edge (although it's easier if you convert picometers to centimeters first):

$$V = (383.3 \times 10^{-10}\text{ cm})^3 = 5.631 \times 10^{-23}\text{ cm}^3$$

Density is mass over volume, so the density of Iridium is:

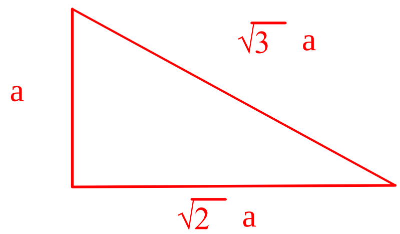
$$\frac{1.277 \times 10^{-21}\text{ g}}{5.631 \times 10^{-23}\text{ cm}^3} = 22.68\text{ g/cm}^3$$

46) You are given a small bar of an unknown metal X. You find the density of the metal to be 10.5 g/cm^3. An X-ray diffractions experiment measures the edge of the face-centered cubic unit cell as 409 pm. Identify X.

This problem is the reverse of the last one. You still need to find the volume of the unit cell, which works out to be $6.84_2 \times 10^{-23}$ cm^3. Once you have that, the mass of the unit cell is the product of the volume and the density, or $7.18_4 \times 10^{-22}$ g. Of course, that is for 4 atoms, so if you divide by four and multiply by Avagadro's number, you'll get a molecular weight of 108, which matches silver, Ag, pretty well.

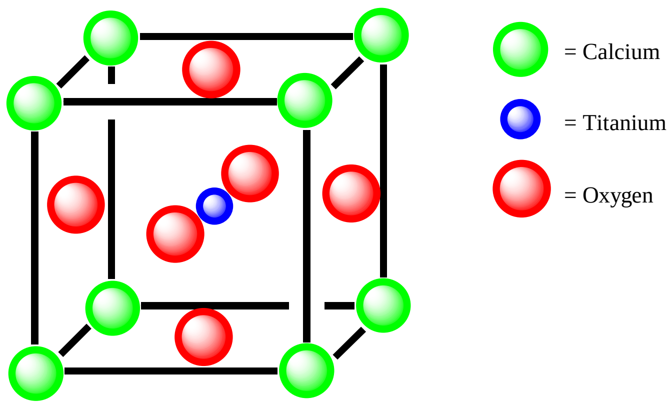
48) Barium has a body-centered cubic structure. If the atomic radius of barium is 222 pm, calculate the density of solid barium.

The challenge in this problem is converting the radius of barium to the volume of the unit cell. For body-centered cubic unit cells the only way to get a diagonal that goes completely through atoms is to go from one corner, through the center of the cube, to the other corner. That gives you a right triangle like the one shown below.

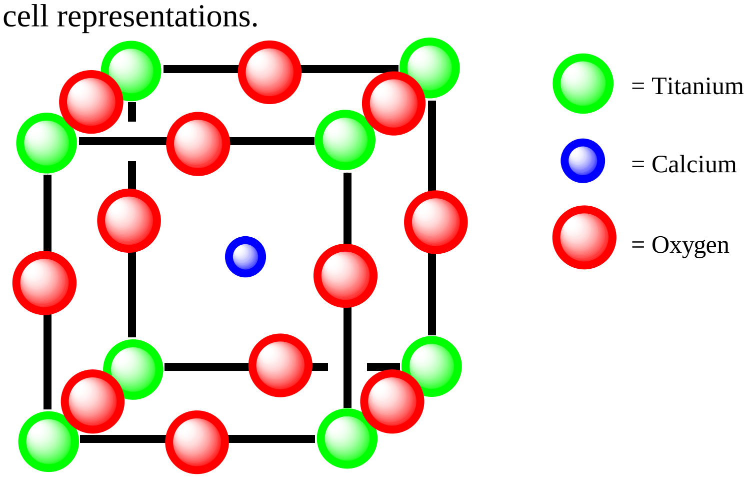


The long side could also be described as having a length of 4r, so we end up with the equation: $\sqrt{3}\ a = 4r$. If you use 222 x 10-10 cm for r, you can get the length of a side by solving for a. Once you have a, V = a3. From there, work the problem just like #44 with the exception that a body-centered cubic structure only has 2 atoms per unit cell, not 4. If you work the problem correctly, you should get an answer of 3.40 g/cm^3.

70) Perovskite is a mineral containing calcium, titanium, and oxygen. The following diagram represents the unit cell.



a. What is the formula for perovskite? $CaTiO_3$
b. An alternative way of drawing the unit cell of perovskite has calcium at the center of each cubic unit cell. What are the positions of the titanium an oxygen atoms in this representation of the unit cell? Show that the formula for perovskite is the same for both unit cell representations.



c. How many oxygen atoms surround a given Ti atom in each representations of the unit cell?

Titanium is in an octahedral hole, so it is surrounded by 6 oxygen atoms.

72) Define each of the following:

a. condensation – going from the gas phase to the liquid phase
b. evaporation – going from the liquid phase to the gas phase
c. sublimation – going from the solid phase to the gas phse
d. supercooled liquid – a liquid that is cooled below its freezing point with changing to a solid

86) A 20.0 g sample of ice at -10.0 ^oC is mixed with 100.0 g of water at 80.0 ^oC. Calculate the final temperature of the mixture assuming no heat loss to the surroundings. The heat capacities of $H_2O(s)$ and $H_2O(l)$ are 2.08 and 4.18 J g^{-1} $^oC^{-1}$, respectively, and the enthalpy of fusion for ices is 6.01 kJ/mol.

This is a review problem from early thermodynamics last semester. The important assumption is that the heat gained by the ice must be equal to the heat lost by the water, so:

$$q_{ice} = - q_{water}$$

The heat gained by the ice is actually three changes added together: raising the ice to 0 oC, melting the ice, and finally raising the temperature of the melted ice. The water heat change is just a single value. Your overall equation should look something like this:

$$m_{ice}C_{ice}\Delta T_{ice} + n_{ice}\Delta H_{fus} + m_{ice}C_{water}\Delta T = -(m_{water}C_{water}\Delta T_{water})$$

$$20.0\text{ g }(2.08\text{ J/g}^oC)(10\ ^oC) + 1.11\text{ mol }(6.01\text{ kJ/mol}) + 20.0\text{ g }(4.18\text{ J/g}^oC)(T_f - 0.0) = - [100.0\text{ g }(4.18\text{ J/goC})\ (T_f - 80.0\text{ oC})]$$

If you work through the math, you should come up with a final temperature of 52.5 ^oC once the system comes to thermal equilibrium.

90) Use the accompanying phase diagram for sulfur to answer the following questions.

a. How many triple points are in the phase diagram? 3
b. What phases are in equilibrium at each of the triple points?

153 ^oC, 1420 atm has rhombic, monoclinic, and liquid all in equilibrium
115.18 ^oC, 3.2 x 10^{-5} atm has monoclinic, liquid, and gas all in equilibrium
95.31 ^oC, 5.1 x 10^{-6} atm has rhombic, monoclinic, and gas all in equilibrium

c. What pahse is stable at room temperature and 1.0 atm pressure? Rhombic
d. Can monoclinic sulfur exist in equilibrium with sulfur vapor? Yes, over a brief range.
e. What are the normal melting point and normal boiling point of sulfur? 115.21 and 444.6 ^oC respectively.
f. Which is the denser solid phase, monoclinic or rhombic sulfur? Rhombic is more dense according to the slope of the line separating the phases.