# Of note

- Quiz 5 and homework 2 have been posted
- I will be out of town until monday evening. Don't expect prompt replies to emails, but I will try to reply to all queries ASAP.
- Logic:If I don't accept late HW and the data base is reset at 5pm, doesn't it seem likely that you shouldn't submit work early?
- Web Pages 170 and 171 are working now. The assignment on #170 is changed to 10 out of 15. Page 169 is dropped from the assignment.

# Entropy continued

- Over the next several weeks, you should read sections 8.13 and 8.14. Yes this material will be on an exam sometime.

- Definitions and conventions
  - The symbol for entropy is S
  - S increases with increasing "state options"
  - $\Delta S = S_2 - S_1$
  - $\Delta S > 0$ entropy favored (ex: solid => liquid)
  - $\Delta S < 0$ entropy disfavored (ex: gas => liquid)

- First attempt at the second law: "Only processes with $\Delta S > 0$ will occur spontaneously."

# Melting an ice cube revealed

- A cube of ice with a mass of 14.5g is dropped into 120g of water(l) at $87^o$. What is the resulting temperature?

- $q_{gain}=-q_{lost}$
- $n*\Delta H_{fus}+4.184*m_1*(T_f-0)=-4.184*m_2*(Tf-87)$
- This is the type of problem that really lends itself to simplification by solving for everything possible before doing any real algebra
- $4840 +60.7*T_f=-502T_f+43700$ (why do we use 4840 and 43700, instead of 4.84 and 4.37?)
- Tf=$69^o$
- Alternatively, melting the ice absorbs 4840J from the 87deg water
- $4840=-4.184*m2* \Delta T \Rightarrow \Delta T =-9.6^o$
- now you effectively have 14.5g of $0^o$ water and 120g of $77.4^o$ water
- $4.184*m_1*(T_f-0)=-4.184*m_2*(Tf-77.4)$
- $60.7*T_f=-502T_f +38800$
- $T_f=69^o$

# A little more about unit cells and density

Below is a unit cell for a simple cubic structure.

1. Note that there is 1/8 of an atom at each corner. Thus the total atom count in the unit cell is one

2. The edge of the cube is 2*r. Since the volume is the edge cubed, the volume is $8r^3$.

3. The density of the material should then be d=Ma/$8r^3$

4. All simple cubic materials will follow this relationship.
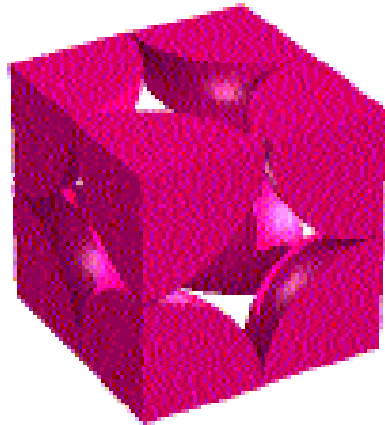
# The Actual Equations

- $d \propto$ (number of atoms in the unit cell)$*M_{atom}/r^3$

- If one looks at the cubic packings: simple cubic, body centered cubic and close packed(hcp or ccp), several things become apparent:

1. For each of these, the number of of atoms per unit cell($N_c$) is constant.

2. The volume of the cube will be a function of the geometry and the atomic radius and can be written $V=C*r^3$

3. The above two can be combined to yield a constant for each structure type and the general formula written as: $d=N_c*M_{atom}/C*r^3$

4. $N_c$ and C can be combined to a single constant which is solely the result of the structure. ($C_{geom}$) thus $d= C_{geom}*(M_{atom}/r^3)$

5. If M is in gm and r is in cm, this will give a "normal" density. Otherwise (for instance, M in amu and r in picometers), some conversions are needed.

6. For the three structures, the constants are:

    simple cubic: 0.1250

    bodycentered: 0.1624

    hcp or ccp: 0.1768

    Note how the increase in the constant is in agreement with the expected density increases

# Thoughts on the usefulness of this

- Given the preceding discussion and the resultant equations, several questions should arise. The assigned web page will demonstrate the basic applications
- How do you know whether it is simple, bcc or ccp/hcp?
  - Identifying a given crystal as cubic (or one of the Bravais alternatives) can often be done by examining the crystal under a microscope. Ever notice the gross shape of a salt crystal?
  - If one knew that the material was cubic and knew r, then combining that with the density gives the exact type.
  - To get a more detailed structural analysis requires methods such as X-ray crystallography (10.7), which is far more complex than the book would lead you to believe. This is seen in that the Braggs received a Noel prize for their efforts in this area.
  - This link provides a very nice discussion of how X-ray photographs can be used to assign the unit cell structure to sucrose
    http://www.luc.edu/faculty/spavko1/c105/disc/o-31lab.htm
- It is not uncommon to find structures with a mix of hcp and ccp.
- What happens when there's more than one element present (NaCl?)

# Compound Lattices

- Simple cubic, bcc and hcp/ccp can only the used for single element systems which can be approximated as equal sized spheres. Don't be mislead by the different colors used in the text. In situations where this is not the case, one gets a compound lattice, which is often described as two intertwined lattices or by one ions filling holes left in the lattice of the other ion.

- A simple cubic structure has voids in the cube centers. When a close packed array of anions forms, you get 2 tetrahedral holes per anion and one octahedral hole per anion.

- The three primary structures for 1:1 salts are CsCl, NaCl and ZnS where the ratios are 8:8, 6:6 and 4:4.

# 1:1 Salts

- CsCl-anions can be viewed as simple cubic with the cations at the center of the cubes. The coordination number(CN) is 8:8

- NaCl The chloride ions have a ccp lattice. The sodium ions occupy octahedral holes between the chlorides with the overall effect of each ion being surrounded by 6 ions of opposite charge. CM= 6:6

- ZnS
  - Zinc Blende-anions are ccp and cations fill ½ of the tetrahedral holes
  - Wurtzite-anions are hcp and cations fill ½ of the tetrahedral holes
  - Both are CN=4:4

# Radius Ratio Rule

- For a simple 1:1 salt, the type of structure which will be observed can be predicted, to a limited extent, by the relative sizes of the anion and cation. In general, not surprising the anions, are larger.

- As the basic thought consider the size of the "hole" that exists when the anions just touch. Also, keep in mind that the relative hole sizes are CsCl>NaCl>ZnS. The best cation is one which is at least large enough to fill the hole completely. A cation smaller than that does not do an effective job of separating the anions. As the cation gets smaller relative to the anion, one must go to a structure which also has smaller holes. Thus, the progression should be that as the $r^-/r^+$ increases, one will move from CsCl to NaCl to ZnS. An alternative view is to state that the larger the cation is relative to the anion, the more anions can "surround it" and the higher the CN. Thus, the ratio $r^-/r^+$ can be used as a predictor of the structure of the solid. The numbers below are based on simple geometric arguments, and you should not consider them as absolute measures of the likely structure. Also, don't panic, you won't have to do the calculations, just know the principle.

    - $1 < r^-/r^+ < 1.37$  CsCl
    - $1.37 < r^-/r^+ < 2.44$  NaCl
    - $2.44 < r^-/r^+ < 4.44$  ZnS

# Exemplary non 1:1

- $CaF_2$(fluorite)-simple cubic fluorides with calcium in every other cube center CN=8:8
- $Al_2O_3$(corundum)-hcp anions with cations in 2/3 of the octahedral holes. This is found in quite a few $M_2O_3$ oxides($Fe_2O_3$)
- $MgAl_2O_4$(spinel structure)-oxides are ccp.1/8 of the of the tetrahedral holes are occupied by the $Mg^{2+}$ and ½ of the octahedral holes are occupied by the $Al^{3+}$. There is an alternative called the reverse spinel-what do you think that means?
- $CaTiO_3$(perovskite structure)-oxides and $Ca^{2+}$ form a ccp array with the $Ti^{4+}$ in those octahedral holes formed exclusively by the oxides (things do get complex-but notice that there evidently are rules being followed.)
- As you would expect, the unit cells of any salt can be quite complex and contain many atoms (and parts thereof). This link leads to a site with numerous structures, if you wish to sample them..

http://cst-www.nrl.navy.mil/lattice/index.html

# Some Properties of Fluids

- Surface tension-work required to expand the surface or for a molecule to "force" its way to the surface. The stronger the surface tension, the larger are the drops that the liquid will form. Have you ever noticed how some liquids, such as gasoline, are hard to dispense dropwise vs the ease with water forms drops?

- Viscosity-resistance to flow

- How are the above two related to intercomponent forces?

# Evaporation and Vapor Pressure

- What is evaporation?
- Escape from the **surface** of the liquid to the vapor phase.
- How are evaporation the vapor pressure related
- Vapor pressure is the pressure exerted when the rate of evaporation equals the rate of return in a closed system. This is an equilibrium condition and is often termed the equilibrium vapor pressure.
- How do you explain evaporation? In particular, why do different materials evaporate at different rates and how does temperature affect evaporation (and vapor pressure). What aspect of energies, discussed previously ,is this related to?
- Evaporation rate is dependent on the surface area, but vapor pressure is not. Why?
- What differentiates evaporation and boiling and what is the normal boiling point?
- Ebullition-the boiling action (or a sudden outburst of

# Phase diagrams

- The relationships between the three phases can be illustrated with a phase diagram. The red line represents the solid liquid line for water, the blue line for other substances. A system which meets the conditions of being "on the line" has the phases in equilibrium.
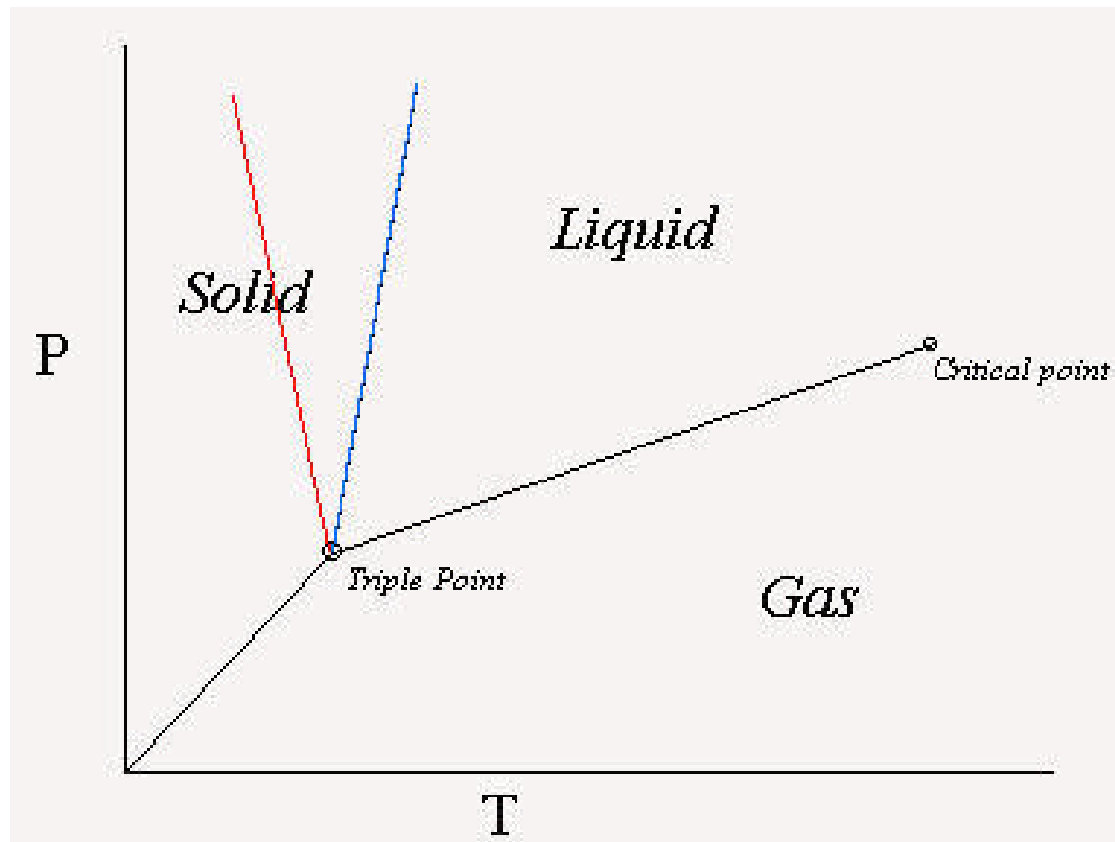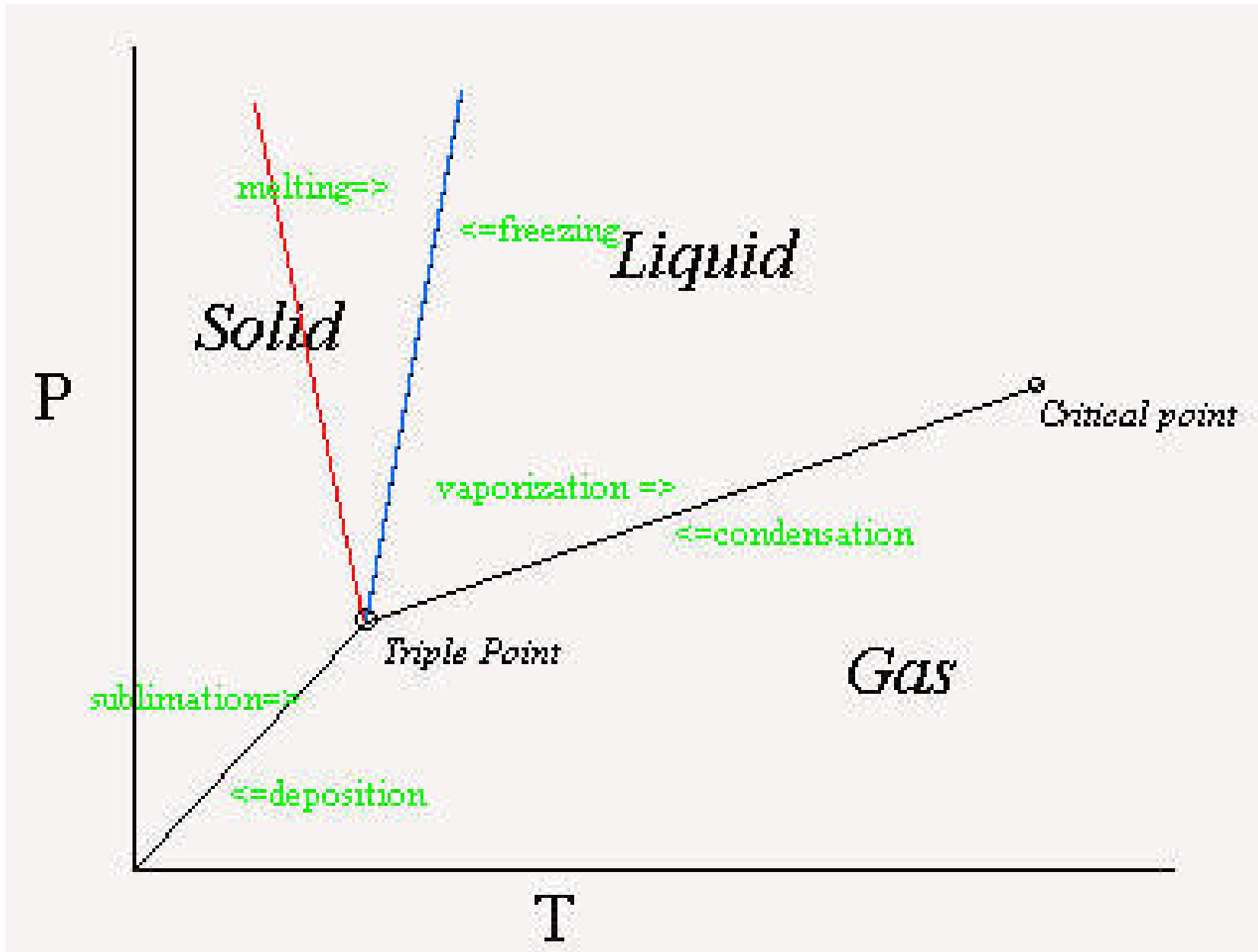
# What's the deal with water?

- Only water expands upon freezing?
- Why?
- What are the consequences of this behavior with regards to your day to day living?
- What are the consequences with regards to life in the universe?

# Boiling Point and Applied Pressure the Clausius-Clapeyron Equation

- Logically it follows that if the boiling point is the temperature at which the vapor pressure equals the applied pressure, if the applied pressure decreases, the boiling temperature should also decrease. However, this is, not surprisingly, not a simple linear function. Given the complexity of this function, calculations are limited to the homework assignment. However, you should familiarize yourself with it's basic structure, as you will see its like later.

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$