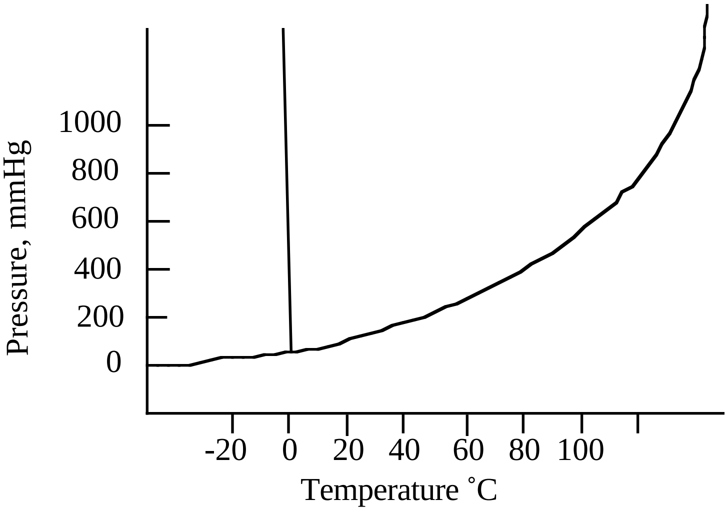
Chem 1515
Problem Set #2
Fall 2001

Name____________________________
TA Name ________________________
Lab Section #______

ALL work must be shown to receive full credit. **Due at the beginning of lecture on Friday, September 7, 2001.**

PS2.1. In the phase diagram for water shown below;



a) determine the physical state of water at
  i) 900 mmHg and 40 ˚C **liquid**
  ii) 500 mmHg and 30 ˚C **liquid**
  iii) 300 mmHg and 90 ˚C **gas**

b) At 400 mm Hg what is the approximate temperature needed to convert water from a solid to a liquid? **0 ˚C**

c) What is the approximate pressure at which water changes from a liquid to a gas at 80 ˚C? **350 mmHg**

PS2.2. Carbon disulfide, CS_2, has a vapor pressure of 298 mm Hg at 20 ˚C. A sample of 6.00 g of CS_2, is placed into a stoppered flask at 20 ˚C.

a) What is the maximum volume the flask can have if equilibrium is to be established between liquid and vapor?

To do this calculation we will calculate the volume of the container at 20 ˚C of the 6.00 g of CS_2 when the pressure exerted is the equilibrium vapor pressure. At this pressure using the Ideal Gas Law the assumption is the CS_2 is ALL in the vapor phase. Since the pressure is 298 mmHg, but assuming all the sample is in the gas we are at the maximum volume of the container.

$$6.00 \text{ g } CS_2\left(\frac{1 \text{ mol } CS_2}{76.0 \text{ g}}\right) = 0.0789 \text{ mol } CS_2$$

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$298 \text{ mmHg}\left(\frac{1 \text{ atm}}{760 \text{ mmHg}}\right) = 0.392 \text{ atm}$$

$$V = \frac{0.0789 \text{ mol } (0.0821 \frac{\text{L·atm}}{\text{mol·K}})(293 \text{ K})}{0.392 \text{ atm}} = 4.84 \text{ L}$$

b) If the flask has a volume of 3.0 L, what will be the pressure of CS_2?

Decreasing the volume for an ideal gas at constant temperature and mol always increases the pressure of the gas in the container. However, in this case the pressure exerted when the volume is 4.84 L is exactly equal to the equilibrium vapor pressure of liquid CS_2. Any volume decrease will cause the pressure of the vapor to increase. But since the pressure can not exceed the equilibrium vapor pressure decreasing the volume will cause condensation of the vapor to occur. Decreasing the volume will cause an instantaneous increase in pressure, to keep the pressure at the equilibrium condensation begins and continues at the volume decreases. The pressure exerted by the gas remains at 298 mmHg as the volume is lowered to 3.0 L.

c) If the flask has a volume of 6.0 L, what will be the pressure of CS_2?

Increasing the volume of an ideal gas always decreases the pressure (at constant temperature and mols). A pressure less than the equilibrium vapor pressure is allowed. When the pressure is less than the equlibrium vapor pressure no liquid is present in the system. We can use the Ideal gas law equation to calculate the pressure when the volume is increased to 6.0 L since the sample is completely in the gas phase.

$$P_1V_1 = P_2V_2$$

$$P_2 = \frac{P_1V_1}{V_2} = \frac{298 \text{ mmHg} \cdot 4.84 \text{ L}}{6.0 \text{ L}} = 240 \text{ mmHg}$$

PS2.3. Indicate all the various types of intermolecular attractive forces that may operate in each of the following:

a) $C_2H_6(l)$; **London dispersion only**

b) $H_2S(l)$; **Dipole-dipole and London dispersion**

c) $CH_3NH_2(l)$; **Hydrogen-bonding and London dispersion**

d) $MgCl_2(s)$ **Ionic**

PS2.4. What is the strongest intermolecular attraction, or bond, that must be broken when each of the following substances is melted?

a) nitrogen monoxide **NO is a polar molecule so dipole-dipole and London dispersions forces : since nitrogen and oxygen are both second period elements the dipole-dipole force is more important than the dispersion forces.**

b) boron trifluoride **BF_3 is a nonpolar molecule so London dispersion force is the only force in this case so it is the most important by default.**

c) ammonium chloride **Ionic interaction and London dispersion forces : but LDF are extremely small compared to ionic bonds.**

d) bromine **Br_2 is a nonpolar molecule so only London dispersion forces are the only forces.**

e) propane **$CH_3CH_2CH_3$ is a nonpolar molecule so only London dispersion forces are the only forces.**

PS2.5. Arrange the following substances in order of increasing boiling point;

$$I_2, F_2, Cl_2, Br_2$$

Explain why you arranged the substances in the order you determined.

The correct order of increasing boiling point is;

$$F_2 < Cl_2 < Br_2 < I_2,$$

This order is based on the increasing intermolecular attractive forces moving from F_2 to Cl_2 to Br_2 to I_2. The intermolecular attractive force in all of these elements is London dispersion forces. Moving from F_2 to Cl_2 to Br_2 to I_2 the number of electrons increase. In particular the valence electrons are located further and further from the nucleus. The further the valence electrons are from the nucleus the more polarizable those electrons are, and stronger the attractive forces.

PS2.6. For each of the following pairs of substances predict which will have the higher boiling point and indicate why:

a) CO_2 or OCS **OCS will have the higher boiling point for two reasons; it is a polar compound while CO_2 does not, so OCS has some dipole-dipole forces, and since S will have a higher polarizability compared to O we would expect a greater contribution from the dispersion forces.**	b) CH_3CH_2OH or $HOCH_2CH_2OH$ **Both compounds have hydrogen bonding attractive forces. Ethylene glycol will have the higher boiling point compared to ethanol, because it has one more OH functional group than ethanol. The additional OH means more hydrogen bonding is possible.**
c) HCl or KCl **KCl will have the higher boiling point because it is an ionic compound and the interparticle attractive forces are among the strongest-ionic bonds. HCl is polar covalent and the dipole-dipole and dispersion forces are very weak compared to the ionic bond in KCl.**	d) N_2 or Ba **Ba will have the higher boiling point due to the stronger metallic bonds that occur in the Ba solid. N_2 is a nonpolar molecule that has only dispersion forces which are very weak compared to metallic bonds.**

PS2.7. In terms of intermolecular attractive forces explain each of the following;

a) even though NH_3 or CH_4 have similar molar masses, NH_3 has a much higher normal boiling point (–33 ˚C) than CH_4 (–164 ˚C).

The intermolecular attractive forces occurring in, NH_3 are hydrogen bonding and London dispersion forces. The intermolecular attractive forces occurring in, CH_4 are only London dispersion forces. Hydrogen-bonding attractive forces are stronger forces compared to dispersion forces when atoms are in the second period. Therefore, NH_3 has a higher boiling point compared to CH_4.

b) at 25 ˚C and 1.0 atmosphere, ethane (C_2H_6) is a gas and hexane (C_6H_{14}) is a liquid.

The intermolecular attractive forces in both ethane and hexane are London dispersion forces only. Hexane has many more electrons compared to ethane. With more electrons the molecule is more polarizable and the attractions between hexane molecules is greater compared to ethane. Therefore, hexane has a higher boiling point compared to ethane. NOTE: do not use a molar mass argument! Dispersion forces are based on electrons, not the molar mass.

c) Si melts at a much higher temperature (1410 ˚C) than Cl_2 (–101 ˚C).

The interparticle forces in Si are extended covalent. That is, each silicon atom is covalently bonded to four adjacent Si atoms, in a macromolecular structure. Chlorine on the other hand is a nonpolar diatomic molecule and the only intermolecular attractive forces between Cl_2 molecules are London dispersion forces. To melt Si strong covalent bonds must be broken, compared to overcoming weak London dispersion forces between individual chlorine molecules. Therefore the melting point of Si is considerably higher than Cl_2.

PS2.8. Indicate the type of crystal (molecular, metallic, extended covalent, or ionic) each of the following would form upon solidification:

a) CO_2 ; **molecular**

b) SiO_2 ; **extended covalent**

c) Si ; **extended covalent**

d) CH_4 ; **molecular**

e) Ru ; **metallic**

f) I_2 ; **molecular**

g) KBr ; **ionic**

h) H_2O ; **molecular**

i) NaOH ; **ionic**

j) U ; **metallic**

k) PH_3 ; **molecular**

l) $CaCO_3$. **ionic**

PS2.9. Europium metal crystallizes in a body-centered cubic unit cell. The density of europium is 5.26 $\frac{\text{g}}{\text{cm}^3}$. Calculate the edge length of the unit cell and the atomic radius of europium.

PS2.10. Aluminum crystallizes in a face-centered cubic unit cell and has a density of 2.70 $\frac{\text{g}}{\text{cm}^3}$. What are the unit cell dimensions (edge length)?