Chem 1515.001 - 006
Problem Set #2
Spring 2002

Name____________________________________

TA’s Name _________________________________

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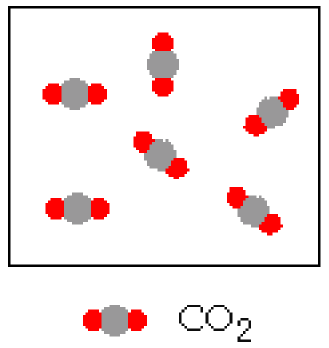
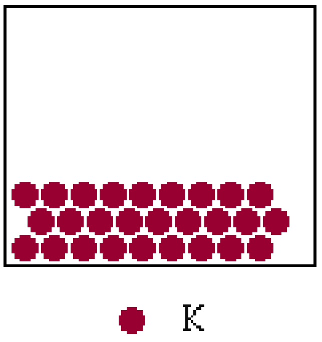
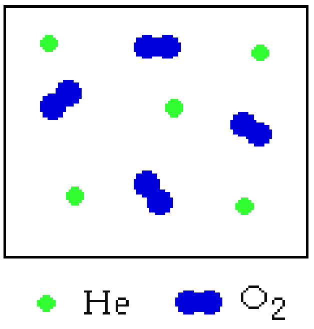
ALL work must be shown to receive full credit. **Due in lecture, at 8:30 a.m. on Friday, February 1, 2002.**

PS2.1. Using the PLE4 (http://intro.chem.okstate.edu/PLE412502/PLMPhase.html) discussed in class as a source, describe, in terms of a particulate level view, what happens as heat is added to a sample of a pure substance initially in the solid phase until the sample is completely vaporized.

When heat is added to the sample, initially in the solid phase, the particles begin to vibrate in position. As more heat is added the particles vibrate even more until, they begin to move (translate). Movement only begins when sufficient heat is added that the particles can overcome the attractive forces holding them in the solid state. At the macroscopic level this increased translation motion is what we recognize as melting. The particles in the liquid phase are more mobile. The additional energy the particles have in the liquid phase allow the particles to constantly make and break attractive forces between adjacent particles. As more heat is added some of the particles will have sufficient energy to escape the liquid phase, by completing overcoming all attractive forces with adjacent particles, and enter the vapor phase. In the vapor phase the particles are not attracted to each other because their individual kinetic energy far exceeds the attractive energy they might have. So collisions between particles in the gas phase are elastic. As more heat is added more particles escape the liquid phase, eventually all of the particles (evaporate) escape into the vapor phase

PS2.2. In the boxes below diagram the specified system as viewed at the atomic level in the space provided. Be sure to clearly label each of the substances in your diagram.

		
A sample CO_2 at 25 ˚C	A sample of potassium at 25 ˚C	A mixture of oxygen and helium at 25 ˚C

PS2.3. Using a substance of your choice, write a chemical equation describing the condensation process and a chemical equation describing the freezing process. For each process discuss the change in enthalpy and entropy that occurs. For each process describe the conditions (in terms of temperature) that favor a spontaneous change, and the conditions that do not favor a spontaneous change.

$H_2O(g) \rightarrow H_2O(l)$ condensation
$H_2O(l) \rightarrow H_2O(s)$ freezing

In condensation heat is released (exothermic, $-\Delta H$) and the liquid state is more ordered ($-\Delta S$) compared to the gaseous state.

$$H_2O(g) \rightarrow H_2O(l) + \text{heat}$$

In freezing heat is released (exothermic, $-\Delta H$) and the solid state is more ordered ($-\Delta S$) compared to the liquid state.

$$H_2O(l) \rightarrow H_2O(s) + \text{heat}$$

Since ΔH is negative and ΔS is negative, both processes are favored (spontaneous) when the temperature is low and nonspontaneous when the temperature is high. High and low temperature are different for the two processes. What are those temperatures? We know from our own experience, in the case of water, that water in the gas phase will spontaneous occur when the temperature is less than 100 ˚C. Water vapor will not spontaneously condense above 100 ˚C. The same argument is used for freezing. Freezing is spontaneous below 0 ˚C, and nonspontaneous above 0 ˚C.

PS2.4 a. How much heat is required to convert 75.0 g of $H_2O(s)$ at -12.0 °C to $H_2O(l)$ at 75.0 °C?

Step 1) : $H_2O(s)$ at -10 ˚C to $H_2O(s)$ at 0 ˚C
Step 2) : $H_2O(s)$ at 0 ˚C to $H_2O(l)$ at 0 ˚C
Step 3) : $H_2O(l)$ at 0 ˚C to $H_2O(l)$ at 100 ˚C

$$75.0 \text{ g } H_2O\left(\frac{1 \text{ mol}}{18.0 \text{ g}}\right) = 4.17 \text{ mol } H_2O$$

Step 1):

$$4.17 \text{ mol } H_2O\left(\frac{37.6 \text{ J}}{\text{mol}\cdot{}^\circ\text{C}}\right)(12\ {}^\circ\text{C}) = \quad 1.88 \times 10^3 \text{ J}$$

Step 2):

$$4.17 \text{ mol } H_2O\left(\frac{6010 \text{ J}}{\text{mol}\cdot{}^\circ\text{C}}\right) = \quad 2.51 \times 10^4 \text{ J}$$

Step 3):

$$4.17 \text{ mol } H_2O\left(\frac{75.2 \text{ J}}{\text{mol}\cdot{}^\circ\text{C}}\right)(75\ {}^\circ\text{C}) = \quad 2.35 \times 10^4 \text{ J}$$

TOTAL 5.04×10^4 J (50.4 kJ)

b) How much heat is produced when 75.0 g of $H_2O(g)$ at 115 °C is converted to $H_2O(l)$ at 75.0 °C?

Step 1) : $H_2O(g)$ at 115 ˚C to $H_2O(g)$ at 100 ˚C
Step 2) : $H_2O(g)$ at 100 ˚C to $H_2O(l)$ at 100 ˚C
Step 3) : $H_2O(l)$ at 100 ˚C to $H_2O(l)$ at 75 ˚C

$$75.0 \text{ g } H_2O\left(\frac{1 \text{ mol}}{18.0 \text{ g}}\right) = 4.17 \text{ mol } H_2O$$

Step 1):

$$4.17 \text{ mol } H_2O\left(\frac{33.1 \text{ J}}{\text{mol}\cdot{}^\circ\text{C}}\right)(15\ {}^\circ\text{C}) = \quad 6.90 \times 10^2 \text{ J}$$

Step 2):

$$\mathbf{4.17\ mol\ H_2O\left(\frac{40670\ J}{mol\cdot{}^\circ C}\right) = \qquad 1.70 \times 10^5\ J}$$

Step 3):

$$\mathbf{4.17\ mol\ H_2O\left(\frac{75.2\ J}{mol\cdot{}^\circ C}\right)(25\ {}^\circ C) = \qquad 7.84 \times 10^3\ J}$$

TOTAL 1.78 x 10^5 J (178 kJ)

PS2.5. Ethyl alcohol melts at -114.5 °C and boils at 78.4 °C. The enthalpy of vaporization for ethyl alcohol at 78.4 °C is 38.56 kJ mol^{-1} and the enthalpy of fusion is 4.60 kJ mol^{-1}. If the specific heat of ethyl alcohol vapor is taken to be 1.43 J g^{-1} °C^{-1}, and that for the liquid 2.46 J g^{-1} °C^{-1}, how much heat is required to convert 10.0 g of ethyl alcohol at -100 °C to the vapor phase at 100 °C?

Step 1): $C_2H_5OH(l)$ at -100˚C to $C_2H_5OH(l)$ at 78.4˚C
Step 2): $C_2H_5OH(l)$ at 78.4˚C to $C_2H_5OH(g)$ at 78.4˚C
Step 3): $C_2H_5OH(g)$ at 78.4˚C to $C_2H_5OH(g)$ at 100˚C

$$\mathbf{10.0\ g\ C_2H_5OH\left(\frac{1\ mol}{46.0\ g}\right) = 0.217\ mol\ C_2H_5OH}$$

Step 1): $C_2H_5OH(l)$ at -100˚C to $C_2H_5OH(l)$ at 78.4˚C

$$\mathbf{10.0\ gm\ C_2H_5OH\left(\frac{2.46\ J}{g\cdot{}^\circ C}\right)(178.4\ {}^\circ C) = 4.39 \times 10^3\ J}$$

Step 2): $C_2H_5OH(l)$ at 78.4˚C to $C_2H_5OH(g)$ at 78.4˚C

$$\mathbf{0.217\ mol\ C_2H_5OH\left(\frac{38560\ J}{mol\cdot{}^\circ C}\right) = \qquad 8.37 \times 10^3\ J}$$

Step 3): $C_2H_5OH(g)$ at 78.4˚C to $C_2H_5OH(g)$ at 100˚C

$$\mathbf{10.0\ gm\ C_2H_5OH\left(\frac{1.43\ J}{g\cdot{}^\circ C}\right)(21.6\ {}^\circ C) = 3.08 \times 10^2\ J}$$

Heat required = 13.1 kJ

PS2.6a. Define the term equilibrium vapor pressure.

The pressure due to particles of a substance in the vapor phase above its liquid in a closed container at a given temperature.

The maximum pressure exerted by the vapor above a liquid at a given temperature.

The pressure exerted by the vapor at given temperature when the rate of condensation equals the rate of evaporation.

b) Use a vapor-pressure table (check the Database link on the class web site) to look up the equilibrium vapor pressure of a sample of water at 85 °C and at 70 °C.

The vapor pressure of water at 85 ˚C is 433.6 mm Hg and at 70 ˚C the vapor pressure is 233.7 mm Hg.

c) Consider two closed containers each partially filled with liquid water one at 85 °C and the other at 70 °C. Can the pressure of water vapor in the gas phase in either container ever exceed the equilibrium vapor pressure at the particular temperature? Explain why or why not.

No. At a given temperature we cannot have a pressure due to the vapor above a liquid greater than the equilibrium vapor pressure. If we attempt to add additional water, in the vapor phase, to a system already at equilibrium, the rate of condensation increases until the vapor pressure re-establishes equilibrium. The net result is there is no change in the vapor pressure.

PS2.7. A sample of water in the vapor phase (no liquid present) in a flask of constant volume exerts a pressure of 440 mm Hg at 100 °C. The flask is slowly cooled.

a) Assuming no condensation, use the Ideal Gas Law to calculate the pressure of the vapor at 85 °C; at 70 °C.

$$\textbf{@85˚C}\ \ P_2 = \frac{P_1 \cdot T_2}{T_1} = \frac{440\text{ mm Hg} \bullet 358\text{ K}}{373\text{ K}} = 422\text{ mmHg}$$

$$\textbf{@70˚C}\ \ P_2 = \frac{P_1 \cdot T_2}{T_1} = \frac{440\text{ mm Hg} \bullet 343\text{ K}}{373\text{ K}} = 405\text{ mmHg}$$

b) Will condensation occur at 85 °C; 70 °C? Explain.

Since the calculated pressure of the sample in the vapor at 85 ˚C is less than the equilibrium vapor pressure no condensation occurs. Condensation occurs sometime before 70˚C because the calculate pressure exerted by the vapor is greater than the equilibrium vapor pressure at that temperature.

c) On the basis of your answers in a) and b), predict the pressure exerted by the water vapor at 85 °C; at 70 °C.

The pressure due to the vapor at 85˚C is 422 mm Hg, at 70˚C the vapor pressure is 233.7 mm Hg.

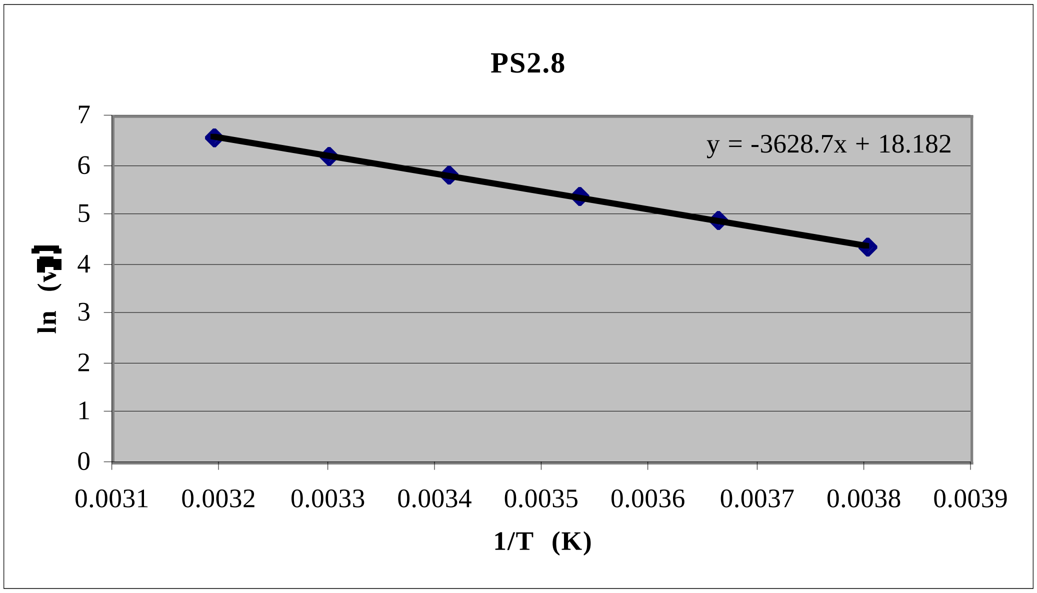
PS2.8. Consider the following data for the dichloromethane (CH_2Cl_2)

Temperature (˚C)	Vapor pressure (mm Hg)
-10.0	79.5
0	134.3
10.0	212.8
20.0	330.1
30.0	494.3
40.0	725.3

a) Use graphing software (Microsoft Excel) to plot ln(vp) vs. T^{-1} (K^{-1}) for dichloromethane and use your graph to determine the slope of the best line through the data. The heat of vaporization of a liquid can be obtained from such a plot. The relationship is given as,

$$\text{Slope} = -\frac{\Delta H^\circ_{vap}}{8.314\text{ J mol}^{-1}\text{ K}^{-1}}$$

Calculate the heat of vaporization for dichloromethane. (Your plot must be turned in with the problem set, so be sure to clearly label your graph. Hand draw graphs are NOT acceptable.)



$$\mathbf{-3628.7 = -\frac{\Delta H^\circ_{vap}}{8.314\ J\ mol^{-1}\ K^{-1}}}$$

$$\mathbf{\Delta H^\circ = 30.2\ kJ\ mol^{-1}}$$

b) Using the graph, determine the temperature of a sample of dichloromethane when the vapor pressure is 462 mmHg.

$$\mathbf{\ln (vp) = -3628.7\left(\frac{1}{T}\right) + 18.182}$$

$$\mathbf{\ln (462\ mm\ Hg) = -3628.7\left(\frac{1}{T}\right) + 18.182}$$

$$\mathbf{6.136 = -3628.7\left(\frac{1}{T}\right) + 18.182}$$

$$\mathbf{6.136 - 18.182 = -3628.7\left(\frac{1}{T}\right)}$$

$$\mathbf{-12.05 = -3628.7\left(\frac{1}{T}\right)}$$

$$\mathbf{\frac{-12.05}{-3628.7} = \left(\frac{1}{T}\right)}$$

$$\mathbf{T = 301\ K}$$

c) Using the graph, determine the vapor pressure of a sample of dichloromethane at -2.35 °C.

$$\mathbf{\ln (vp) = -3628.7\left(\frac{1}{T}\right) + 18.182}$$

$$\mathbf{\ln (vp) = -3628.7\left(\frac{1}{270.6}\right) + 18.182}$$

$$\mathbf{\ln (vp) = -13.41 + 18.182}$$

$$\mathbf{\ln (vp) = 4.77}$$

$$\mathbf{vp = 118\ mm\ Hg}$$

PS2.9a. The normal boiling point of acetone, $(CH_3)_2CO$ is 56.2 °C and its $\Delta H°_{vap}$ = 32.0 kJ mol^{-1}. Draw a Lewis structure for acetone and calculate the temperature at which acetone has a vapor pressure of 593. mmHg.

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

$$\ln \frac{593}{760} = \frac{-32000 \frac{J}{mol}}{8.314 \frac{J}{mol \bullet K}}\left(\frac{1}{T_1} - \frac{1}{329.2K}\right)$$

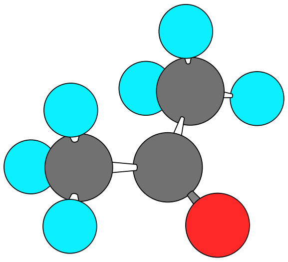
$$\ln (0.780) = -3848.9\left(\frac{1}{T_1} - \frac{1}{329.2}\right)$$

$$-0.248 = -3848.9\left(\frac{1}{T_1} - \frac{1}{329.2}\right)$$

$$6.45 \times 10^{-5} = \left(\frac{1}{T_1} - \frac{1}{329.2}\right)$$

$$\frac{1}{T_1} = 3.10 \times 10^{-3} \qquad T_1 = 322\ K$$

Lewis structure



b) Using data in part a of this problem, calculate the vapor pressure of acetone when the temperature is –15.5 °C.

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

$$\ln \frac{vp_1}{760} = \frac{-32000\ J \frac{J}{mol}}{8.314 \frac{J}{mol \bullet K}}\left(\frac{1}{257.5} - \frac{1}{329.2K}\right)$$

$$\ln \frac{vp_1}{760} = -3848.9\left(\frac{1}{257.5} - \frac{1}{329.2}\right)$$

$$\ln \frac{vp_1}{760} = -3.26$$

$$e^{\ln \frac{vp_1}{760}} = e^{-3.26}$$

$$\frac{vp_1}{760} = 0.0386$$

$$vp = 29.3\ mm\ Hg$$

PS2.10. Calculate the $\Delta H˚_{vap}$ for carbon disulfide if its vapor pressure at –5.1 ˚C is 100 mm Hg and at 45.5 ˚C its vapor pressure is 755 mm Hg..

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

$$\ln \frac{100\ mm\ Hg}{755\ mm\ Hg} = \frac{-\Delta H}{R}\left(\frac{1}{267.9} - \frac{1}{318.5}\right)$$

$$\ln\ 0.132 = \frac{-\Delta H}{8.314 \frac{J}{mol \bullet K}}(5.93 \times 10^{-4})$$

$$-2.02 = \frac{-\Delta H}{8.314 \frac{J}{mol \bullet K}}(5.93 \times 10^{-4})$$

$$\frac{2.02 \cdot 8.314 \frac{J}{mol \bullet K}}{5.93 \times 10^{-4}} = \Delta H$$

$$\Delta H = 28.4\ kJ$$