Chapter 10- Liquids and Solids Study Guide

(Key)

10.1 Intermolecular Forces

There are two types of forces:
- **Intramolecular Forces-** Forces within molecule (sharing electrons in a molecule)

- **Intermolecular Forces** - Forces Between Molecules

There are three kinds of forces that are discussed in this section: (Intermolecular)
- **Dipole-Dipole forces** -when the ⊕ end of a polar molecule attracts the ⊖ end of another. (only about 1% as strong as ionic or covalent).
- **Hydrogen bonds** - Dipole-Dipole with hydrogen -very strong
- **London dispersion forces** - A force that exists between noble gases or non-polar molecules- weak

Example 10.1A London Dispersion Forces

The boiling point of Argon is –189.4 °C.
   a. Why is it so low?
   b. How does this boiling point help prove that London Dispersion forces exist?
   c. The boiling point of Xenon is –119.9 °C. Why is it higher than that of Argon?

Solution
   a. Argon does not interact with other substances because it is so small and has a complete octet of valence electrons. Argon must be made quite cool to allow liquefication via London dispersion forces.
   b. If these forces did not exist, Argon would never liquefy.
   c. Xenon is bigger and has more electrons than Argon. The likelihood of momentary dipoles is greater. (It has greater polarizability than Argon).

Example 10.1B The Effect of Intermolecular Forces.

Put the following substances in order from lowest to highest boiling points: C_2H_6, NH_3, F_2

Solution

$F_2 < C_2H_6 < NH_3$

F_2 can only exhibit intermolecular London forces. C_2H_6 is not especially polar, but it does have very slight electronegativity difference between the carbon and hydrogen atoms. NH_3 exhibits hydrogen bonding, thus giving it a relatively high boiling point.

Problems:
1. Of HF, HCl and HBr, which has the highest boiling point? Why? Which has the lowest?

HF has the highest BP.

HCl has the lowest.

Large H bonding among the smallest molecules with most polar H-X bond Small size of F allows for closest dipole interaction.

1

2. Propane, C_3H_8 is a gas at room temp.; hexane, C_6H_{14}, is a liquid; and dodecane, $C_{12}H_{26}$ is a solid. Explain.

All other conditions being equal, the higher M.W. of non-polar compounds the greater the London forces (more momentary dipoles)

3. Which would you expect to have a lower melting point, C_3H_8 or CH_3OH? Why?

C_3H_8 -it is non-polar, it has weak london forces CH_3OH has H bonding

10.2 The Liquid State

The following review questions will serve to test your understanding of the material in this section.

- Why do liquids tend to bead up when on solid surfaces?

The molecules have an uneven pull.

The interior molecules have pull on all sides. The surface molecule have uneven pull.

- What are cohesive forces? Adhesive forces? What causes these forces?

Cohesive-intermolecular forces among molecules of Liquid

Adhesive- forces between Liquid + container

The surface has polar bonds (O in glass)

- What is surface tension? Why does it arise?

Surface Tension is the resistance of a liquid to increase its surface area.

It happens when Liq- molecules absorb energy to increase their surface area.

- Why does water from a concave meniscus when in a thin tube? Why does mercury form a convex meniscus?

Water is polar, glass is polar.

water's adhesive forces w/ glass is greater than cohesive forces w/ itself.

Hg is non-polar, glass is polar. Mercury's cohesive forces w/ itself is greater than adhesive forces w/ glass.

- What is viscosity? What is a requirement for a liquid to be viscous?

A measure of a liquid's resistance to flow.

Large intermolecular forces

- Why do models of liquids tend to be more complex than those for either solids or gases?

Liquids have both strong intermolecular forces (solids) AND significant molecular motions (gas)

Example 10.2 Properties of Liquids

Which would have a higher surface tension, H_2O or C_6H_{14}? Why? Would the shape of the H_2O meniscus in a glass tube be the same or different than C_6H_{14}?

Solution

Water, having a large dipole moment, has relatively large cohesive forces. Hexane, C_6H_{14}, is essentially nonpolar. It has low cohesive forces. Water would therefore have the higher surface tension.

The water meniscus is concave because the adhesive forces of water to polar constituents on the surface of the glass are stronger than the cohesive forces. Hexane would have a convex meniscus. It has very small adhesive forces, and the slightly larger cohesive forces would dominate.
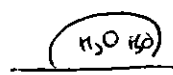
Problems:

4. Why does water "bead up" more on a car that is waxed than isn't?

There are fewer adhesive forces between the non-polar wax and water molecules than among water molecules

5. Would mercury bead up more on a waxed or unwaxed car?

Unwaxed car.

0.8 Vapor Pressure and Changes of State

Your book introduces some very useful terms in this section. You need to be able to define **vaporization, enthalpy of vaporization, condensation, sublimation, enthalpy of fusion, melting point and boiling point.**

Dynamic equilibrium is a concept that you will be using a great deal for the rest of the year. It means that *two opposing processes are occurring at the same rate*. The net effect is no observable change. But the system is not static. In this section, **the equilibrium vapor pressure** means that evaporation and condensation by a liquid are occurring at the same rate. The net effect is to have a constant vapor pressure exerted by the liquid.

The vapor pressure of a liquid varies with the molecular weight of the liquid and other molecular properties such as polarity and hydrogen bonding.

A heavier substance will have a lower vapor pressure than a lighter substance, all other things being equal, because the atoms are more polarizable, leading to larger intermolecular forces. A substance with hydrogen bonding interactions will have a lower vapor pressure (will be less volatile) than a nonpolar substance. Your book introduces the Clausisus-Clapeyron equation which interrelates vapor pressure, temperature and enthalpy of a liquid.

$$\ln\left[\frac{P_{T_1,vap}}{P_{T_2,vap}}\right] = \frac{\Delta H_{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Where T_1 and T_2 are temperatures in Kelvins, ΔH_{vap} is the enthalpy of vaporization of a liquid, and $P_{T_1, vap}$ and $P_{T_2, vap}$ are vapor pressures of the liquid temperatures T_1 and T_2.

Example 10.8A Clausius-Clapeyron Equation

The vapor pressure of 1-propanol at 14.7 °C is 10.0 mm Hg. The heat of vaporization is 47.2 kJ/mol. Calculate the vapor pressure of 1-propanol at 52.8 °C.
Solution
Let's list what we are given.

$\Delta H_{vap} = 47.2$ kJ/mole   R = 8.314 J/mol K = 0.008314 kJ/mol K
$T_1 = 14.7\,°C = 287.7$ K $T_2 = 52.8\,°C = 325.8$ K
$P_{T_1\ vap} = 10.0$ mm Hg $P_{T_2\ vap} = ?$

Substituting,

$$\ln\left[\frac{10.0}{x}\right] = \frac{47.2\ kJ/mol}{0.008314\ \frac{kJ}{mol\cdot K}}\left[\frac{1}{325.8\,K} - \frac{1}{287.9\,K}\right] \Rightarrow \ln\left[\frac{10.0}{x}\right] = 5677\left(-4.06\times10^{-4}\right)$$

$$\ln\left[\frac{10.0}{x}\right] = -2.305$$

Taking the antilog of both sides,
X/10 = 10.02
$X = P_{T_2\ vap} = 100.2 = 100.2$ mm Hg

3

Heating Curves

Look at Figure 10.42 below (a clearer version is in your textbook). This illustrates the **heating curve** for water. Note two important observations.

- The temperature of a substance remains constant during a phase change.
- The temperature rises when heat is input while a substance is in one phase.

Figure 10.42
The heating curve for a given quantity of water where energy is added at a constant rate. The plateau at the boiling point is longer than the plateau at the melting point because it takes almost seven times more energy (and thus seven times the heating time) to vaporize liquid water than to melt ice. The slopes of the other lines are different because the different states of water have different molar heat capacities (the energy required to raise the temperature of 1 mole of a substance by 1 °C).
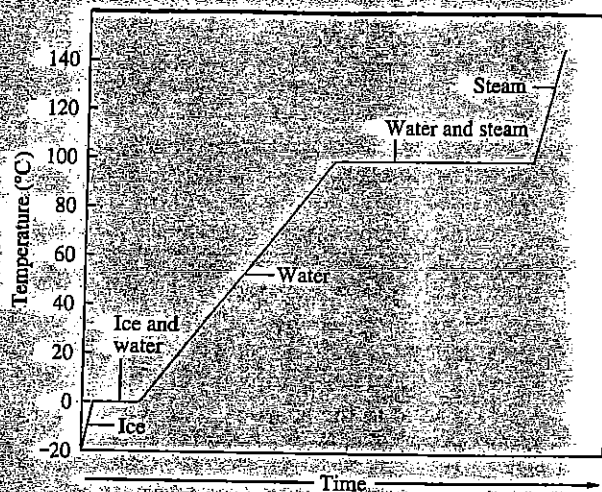
You can find the amount of energy required to convert water from ice at T_1 to steam at T_2 by using the following information.

- Specific heat capacity of ice (2.1 J/g°C)
- ΔH_{fusion} of water (6.0 kJ/mol)
- Specific heat capacity of liquid water (4.18 J/g°C)
- ΔH_{vap} of water (43.9 kJ/mol)
- Specific heat capacity of steam (1.8 J/g°C)

How much of the information will be used will depend on the problem you have to solve.

Example 10.8B Heating Curve
How much energy does it take to convert 130 g of ice at -40 °C to steam at 160 °C?

Strategy
There are 5 steps involved in the conversion from ice to steam.
1. Heating ice from -40 °C to the melting point.
2. Melting ice to form liquid water.
3. Heating liquid water to its boiling point.
4. Boiling liquid water to form steam.
5. Heating to 160 °C.

The total energy required is the sum of the energy required in each of the 5 steps. The appropriate constants for each step are given in the discussion preceding this problem. The units of heat capacity contain °C because the temperature is rising in each of these steps. The units "enthalpy of fusion and vaporization" do not because the temperature is constant during a phase change.

Solution
Energy used = sum of energies from individual steps. There are 7.22 mol of water in 130 g.

Step 1 = 40 °C x 130 g x 2.1 J/g°C =	10.92 kJ
Step 2 = 7.22 mol x 6.0 kJ/mol =	43.3 kJ
Step 3 = 100 °C x 130 g x 4.18 J/g°C =	54.6 kJ
Step 4 = 7.22 mol x 43.9 kJ/mol =	317.0 kJ
Step 5 = 60 °C x 130 g x 1.8 J/g°C =	14.04 kJ
Total Energy =	**440. kJ**

4

11. Consider the following relationship between vapor pressure and the standard heat of vaporization for any pure liquid:

$$\text{Slope} = \frac{\Delta(\ln P)}{\Delta(\frac{1}{T})} = \frac{3.65 - 4.45}{3.265 \times 10^3 - 3.115 \times 10^3} = \frac{-.8}{1.5 \times 10^4} = -5333 \, K$$
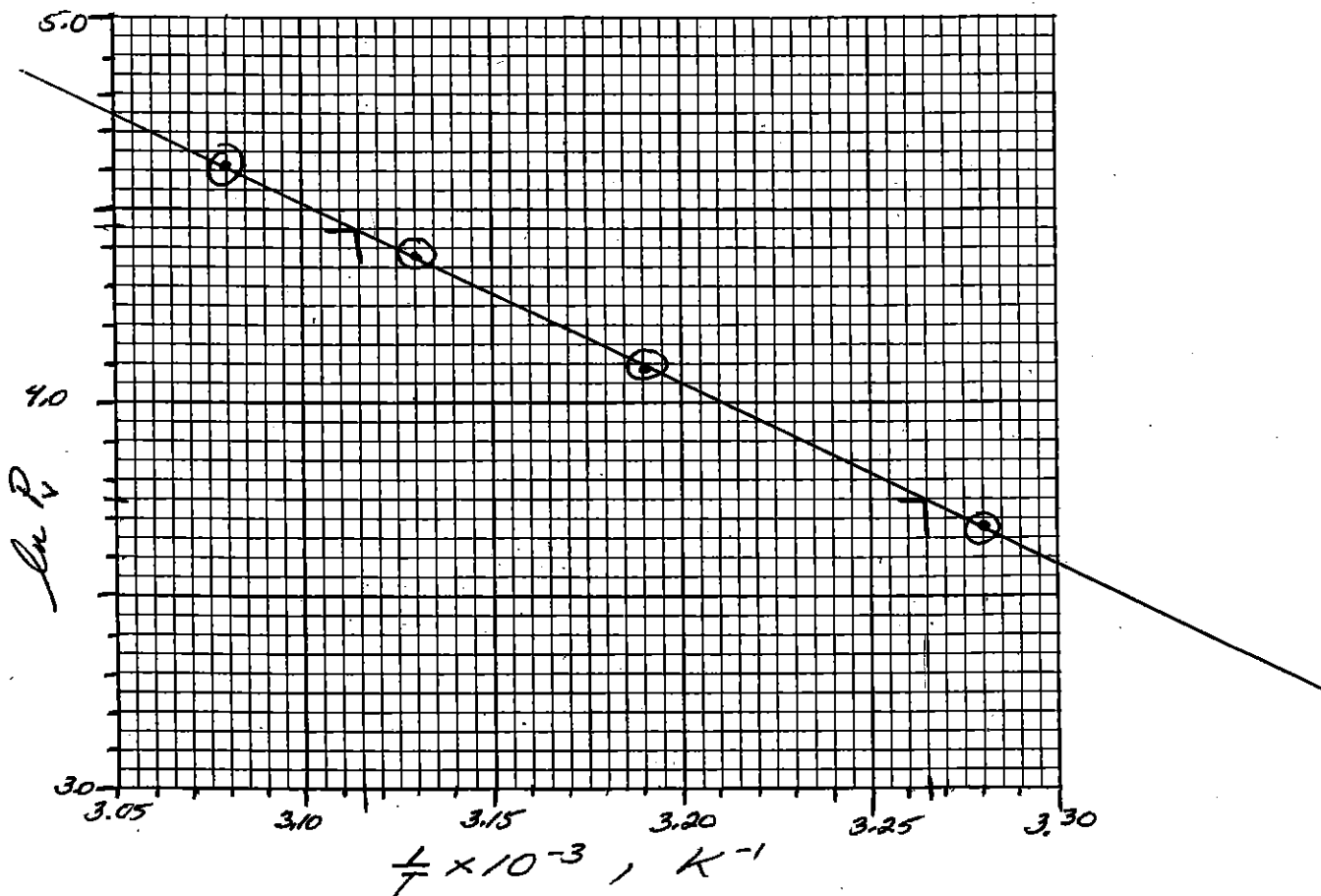
$$\text{Slope} = \frac{\Delta H}{R}$$

$$\Delta H_{vap} = (\text{slope})(R) = (-5333 \, K)(8.31 \frac{J}{mol \cdot K}) = -44,320 \, J/mol$$

$$\boxed{-44.32 \frac{kJ}{mol}}$$

The following data are for the vapor pressure of toluene, a common solvent.

t (°C)	32.0	40.0	47.0	52.0
T (K)	305	313	320	325
1/T (K⁻¹)	3.28×10^{-3}	3.19×10^{-3}	3.13×10^{-3}	3.08×10^{-3}
P_v (torr)	40.0	60.0	80.0	100.
ln P	3.69	4.09	4.38	4.61

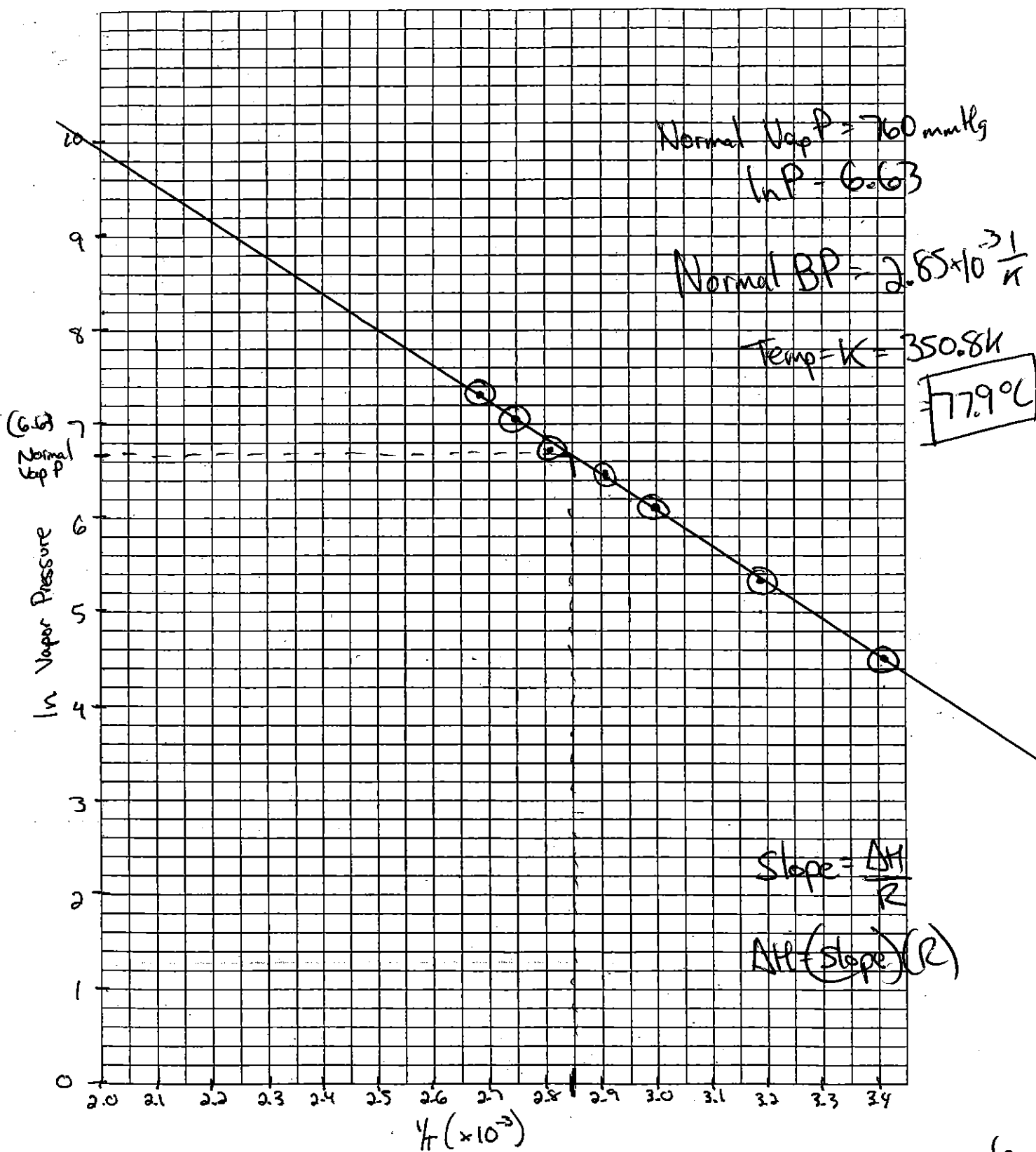Plot ln P vs. 1/T and use your graph to estimate the heat of vaporization for toluene.

$$\frac{1}{T} \times 10^{-3}, \quad K^{-1}$$

5

21. Using the following vapor pressure data for CCl_4, make a graph and determine the normal boiling point of the liquid.

Temp (°C)	20.0	40.0	60.0	70.0	80.0	90.0	100.0
V.P. (torr)	91.0	213.0	444.3	617.4	836.0	1110	1459
T (K)	293	313	333	343	353	363	373
$\frac{1}{T}$ (K⁻¹)	3.46×10^3	3.19×10^3	3×10^3	2.92×10^3	2.83×10^3	2.75×10^3	2.68×10^7
ln P	4.51	5.36	6.10	6.43	6.73	7.01	7.29

Normal Vap P = 760 mmHg

ln P = 6.63

Normal BP = $2.85 \times 10^{-3} \frac{1}{K}$

Temp = K = 350.8K

= 77.9°C

Slope = $\frac{\Delta H}{R}$

$\Delta H = (Slope)(R)$

(6.63)
Normal
Vap P

ln Vapor Pressure

$\frac{1}{T} (\times 10^{-3})$

6

T_1 P_1 $R = 8.31 \, J/mol \cdot K = .00831 \frac{kJ}{mol \cdot K}$

22. The vapor pressure of water at 25 deg C is 23.8 torr. Confirm the value of 43.9 kJ/mol for the heat of vaporization of water. (Use data for the normal boiling point as well as the vapor pressure given.) $T_2 = 100°C$ $P_2 = 760 \, torr$

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

$$-3.46 = \frac{\Delta H}{831}\left(\frac{1}{373} - \frac{1}{298}\right)$$

$$\ln\left(\frac{23.8}{760}\right) = \frac{\Delta H}{8.31 \, J/mol \cdot K}\left(\frac{1}{373} - \frac{1}{298}\right)$$

$$\Delta H = 42612 \, J/mole = \boxed{42.7 \frac{kJ}{mol}}$$

pretty close.

23. On top of one of the peaks in Rocky Mountain National Park the pressure of the atmosphere is 550 torr. Determine the boiling point at this location. $P_2 = 760 \, torr$ $T_2 = 373 \, K$

P_1 $T_1 = ?$

$$\ln\left(\frac{760 \, torr}{550 \, torr}\right) = \frac{43.9 \, kJ/mol}{.008314 \, kJ/mol \cdot K}\left(\frac{1}{T_2} - \frac{1}{373}\right)$$

$$.323 = 5280\left(\frac{1}{T_2} - \frac{1}{373}\right) \qquad \frac{1}{T_2} = .00274 \qquad T_2 = 364.6 \, K$$

$$\boxed{T_2 = 91.7°C}$$

24. Octane, C_8H_{18}, is a principal component of gasoline. It has a vapor pressure of 145 mm Hg at 75.0°C and 20.0 mm Hg at 32.0°C. Use the Clausius-Clapeyron equation to estimate the:

T_1 348K P_2 T_2 305K

    a. Heat of vaporization of octane.

    b. Vapor pressure of octane on a warm day (85°F) $P_2 = ?$

a) $$\ln\left(\frac{145 \, mm \, Hg}{20 \, mm \, Hg}\right) = \frac{\Delta H}{8.314 \frac{J}{mol \cdot K}}\left(\frac{1}{305 K} - \frac{1}{348 K}\right)$$

$$1.981 = \Delta H(4.852 \times 10^{-5})$$

$$\Delta H = 40654 \, J/mol$$

$$\Delta H = 40.6 \, kJ/mol$$

b) $85°F = \underline{\quad}°C$ $°C = \frac{85-32}{1.8} = 29.4°C = 302.4 K$

$$\ln\left(\frac{145}{P_2}\right) = \frac{40.6}{.008314}\left(\frac{1}{302.4} - \frac{1}{348 K}\right)$$

$$\ln(145) - \ln P_2 = 2.12$$

$$-\ln P_2 = \cancel{2.12} \\ -2.86$$

$$\ln P_2 = 2.86 \qquad \boxed{P_2 = 17.5 \, mm \, Hg}$$

25. Isopropanol, C_3H_8O, is also known as rubbing alcohol. The heat of vaporization is 42.1 kJ/mol. How much heat is needed to evaporate 25 g of isopropanol?

$$25 \, g \, C_3H_8O\left(\frac{1 \, mol \, C_3H_8O}{60 \, g}\right)\left(\frac{42.1 \, kJ}{mole}\right) = \boxed{17.5 \, kJ}$$

7

26. How much isopropanol must evaporate to cool 1 kg from 25 °C to 20°C? (the sp. Heat of isopropanol is 2.59 J/g°C)

$$Q = mc\Delta t = (1000_g)(2.59 \text{ J/g°C})(20°C - 25°C) = -12,950 \text{ J}$$

$$\Delta H = 40.1 \frac{kJ}{mol}$$
$$42,100 \text{ J/mol}$$

$$Q_{vap} = (\Delta H_{vap})(mol)$$

$$mol_{isoprop} = \frac{Q}{\Delta H} = \frac{12,950 \text{ J}}{42,100 \text{ J/mol}} = .3076 \text{ mol} \left(\frac{60_g}{mol}\right)$$

$$\boxed{18.5_g \text{ isopropanol}}$$

27. What quantity of heat is required to melt 1.0 kg of ice at its melting point?

$$1000_g \text{ ice} \left(\frac{1 \text{ mole}}{18_g}\right)\left(\frac{6 \text{ kJ}}{mole}\right) = \boxed{333.3 \text{ kJ}} \quad \Delta H_{fus} = 6 \text{ kJ/mol}$$

28. What quantity of heat is required to vaporize 1.0 kg of ice?

① Melt ice
② Heat melted ice
③ Vaporize melted ice.

① $1000_g \text{ ice} \left(\frac{1 \text{ mole}}{18_g}\right)\left(\frac{6 \text{ kJ}}{1 \text{ mole}}\right) = 333.3 \text{ kJ}$

② $Q = mc\Delta t = (1000_g)(4.184 \text{ J/g°C})(100°C) = 418,400 \text{ J} = 418.4 \text{ kJ}$

③ $1000_g \text{ water} \left(\frac{1 \text{ J}}{18_g}\right)\left(\frac{43945}{mole}\right) = 2439 \text{ kJ}$

$$\boxed{3,190 \text{ kJ}}$$

29. What is the final temperature when 10 g of water at 0 °C is added to 100 g of water at 75 °C?

$$Q_{cold\ water\ gained} = Q_{Hot\ water\ lost}$$

$$M_c C_c \Delta t_c = -M_H C_H \Delta t_H$$

$$(10_g)(4.184 \text{ J/g°C})(T_f - 0°C) = -(100_g)(4.184 \text{ J/g°C})(T_f - 75°C)$$

$$T_f = -10(T_f - 75) \qquad T_f = -10T_f + 750$$

$$11T_f = 750$$

$$\boxed{T_f = 68.2°C}$$

30. If 10 g of ice at 0°C comes into contact with 10 g of water at 50 °C, calculate the final temperature reached by the system at equilibrium.

Heat gained by ice = Heat lost by warm H_2O

$$10_g \text{ ice} \left(\frac{1 \text{ mole}}{18_g}\right)\left(\frac{6 \text{ kJ}}{mole}\right) = \frac{3.33 \text{ kJ}}{\text{needed to melt all ice}}$$

$$Q = mc\Delta t = (10_g)(4.184 \text{ J/g°C})(0 - 50) = -2.09 \text{ kJ}$$

-Not enough heat contained in warm water to melt all ice.

$$\boxed{t_f = 0°C}$$

31. What is the final temperature of 10 g of ice at 0°C is added to 100 g of water at 75 °C? (ΔH_f = 6.0 kJ/mol, heat capacity of water is 4.2 J/g°C)

$$10_g \text{ ice} \left(\frac{1 \text{ mol}}{18_g}\right)\left(\frac{6 \text{ kJ}}{mole}\right) = \frac{3.33 \text{ kJ}}{\text{Needed to melt all ice.}}$$

Heat to melt ice + Heat to warm melted ice = Heat lost by warm water

$$3,330 \text{ J} + (10_g)(4.184 \text{ J/g°C})(t_f - 0) = -(100_g)(4.184 \text{ J/g°C})(t_f - 75)$$

$$3,330 \text{ J} + 41.84 t_f = -418.4(t_f - 75) = -418.4 t_f + 31,380$$

$$460.24 t_f = 28,050 \qquad \boxed{t_f = 60.9°C}$$

32. If 10 g of ice at 0°C comes in contact with 50 g of water at 10°C, calculate the final temperature reached by the system at equilibrium.

$$10_g \text{ ice} \left(\frac{1 \text{ mole}}{18_g}\right)\left(\frac{6 \text{ kJ}}{mole}\right) = \frac{3.33 \text{ kJ}}{\text{needed to melt ice.}}$$

$$Q_{warm\ water} = mc\Delta t = (50)(4.184)(10 - 0) = 2092 \text{ J} = 2.09 \text{ kJ}$$

-Not enough heat in warm water to melt all of the ice. $\boxed{t_f = 0°C}$

8

crit temperature- temp when vapor can't be liquified regardless of pressure.
crit pressure - pressure required to produce liquification at the crit. temp.
crit point- the point on a phase diagram where crit P - crit T meet.

Triple Point-
-solid + liquid
phase have same
vapor pressure

10.9 Phase Diagrams

The beauty of this section is that it helps explain a large number of real world phenomena. (See the Chemical Impact on diamonds near the end of this chapter in your book.)

You should be able to define the following terms: **phase diagram, critical temperature, critical pressure, critical point and triple point.** You should be able to answer the following general questions regarding material presented in this section.

A. Why does the solid/liquid line in the phase diagram of water have a negative slope? Why is it positive for carbon dioxide?

if there is a negative slope, the density of the solid is less than the liquid

$D_{ice} < D_{water}$ - negative slope $D_{solid\,CO_2} > D_{liq\,CO_2}$ - positive slope.   The MP for ice decreases as P increases

B. Why does it take longer to cook an egg in the Rocky Mountains than at sea level?

There is a higher elevation in the Rockies, so there is less external atmospheric pressure, and water boils at a lower temp. Therefore, it must be heated for a longer time to absorb the same amount of heat.

C. How does the phase diagram for water help explain why your blades glide on a liquid layer when you ice skate?

The blades exert a large Pressure on the ice and it melts. As the blades move away, the pressure on the ice decrease and the liquid refreezes.

D. How does the phase diagram for carbon dioxide help explain how a CO_2 fire extinguisher works?

CO_2 is a liquid at 25°C w/ very high pressure
As Liquid CO_2 is let out and since the pressure drops, it vaporizes.
CO_2 is heavier than air. It also cools, so it puts out fire

E. Snow sometimes sublimes. How can this be so in spite of the phase diagram?

The atmosphere is not a closed system. The pressure is from the atmosphere, not from a piston. Vapor can escape to surroundings as soon as it is formed. Vapor does not have equilibrium w/ solids and ice disappears.

Example 10.9 Phase Diagrams

What phase changes does water undergo (see diagram below or a cleaner version in Fig 10.47 in book) as the pressure changes while the temperature is held constant at -12°C?
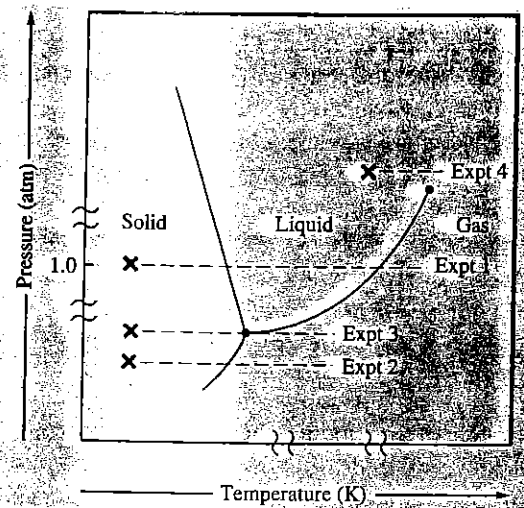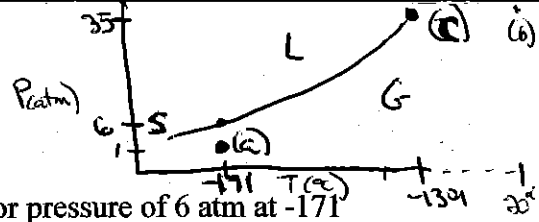

Figure 10.48
Diagrams of various heating experiments on samples of water in a closed system.

Solution

At very low pressures, water exits as a gas at -12°C. As the pressure in increased, it turns into a solid. At very high pressures the water will liquefy.

9

(top right, graph with handwritten annotations)

35

$P_{(atm)}$

L

G

S

•(c) (b)

•(a)

-171 $T(°C)$ -139 20

Problems

33. The critical point of CO is -139°C, 35 atm. Liquid CO has a vapor pressure of 6 atm at -171 °C. Which of the following statements must be true?
   a. CO is a gas at -171°C and 1 atm. T
   b. A tank of CO at 20°C can have a pressure of 35 atm. T
   c. CO gas cooled to -145°C and 40 atm pressure will condense. T
   d. The normal boiling point of CO lies above -171°C. F

34. How is the change in density for a solid-to-liquid phase change related to the slope of the liquid-solid line of a phase diagram?

   If the solid is more dense, the s/L line is a positive slope.
   If the solid is less dense, the S/L line is a negative slope.

35. Iodine has a triple point at 114°C, 90 mm Hg. Its critical temperature is 535°C. The density of the solid is 4.93 g/cm³, while that of the liquid is 4.00 g/cm³. Sketch a phase diagram for iodine and use it to fill in the blanks below, either as "liquid" or "solid."
   a. Iodine vapor at 80 mm Hg condenses to the ___Solid___ phase when cooled sufficiently.
   b. Iodine vapor at 125°C condenses to the ___Liquid___ phase when enough pressure is applied.
   c. Iodine vapor at 700 mm Hg condenses to the ___Liquid___ phase when cooled above the triple point tempearature.
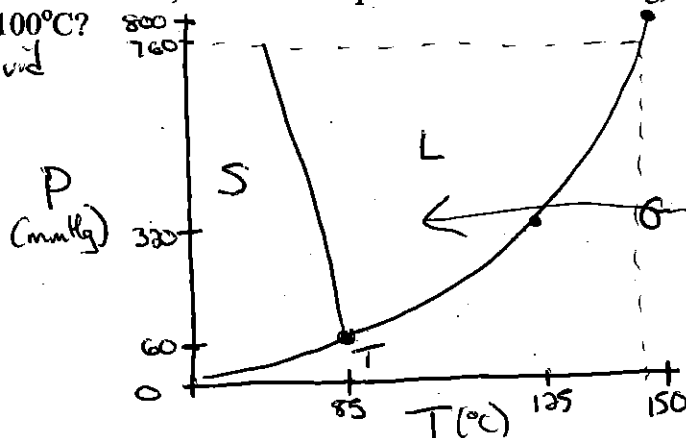
(phase diagram, handwritten)

760
700

P
(mmHg)

S   L   •C

G

90

O

114°C   535°C
Temp (°C)
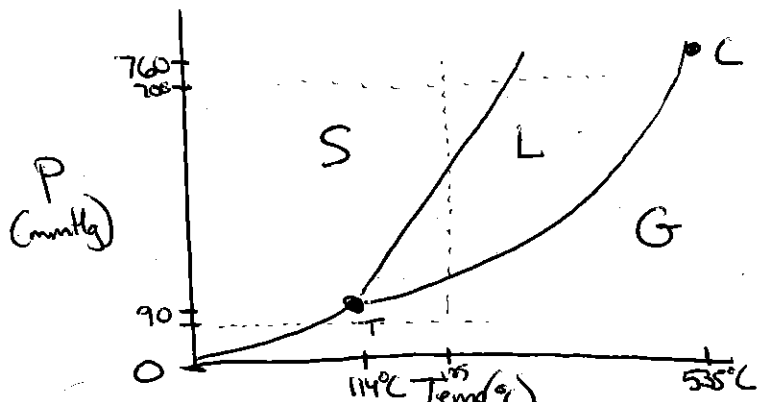
S/L line
has a (+)
slope
because
$D_{Solid} > D_{Liq}$

36. A pure substance A has a liquid vapor pressure of 320 mm Hg at 125°C, 800 mm Hg at 150°C, and 60 mm Hg at the triple point, 85°C. The melting point of A decreases slightly as pressure increases.
   negative slope
   a. Sketch a phase diagram for A.
   b. From the phase diagram, estimate the normal boiling point. ~140°C (Temp @ 760 mmHg)
   c. What changes occur when, at a constant pressure of 320 mm Hg, the temperature drops from 150 to 100°C?

   Gas → Liquid

(phase diagram, handwritten)

800
760

P
(mmHg)   320

S   L   G

60

O

85   125   150
T (°C)

10

Name _____ Period _____ Date _____

Phase Diagrams

Below are two pressure-temperature graphs, called phase diagrams, for water and carbon dioxide. The triple point T is the point at which the liquid, vapor, and solid phases of a material are in equilibrium. The critical point C is the point above which you cannot liquefy a gas. Study the graphs and answer the questions below. Each line represents equilibrium between the phases that it separates.

Pressure versus Temperature, H_2O Pressure versus Temperature, CO_2
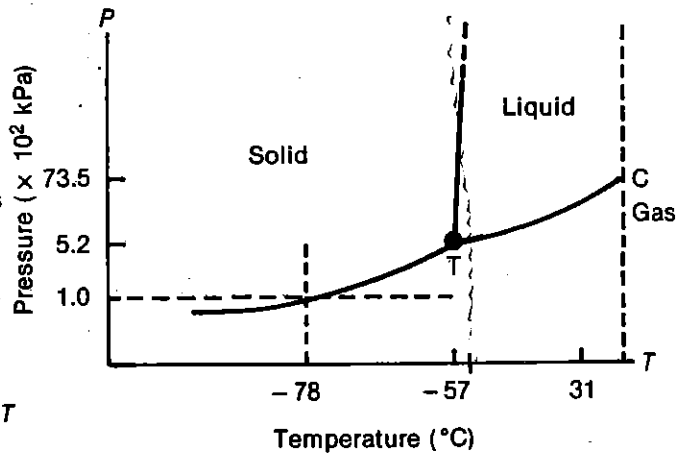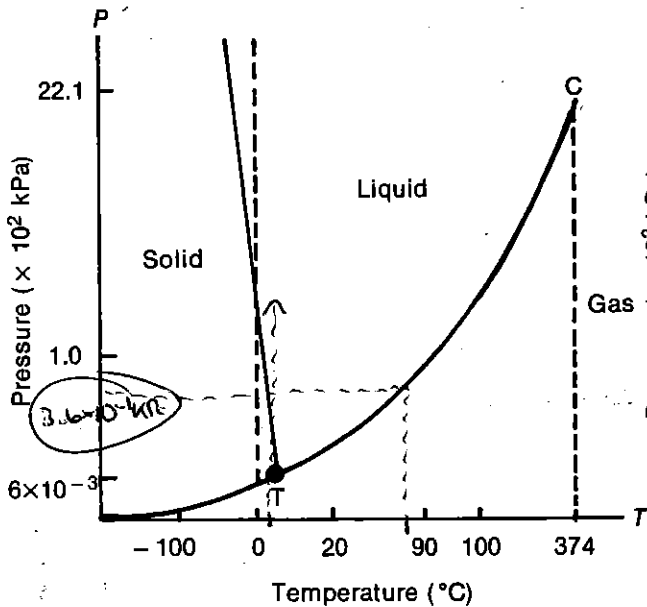
Answer the following questions using the above phase diagrams.   348ʮ

36.6kPa _____ 1. At what pressure will water boil at 75°C?⟨★⟩(tough to estimate (Clausius)
                                  $T_1 = 373k$ $P_1 = 760 mmHg = 1 atm = 1013 kPa$) Calculate using 'Clausius'

374 K   101°C 2. What is the critical temperature of water?

G→S→L _____ 3. If you hold the temperature constant just below the triple point and increase
-57°C, 520kPa (5.13) the pressure, what is the order of the phase change?
                                  4. What is the triple point for carbon dioxide?

G→L→S _____ 5. If you hold the CO_2 temperature constant just above the triple point
                                  and increase the pressure, what is the order of the phase change?
NO _____ 6. At normal atmospheric pressure, can carbon dioxide exist as a liquid?

520 kPa _____ 7. What is the minimum pressure at which carbon dioxide will liquefy?

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

$\ln\left(\frac{P_2}{101.3 kPa}\right) = \frac{43.9 kJ/mole}{.008314 J/mol k}\left(\frac{1}{373k} - \frac{1}{348k}\right)$

$\ln P_2 - \ln 101.3 = -1.017$

$\ln P_2 = 3.601$

$\boxed{P_2 = 36.6 kPa}$

11

There is a temperature, called the **critical temperature,** above which the liquid phase of a pure substance cannot exist. The pressure which must be applied to bring about condensation at that temperature is called the **critical pressure.** Alternatively, one can regard the critical pressure as the vapor pressure of the liquid at its critical temperature.

Table 11.2 lists the critical temperatures of several common substances. The species in the column at the left, all of which have critical temperatures below 25°C, are often referred to as "permanent gases." Applying pressure at room temperature will not condense a permanent gas; it must be cooled as well. The permanent gases are stored and sold under high pressures, often 150 atm or greater; when the valve on the cylinder is opened, the pressure drops as gas escapes, as would be expected from the Ideal Gas Law.

TABLE 11.2 CRITICAL TEMPERATURES					
"PERMANENT GASES"		"CONDENSABLE GASES"		"LIQUIDS"	
Helium	−268°C	Carbon dioxide	31°C	Ether	194°C
Hydrogen	−240	Ethane	32	Ethyl alcohol	243
Nitrogen	−147	Propane	97	Benzene	289
Argon	−122	Ammonia	132	Bromine	302
Oxygen	−119	Chlorine	146	Water	374
Methane	−82	Sulfur dioxide	158	Mercury	1460

The gases listed in the center column of Table 11.2 have critical temperatures above 25°C; they are available commercially as liquids in high pressure cylinders. When we open the valve on a cylinder of propane, the gas that escapes is replaced by vaporization of liquid, and the pressure returns to its original value. Only when the liquid has completely vaporized and the tank is almost empty does the gauge pressure drop.

Phase Diagrams

**15.** Referring to Figure 10.5, state what phase(s) is (are)
present at   *Solid*
  a. −3°C, 5 mm Hg   b. 25°C, 1 atm *Liquid*
  c. 70°C, 20 mm Hg *Vapor*

1. Line AB is a portion of the vapor pressure–temperature curve of liquid water. At any temperature and pressure along this line, liquid water is in equilibrium with water vapor. From the curve we see that at point A, these two phases are in equilibrium at 0°C and about 5 mm Hg (more exactly, 0.01°C and 4.56 mm Hg). At B, corresponding to 100°C, the pressure exerted by the vapor in equilibrium with liquid water is 1 atm. The extension of line AB beyond point B gives the equilibrium vapor pressure of the liquid above the normal boiling point. The line ends at 374°C, the critical temperature of water, where the pressure is 218 atm.

2. Line AC represents the vapor pressure curve of ice. At any point along this line such as point A (0°C, 5 mm Hg) or point C, which might represent −3°C and 3 mm Hg, ice and vapor are in equilibrium with each other.

3. Line AD gives the temperatures and pressures at which liquid water is in equilibrium with ice.

Point A on the phase diagram is the only one at which all three phases, liquid, solid, and vapor, are in equilibrium with each other. It is called the **triple point.** For water, the triple point temperature is 0.01°C. At this temperature liquid water and ice have the same vapor pressure, 4.56 mm Hg.

Temperature (°C)
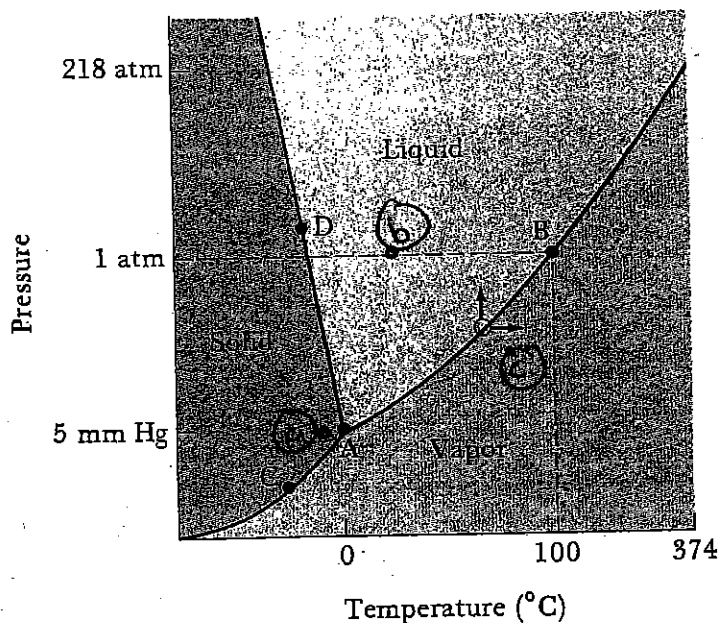
Liquid-Vapor Equilibrium

-Vapor (gaseous form of a liquid)
-open container - evaporation occurs until all liquid is gone.
- closed container - liquid molecules begins to evaporate, but they
  have no place to go, so they become Liquid again.
-increasing the rate of condensation until the rate = rate of evaporation

$$Liquid \rightleftharpoons vapor \quad (forward + reverse \ happening \ at \ same \ rate)$$

(Assume the vapor will follow the ideal gas law, $PV = nRt$)
-Once equilbrium is established, the pressure the vapor exerts on liquid
  remains constant (Vapor pressure)

-Vapor P- varies from liquid to liquid + temp to temp
-If both Liq + Vapor phases are present, the pressure exerted
  by vapor is independent of volume.

A Vaporizer adds moisture to a dry room @ 25°C (298K), where the vapor pressure is 24 mmHg (.0315 atm).

a) What is the mass of the H_2O needed to saturate the air under these conditions if the room's volume is $5 \times 10^4 L$? (treat vapor like an ideal gas).

$$PV = nRT \qquad PV = \left(\frac{mass}{MM}\right)RT$$

$$(.0315 atm)(5 \times 10^4 L) = \left(\frac{mass}{18 \text{ g/mol}}\right)\left(.0821 \frac{L \cdot atm}{mol \cdot K}\right)(298K)$$

$$\boxed{mass = 1,159 \text{ g } H_2O}$$

b) If 1 kg of H_2O is used, what will the pressure of water vapor established in the room be?

$$PV = nRT \qquad PV = \frac{mass}{MM} RT$$

$$P(5 \times 10^4 L) = \left(\frac{1000 \text{ g}}{18 \text{ g/mol}}\right)\left(.0821 \frac{L \cdot atm}{mol \cdot K}\right)(298K)$$

$$\boxed{P = .0272 \text{ atm} = 20.6 \text{ mmHg}}$$

c) Suppose the vaporizer contains 1 kg H_2O. What mass of water will be left when the relative humidity is 50%. @ P_0
(Rel Hum $= \frac{P}{P_0} \times 100 \qquad P = act P \qquad P_0 = Vap P$ @ saturation)

$$P = (.5)(P_0) = (.5)(22.4 \text{ mmHg}) = 11.2 \text{ mmHg} = .0147 \text{ atm}$$

$$PV = nRT \qquad PV = \left(\frac{mass}{MM}\right)RT$$

$$(.0147 atm)(5 \times 10^4 L) = \left(\frac{mass}{18 \text{ g/mol}}\right)\left(.0821 \frac{L \cdot atm}{mol \cdot K}\right)(298K)$$

$$mass = 542.1 \text{ g } H_2O \text{ used to vaporize}$$

$$1000 \text{ g} - 542.1 \text{ g} = \boxed{457.9 \text{ g } H_2O \text{ unused} + \text{ will be in humidifier}}$$