

CHEM 120
Spring 2006
Exam 2

Name: _____

Instructions

Write your answers in blue or black ink. Work done in pencil will be accepted, but you will not be able to appeal any apparent grading mistakes (except simple addition errors). Write neatly. If I can't read it, I can't grade it.

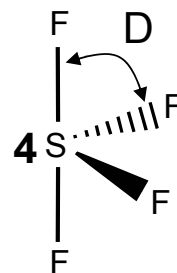
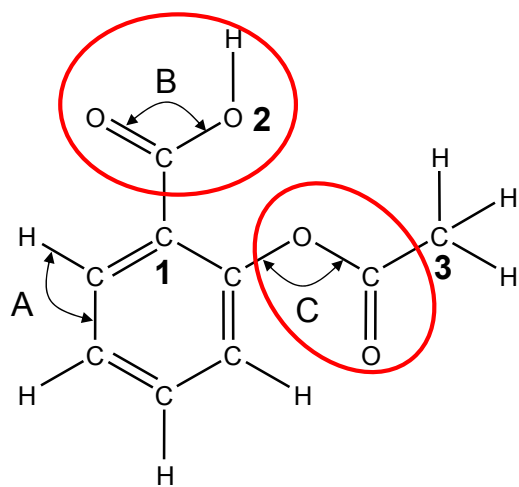
Show all work for full credit! For the word problems write your final answer in a complete sentence. Indicate what you are doing at important steps (you do not need to tell me about every mathematical manipulation you do). If you change your mind on a question, cross out the incorrect answer and clearly indicate your final answer.

There are **10** pages, none blank, and a periodic table.

You may use the back of any page as additional workspace. Please indicate that you have done so.

Problem	Possible Points	Points Received	Estimated Time
1	15		3
2	6		5
3	12		9
4	12		9
5	20		10
6	15		8
7	10		6
Free	10	10	0
Total	100		50
	Bonus		
	Grand Total		

1. Consider the two molecules whose structures are shown below.



a. (8 Points) Give the ideal value for the lettered angles. Place a star next to the one(s) that you expect to be distorted away from these ideal values.

A. 120°

B. 120° *

C. 109.5° *

D. 90.0° *

b. (4 Points) Give the hybridization of the numbered atoms in these structures.

1. sp^2

2. sp^3

3. sp^3

4. sp^3d

c. (3 Points) Circle the polar part(s) of the aspirin molecule.

2. (6 Points) Derive the Clausius-Clapeyron equation $\frac{d(\ln p_{\text{vapor}})}{dT} = \frac{\Delta H}{RT^2}$, which describes the equilibrium between the liquid and gas phases of a substance, from $\Delta G = \Delta H - T\Delta S$ and $\Delta G = -R\cdot T\cdot \ln K$. In this equation p_{vapor} is the vapor pressure of the liquid and ΔH is the enthalpy of vaporization. If you get stuck on the derivative, you may derive the equation in the terms of $\ln p_{\text{vapor}}$. Hint: remember to write down the equilibrium that you are describing.

The equilibrium involved is $\text{liquid} \rightleftharpoons \text{vapor}$.

For this equilibrium $K = p_{\text{vapor}}$. And thus, $\Delta G = -R\cdot T\cdot \ln p_{\text{vapor}}$.

Substituting $\Delta G = -R\cdot T\cdot \ln p_{\text{vapor}}$ into $\Delta G = \Delta H - T\Delta S$ gives $-R\cdot T\cdot \ln p_{\text{vapor}} = \Delta H - T\Delta S$.

Dividing both sides by $-R\cdot T$ gives $\ln p_{\text{vapor}} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$.

Taking the derivative with respect to T (remember that $\frac{dx^n}{dx} = nx^{n-1}$) results in the desired equation.

$$\frac{d(\ln p_{\text{vapor}})}{dT} = \left(-\frac{\Delta H}{R}\right)\left(\frac{dT^{-1}}{dT}\right) + \frac{d}{dT}\left(\frac{\Delta S}{R}\right) = \left(-\frac{\Delta H}{R}\right)(-T^{-2}) + 0$$

$$\frac{d(\ln p_{\text{vapor}})}{dT} = \frac{\Delta H}{RT^2}$$

3. Viscosity is a property of liquids defined as the liquid's resistance to flow. Liquids that flow only slowly (like molasses) are classified as viscous, while those that flow easily are said not to be viscous. Hint: for this problem think about what happens to a liquid at the molecular level when it flows.

a. (4 Points) Water is more viscous than the hydrocarbon octane (C_8H_{18}). Explain.

The process of flowing is described by a ΔG for moving the molecules from one place in space to another. At constant pressure $\Delta G = \Delta H - T\Delta S$. For a flowing liquid ΔH will be positive, because the intermolecular interactions stabilize groupings of molecules and these must be overcome for flow to occur. The ΔS for a flowing liquid is positive, because the energy is being spread out over more particles, or put another way, the particles are moving chaotically (think of the chaotic nature of a flowing stream). Since a viscous material flows slowly (ΔG for flowing is not as negative), and flow is entropically favored (ΔS is positive), the ΔH term for a viscous material must be larger (the passage of its molecules past each other is more hindered).

Water has many strong hydrogen bonds which act to stick water molecules together and thus impede the passage of water molecules past each other. This impeded flow makes water more viscous than octane, which only has dispersion forces acting to hold its molecules together. Even though octane has a higher molecular weight (and thus more dispersion forces), water's higher viscosity implies that hydrogen bonding is the more important effect.

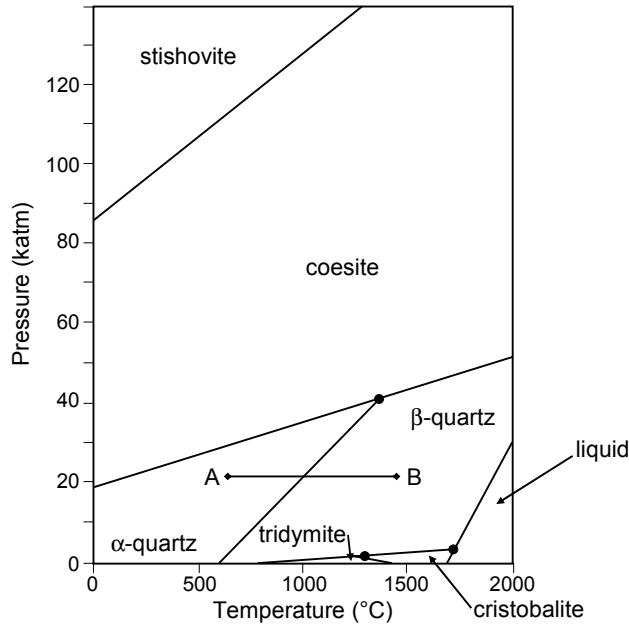
b. (4 Points) Motor oil is much more viscous than water although it is comprised almost exclusively of hydrocarbons (e. g., tetradecane, $C_{14}H_{30}$). Explain.

In the case of tetradecane the dispersion forces must now be significantly stronger than in octane (because it is a bigger molecule) and must now be large enough to hinder the flow of the tetradecane molecules more than hydrogen bonding retards the flow of water.

c. (4 Points) Viscosity decreases as temperature increases (the source of "viscosity breakdown" quoted in TV ads). Explain.

The entropy term for flowing is positive and it will tend to make ΔG for flowing negative (more favorable) as temperature increases. Thus, it is the chaotic nature of a flowing liquid that eventually overcomes the forces holding the liquid's molecules together as the temperature rises and decreases viscosity.

4. Part of the phase diagram of SiO_2 is shown below. Note that the names refer to different solid phases of SiO_2 and that the region corresponding to SiO_2 (g) is not shown.



a. (3 Points) There are three points on the diagram indicated by dots (points A and B are not dots!). What are these points called and what is their significance?

These are triple points and they are where three phases exist together in equilibrium.

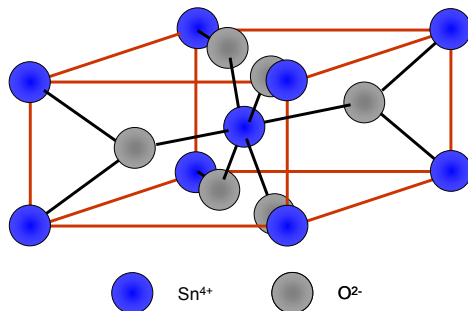
b. (5 Points) Describe what occurs when SiO_2 is heated at 20 katm from point A on the phase diagram to point B on the diagram. Be as specific as possible.

The temperature rises in accord with the heat capacity of α -quartz until 1000 °C. At this temperature the temperature will stop rising as the sample undergoes a phase change from α -quartz to β -quartz. The amount of heat that must be put in depends on ΔH for the phase transition from α -quartz to β -quartz. During this phase change the density of the solid decreases. Once the phase change is over, the temperature will rise again as determined by the heat capacity of β -quartz.

c. (4 Points) According to the phase diagram, cristobalite is the stable form of SiO_2 at temperatures above about 1400 °C and α -quartz is the stable form under normal conditions. Yet, one can pick up cristobalite off the ground and hold it in your hand. Why?

Cristobalite must be metastable. In other words, it is thermodynamically stable, but kinetically inert because all of the pathways that it could take to revert to α -quartz have very high E_a and are thus very slow. Cristobalite is in a thermodynamically unstable state, but can't leave it because there is no way out.

5. On the pre-exam exercise you predicted that SnO_2 (the mineral cassiterite) has a NaCl lattice with half the octahedral holes filled with Sn^{4+} ions. With this structure cassiterite's density is predicted to be 6.66 g/cm^3 . A second possibility is that SnO_2 has the rutile structure, shown below, where Sn^{4+} ions are on the corners and in the center of unit cell and the O^{2-} are inside and on the face of the tetragonal unit cell.



a. (4 Points) Verify that this unit cell gives the correct formula unit for SnO_2 .

There are 8 Sn on the corners, counting as 1/8 each, and 1 in the center, counting as 1, for a total of 4 Sn in the unit cell.

There are 4 O on cell faces, counting as 1/2 each, and 2 in the cell itself, counting as 1, for a total of 4 O in the unit cell.

This makes the formula of the unit cell Sn_2O_4 , or in simplest terms, SnO_2 (there are two formula units in the unit cell).

b. (4 Points) SnO_2 crystallizes with a tetragonal unit cell ($a = b = 4.738 \text{ \AA}$ and $c = 3.188 \text{ \AA}$). How does this simple eliminate the possibility that it crystallizes in the NaCl lattice?

The NaCl lattice is cubic, not tetragonal. Nothing that crystallizes in a tetragonal unit cell can have the NaCl lattice.

c. (8 Points) Predict the density of SnO₂. You are given that 1 Å = 10⁻¹⁰ m and that Avogadro's number is 6.02214x10²³.

Density, d , is given by the equation $d = \frac{m}{V}$, where m is the mass and V the volume of the material or object.

The volume of the SnO₂ unit cell is determined as follows.

$$V = a \times b \times c = (4.738 \times 10^{-10} \text{ m})(4.738 \times 10^{-10} \text{ m})(3.188 \times 10^{-10} \text{ m}) = 7.156_6 \times 10^{-29} \text{ m}^3$$

$$7.156_6 \times 10^{-29} \text{ m}^3 \left(\frac{100 \text{ cm}}{1 \text{ m}} \right)^3 = 7.156_6 \times 10^{-23} \text{ cm}^3$$

The molar mass of SnO₂ is 118.71 g/mole + 2(15.999 g/mole) = 150.70₈ g/mole.

The mass of the unit cell is

$$\left(\frac{2 \text{ SnO}_2 \text{ formula units}}{1 \text{ unit cell}} \right) \left(\frac{1 \text{ mole}}{6.02214 \times 10^{23} \text{ formula units}} \right) \left(\frac{150.70_8 \text{ g}}{1 \text{ mole}} \right) = 5.0051_3 \times 10^{-22} \text{ g}$$

The density is thus.

$$d = \frac{m}{V} = \frac{5.0051_3 \times 10^{-22} \text{ g}}{7.156_6 \times 10^{-23} \text{ cm}^3} = 6.994 \text{ g/cm}^3$$

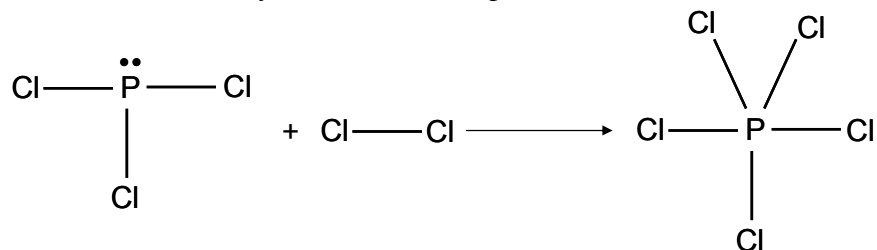
The density of SnO₂ is 6.994 g/cm³.

d. (4 Points) If the density of SnO₂ has been determined to be 6.95 ± 0.05 g/cm³ at the 95% confidence limit, does this support the assertion that SnO₂ has the rutile structure? Explain.

The theoretical density for SnO₂ with the rutile structure is within the 95% confidence interval for the experimental density. The theoretical density predicted for SnO₂ with the NaCl lies outside the experimental result's 95% confidence interval. We can conclude that the NaCl structure is inconsistent with the experimental data. The experimental density supports the assertion that SnO₂ has the rutile structure.

6a. (8 Points) In the gas phase PCl_3 , reacts with Cl_2 to give PCl_5 . For this reaction ΔH is -87.9 kJ/mole. If the bond dissociation energy of a $\text{Cl}-\text{Cl}$ bond is 242 kJ/mole, what is the $\text{P}-\text{Cl}$ bond dissociation energy?

Draw Lewis dot structures for reactants and product.



Set up equation for ΔH in terms of the bonds formed and broken.

$$\Delta H_{\text{rxn}} = \Sigma D_{\text{bonds broken}} - \Sigma D_{\text{bonds formed}}$$

$$\Delta H_{\text{rxn}} = D_{\text{Cl-Cl}} - 2 D_{\text{P-Cl}}$$

$$D_{\text{P-Cl}} = (D_{\text{Cl-Cl}} - \Delta H_{\text{rxn}})/2 = (242 \text{ kJ/mole} + 87.9)/2 = 165. \text{ kJ/mole}$$

The bond dissociation energy of a $\text{P}-\text{Cl}$ single bond is 165 kJ/mole.

b. (4 Points) The bond dissociation energy of a $\text{Cl}-\text{Cl}$ bond can be determined from $\Delta H_f^0(\text{Cl}, \text{g})$. But, in thermodynamic tables $\Delta H_f^0(\text{Cl}, \text{g})$ is listed as $+121.68$ kJ/mole (not 242 kJ/mole!). How do you resolve this apparent discrepancy?

The $\Delta H_f^0(\text{Cl}, \text{g})$ is defined by the reaction $1/2 \text{Cl}_2(\text{g}) \rightarrow \text{Cl}(\text{g})$, while the bond dissociation energy is defined by the reaction $\text{Cl}_2(\text{g}) \rightarrow 2 \text{Cl}(\text{g})$. The bond dissociation energy, in this case, is simply twice the first reaction. So, $D_{\text{Cl-Cl}}$ is twice $\Delta H_f^0(\text{Cl}, \text{g})$.

c. (3 Points) Name the three compounds in this problem.

PCl_3 **phosphorous trichloride**

PCl_5 **phosphorous pentachloride**

Cl_2 **chlorine**

7a. (6 Points) From the following data predict the melting point of PbS.

	ΔH_f^0 (kJ/mole)	S^0 ($J \cdot K^{-1} \cdot \text{mole}^{-1}$)
PbS (solid)	-98.32	91.34
PbS (liquid)	-84.06	100.79

At the melting point the solid and liquid forms of PbS will be at equilibrium, and thus ΔG for the process solid \rightleftharpoons liquid will be 0.

$$\Delta G = \Delta H - T\Delta S = 0$$

$$\Delta H = T\Delta S$$

$$T = \frac{\Delta H}{\Delta S} = \frac{(-84.06 + 98.32) \times 10^3 \text{ J} \cdot \text{mole}^{-1}}{(100.79 - 91.34) \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}} = \frac{14.26 \times 10^3}{9.45} \text{ K} = 1.51 \times 10^3 \text{ K}$$

The melting point of PbS is approximately 1.51×10^3 K.

b. (4 Points) Explain what role the lattice energy (E_{lattice}) and covalent character of the Pb–S bond will have on the melting point.

For a purely ionic compound to melt, the lattice energy, which in general is quite large, must be overcome so that the ions are free to move around in the liquid state. The lattice energy will depend directly on the charge of the ions and inversely on the size of the ions. For a molecular compound to melt the weaker intermolecular interactions must be overcome. Thus, molecular compounds tend to melt at lower temperatures than ionic compounds. If the covalent character in an ionic compound increases then the compound will behave more like a molecule and less like a collection of ions. So during melting, instead of breaking up into ions, it will break up into discrete, neutral pieces (i. e., molecules), as does AlCl_3 . This type of behavior will make the solid's melting point be lower than expected for a pure ionic compound because not all of the bonds in the compound need to be broken for it to melt.

The predicted melting point of PbS is within the range expected for an ionic compound, even one with fairly large ions. We can safely assume that PbS is predominantly an ionic compound with very little covalent character.