

**CHEM 323**  
**Fall 2008**  
**Take-Home Portion of Exam 1**

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. Helpful hint: do your work on a separate sheet of paper and then copy your final answer to this booklet.

Show all work for full credit! For the word problems write your final answer in complete sentences. 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 **11** pages, **1** blank.

You may use your book to look up any needed physical constants, equations, etc. However, you may not work with anyone else, and you may not ask any other faculty members to help you with the specific questions given here. You may ask any chemistry faculty member for help on the concepts involved, and you may ask me anything you want.

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

Problem	Possible Points	Points Received
1	52	
2	26	
3	10	
4	12	
Free	0	0
Total	100	
	Bonus	
	Grand Total	

1. Before beginning work on this problem, download the Excel file containing  $C_{p,m}$  as a function of temperature for mercury from the class web page. Helpful hint: review the basics of Excel and how to prepare graphs in Excel (I will grade you on how closely you adhere to these criteria) at ChemLab.truman under the Data Analysis link.

a. (25 Points) Fit the data using LoggerPro (available on the current student image) to empirical functions in the following way. For data less than about 4 K use the Debye extrapolation. Fit the data between 4 K and the melting point using two quartic functions, one covering the region between 4 K and about 50 K and the other from about 50 K to the melting point. The data for the liquid is to be fit to a cubic function. The functions for the solid must overlap (i. e., have at least one point in common) so that there won't be any breaks.

Prepare a graph of the heat capacity as a function of temperature showing both the data (as points) and the fit (as a single smooth curve through the points). So, even though you used four functions to fit the behavior there is only one line on the graph. Tape your graph in the space provided below and fill in the tables on the next page with the specifics of your fits.

**Figure 1.** Graph of the temperature dependence of  $C_{p,m}$  for solid and liquid mercury. The data were fit to four empirical expressions with the parameters shown in Tables 1-4.

$A =$  \_\_\_\_\_  $\pm$  \_\_\_\_\_  
 RMSE= \_\_\_\_\_  
 Temperature Range = \_\_\_\_\_

**Table 1.** Parameters from the best fit of the low-temperature  $C_{p,m}$  as a function of temperature for solid mercury using the Debye extrapolation ( $C_{p,m} = AT^3$ ). All uncertainties are at 95% confidence.

$A =$  \_\_\_\_\_  $\pm$  \_\_\_\_\_  
 $B =$  \_\_\_\_\_  $\pm$  \_\_\_\_\_  
 $C =$  \_\_\_\_\_  $\pm$  \_\_\_\_\_  
 $D =$  \_\_\_\_\_  $\pm$  \_\_\_\_\_  
 $E =$  \_\_\_\_\_  $\pm$  \_\_\_\_\_  
 RMSE= \_\_\_\_\_  
 Temperature Range = \_\_\_\_\_

**Table 2.** Parameters from the best fit of  $C_{p,m}$  as a function of temperature for solid mercury using the equation  $C_{p,m} = A + BT + CT^2 + DT^3 + ET^4$  on the temperature range shown. All uncertainties are at 95% confidence.

$$A = \quad \pm$$

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$$B = \quad \pm$$

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$$C = \quad \pm$$

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$$D = \quad \pm$$

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$$E = \quad \pm$$

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$$\text{RMSE} =$$

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$$\text{Temperature Range} =$$

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**Table 3.** Parameters from the best fit of  $C_{p,m}$  as a function of temperature for solid mercury using the equation  $C_{p,m} = A + BT + CT^2 + DT^3 + ET^4$  on the temperature range shown. All uncertainties are at 95% confidence.

$$A = \quad \pm$$

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$$B = \quad \pm$$

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$$C = \quad \pm$$

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$$D = \quad \pm$$

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$$\text{RMSE} =$$

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**Table 4.** Parameters from the best fit of  $C_{p,m}$  as a function of temperature for liquid mercury between its melting and boiling points using the equation  $C_{p,m} = A + BT + CT^2 + DT^3$ . All uncertainties are at 95% confidence.

b. (7 Points) Using the results from part *a*, determine  $S_m$  for liquid mercury at 298.15 K. Show your work below (and on the back, if necessary) and compare your value to the value given in the data table in the text. You are given that  $\Delta_{fus}H^0 = 2.30$  kJ/mole for mercury at its melting point (234.308 K).

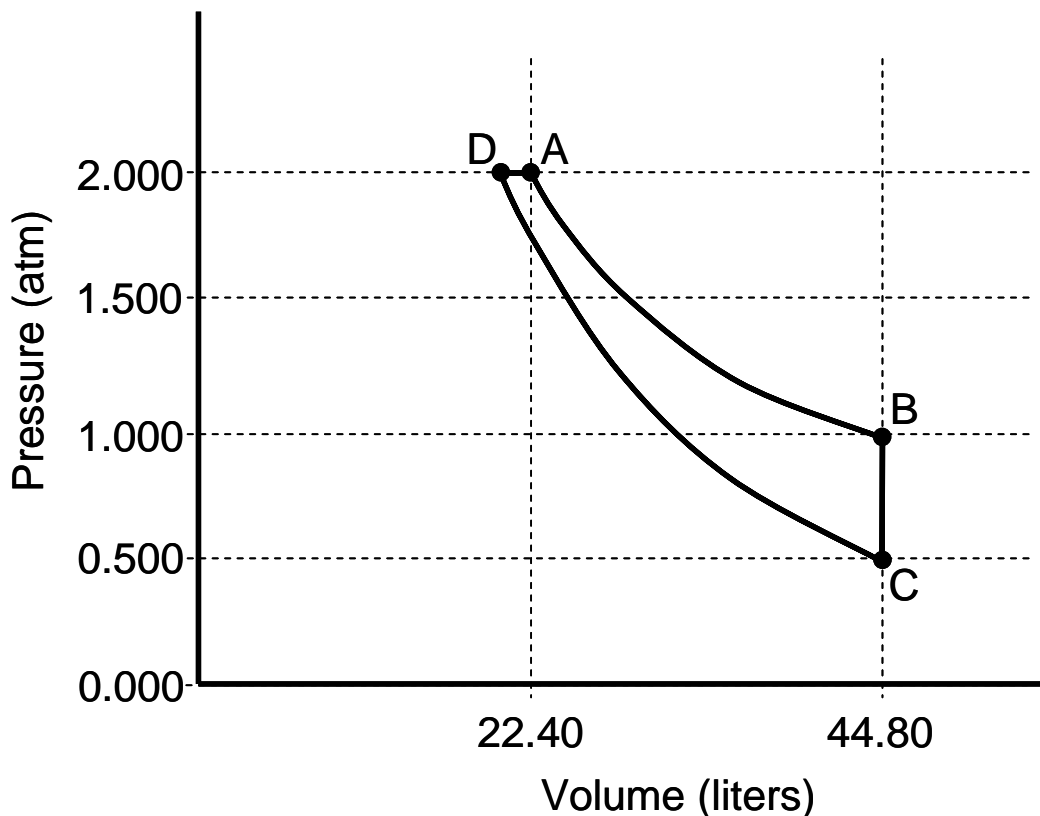
Note that LoggerPro can perform this calculation, but it misses an important term in the entropy expression and it will not necessarily give the correct number of significant figures.

c. (7 Points) By definition  $\Delta_f H^0 = 0$  for an element in its reference state at all temperatures (although the reference state may change with temperature). If we define  $\Delta_f H^0$  for liquid mercury at the melting point as 0, what would be the value of  $\Delta_f H^0$  for liquid mercury at the boiling point (629.73 K) if we didn't set it to 0? Does this amount to a significant difference? Use the appropriate equation(s) from part *a* to answer this question.

d. (6 Points) From your results in part *a*, determine  $C_{p,m}$  at 25.00 °C for mercury and compare it to the value given in the data table in the book. Are they in agreement?

e. (7 Points) Calculate how much heat is required to heat 1.000 mole of liquid Hg from its melting point to liquid Hg at its boiling point. Assume that  $C_{p,m}$  is constant and independent of temperature (use the value of  $C_{p,m}$  at 298.15 K). Compare your answer here to the one in part c. Does assuming  $C_{p,m}$  is constant significantly affect the amount of heat required for this process?

2. (26 Points) A sample consisting of 0.250 mole of an ideal monatomic gas ( $C_{V,m} = \frac{3}{2}R$ ) undergoes the following reversible process. Fill in the table and show your work on the next page (insert extra pages, as needed). If a particular thermodynamic property cannot be determined for a given step write “NA” in the appropriate box.



Step	Type	$q$ (kJ)	$w$ (kJ)	$\Delta U$ (kJ)	$\Delta S$ ( $\text{J}\cdot\text{K}^{-1}$ )	$\Delta H$ (kJ)
a $\rightarrow$ b	isothermal					
b $\rightarrow$ c	isochoric					
c $\rightarrow$ d	adiabatic					
d $\rightarrow$ a	isobaric					
Cycle						



3. (10 Points) How much methane must be burned at constant standard pressure to heat 1.000 kg of liquid water initially at 0.00 °C and convert it completely to steam at 100.00 °C? Assume that there is no heat lost to the surroundings and make whatever other assumptions are required to solve the problem. Relevant data are found in the back of the text.

4a. (6 Points) Many compounds can exist in more than one solid form. These different forms may have very different physical properties as a result of how the molecules are arranged in the solid. An example that we are all familiar with is the different allotropic forms of C (diamond and graphite). Another example of this phenomenon is  $\text{CaCO}_3$  which exists in two solid forms called calcite and aragonite. Using data from your text, and making any necessary assumptions, determine which form of  $\text{CaCO}_3$  is the more stable under standard conditions.

b. (6 Points) Is it possible by changing temperature alone, to change which form of  $\text{CaCO}_3$  is the most stable? If it is possible, predict at the temperature at which this change will occur. Make (and state) the assumptions that you made to solve this problem.