

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.

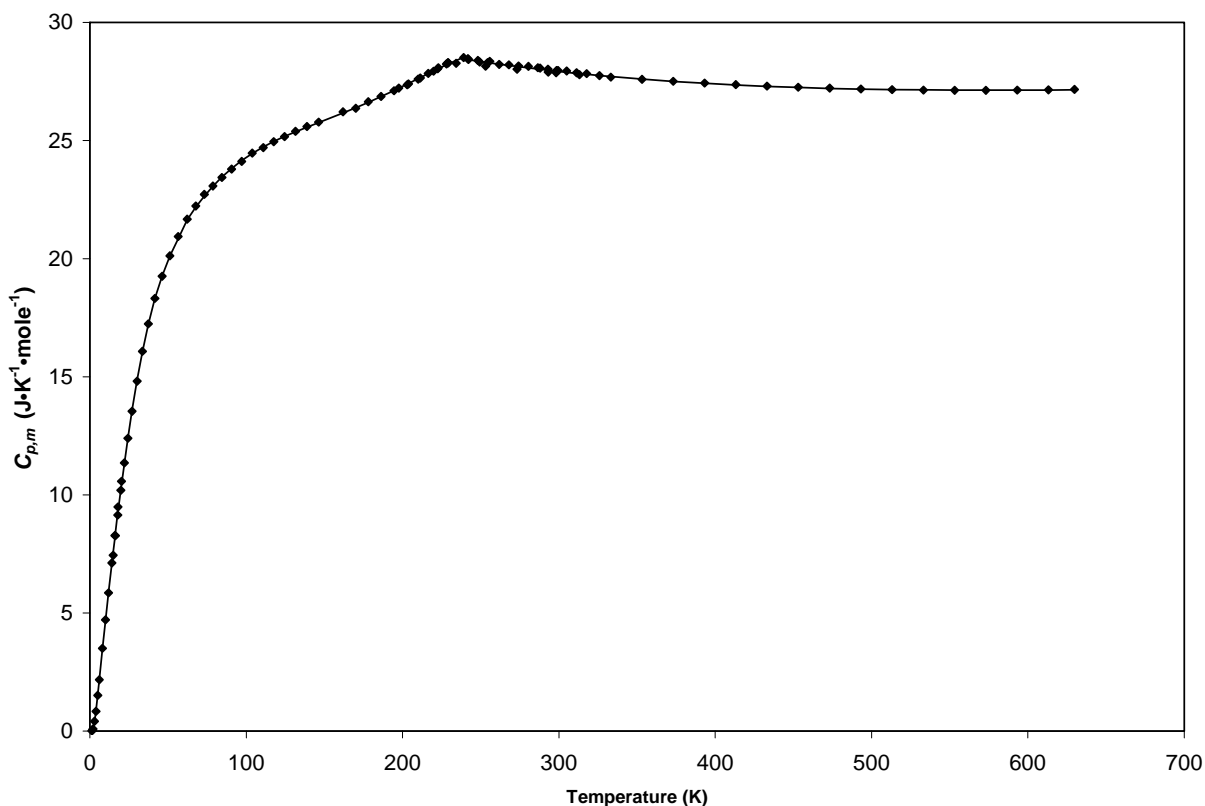


Figure 1. Graph of the temperature dependence of $C_{p,m}$ for solid and liquid mercury. The data were fit to four empirical expressions with the parameters shown in Tables 1-4.

$A =$	0.0134 J·K⁻¹·mole⁻¹	± 0.0005
RMSE=	0.03283	
Temperature Range =	0 – 4 K	

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.

$A =$	-1.8 J·K⁻¹·mole⁻¹	± 0.2
$B =$	0.67 J·K⁻²·mole⁻¹	± 0.04
$C =$	-0.001 J·K⁻³·mole⁻¹	± 0.003
$D =$	-0.00014 J·K⁻⁴·mole⁻¹	± 0.00008
$E =$	0.0000012 J·K⁻⁵·mole⁻¹	± 0.0000008
RMSE=	0.08427	
Temperature Range =	3 – 62 K	

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.

$A =$	$8.9 \text{ J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}$	± 0.5
<hr/>		
$B =$	$0.34 \text{ J}\cdot\text{K}^{-2}\cdot\text{mole}^{-1}$	± 0.01
<hr/>		
$C =$	$-0.0028 \text{ J}\cdot\text{K}^{-3}\cdot\text{mole}^{-1}$	± 0.0002
<hr/>		
$D =$	$0.0000107 \text{ J}\cdot\text{K}^{-4}\cdot\text{mole}^{-1}$	± 0.0000008
<hr/>		
$E =$	$-0.000000015 \text{ J}\cdot\text{K}^{-5}\cdot\text{mole}^{-1}$	± 0.000000001
<hr/>		
RMSE=	0.04084	
<hr/>		
Temperature Range =	$56 - 234 \text{ K}$	
<hr/>		

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.

$A =$	$32.5 \text{ J}\cdot\text{K}^{-1}\cdot\text{mole}^{-1}$	± 0.4
<hr/>		
$B =$	$-0.0248 \text{ J}\cdot\text{K}^{-2}\cdot\text{mole}^{-1}$	± 0.003
<hr/>		
$C =$	$0.000038 \text{ J}\cdot\text{K}^{-3}\cdot\text{mole}^{-1}$	± 0.000008
<hr/>		
$D =$	$-0.000000018 \text{ J}\cdot\text{K}^{-4}\cdot\text{mole}^{-1}$	± 0.000000006
<hr/>		
RMSE=	0.04835	
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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.

Starting with the equation $S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_p}{T} dT$ and including the entire

temperature range from 0 K to 298.15 K and the change of state, we can write the expression shown below. Note the limits on the integration are based on my fits of the data, as shown in Tables 1-4, and your values may differ slightly.

$$S(298.15) = S(0) + \int_0^{4.00} \frac{C_p(\text{solid})}{T} dT + \int_{4.00}^{62.00} \frac{C_p(\text{solid})}{T} dT + \int_{62.00}^{234.308} \frac{C_p(\text{solid})}{T} dT + \frac{\Delta_{fus}H}{T} + \int_{234.308}^{298.15} \frac{C_p(\text{liquid})}{T} dT$$

The expression may be evaluated term by term after substituting the equations from part *a* and dividing by T . Note that $S(0)$ is defined as 0 by the Third Law and that for simplicity units will be left off all of the integrals until the end.

First term.

$$\int_0^{4.00} \frac{C_p(\text{solid})}{T} dT = \int_0^{4.00} \frac{0.0134_1 T}{T} dT = \int_0^{4.00} 0.0134_1 dT = 0.0134_1 T \Big|_0^{4.00} = 0.0536_4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$$

Second term.

$$\begin{aligned} \int_{4.00}^{62.00} \frac{C_p(\text{solid})}{T} dT &= \int_{4.00}^{62.00} \frac{-1.7_6}{T} + 0.66_{59} - 0.0007_9 T - 1.3_6 \times 10^{-4} T^2 + 1.1_8 \times 10^{-6} T^3 dT \\ &= \left(-1.7_6 \ln T + 0.66_{59} T - \frac{0.0007_9}{2} T^2 - \frac{1.3_6 \times 10^{-4}}{3} T^3 + \frac{1.1_8 \times 10^{-6}}{4} T^4 \right) \Big|_{4.00}^{62.00} \\ &= \left(-1.7_6 \ln(62.00) + 0.66_{59}(62.00) - \frac{0.0007_9}{2} (62.00)^2 - \frac{1.3_6 \times 10^{-4}}{3} (62.00)^3 + \frac{1.1_8 \times 10^{-6}}{4} (62.00)^4 \right) \\ &\quad - \left(-1.7_6 \ln(4.00) + 0.66_{59}(4.00) - \frac{0.0007_9}{2} (4.00)^2 - \frac{1.3_6 \times 10^{-4}}{3} (4.00)^3 + \frac{1.1_8 \times 10^{-6}}{4} (4.00)^4 \right) \\ &= (-7.2_6 + 41.2_{-2} - 1.5_1 - 10.8_{-8} + 4.3_{59}) - (-2.4_3 + 2.6_6 - 0.006_3 - 0.0029_0 + 7.5_{52} \times 10^{-5}) = 25.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1} \end{aligned}$$

Third term.

$$\int_{62.00}^{234.308} \frac{C_p(\text{solid})}{T} dT = \int_{62.00}^{234.308} \frac{8.8_9}{T} + 0.34_0 - 0.0027_8 T + 1.07_1 \times 10^{-5} T^2 - 1.5_0 \times 10^{-8} T^3 dT$$

$$= \left(8.8_9 \ln T + 0.34_0 T - \frac{0.0027_8}{2} T^2 + \frac{1.07_1 \times 10^{-5}}{3} T^3 - \frac{1.5_0 \times 10^{-8}}{4} T^4 \right) \Bigg|_{62.00}^{234.308}$$

$$= \left(8.8_9 \ln(234.308) + 0.34_0 (234.308) - \frac{0.0027_8}{2} (234.308)^2 + \frac{1.07_1 \times 10^{-5}}{3} (234.308)^3 - \frac{1.5_0 \times 10^{-8}}{4} (234.308)^4 \right)$$

$$- \left(8.8_9 \ln(62.00) + 0.34_0 (62.00) - \frac{0.0027_8}{2} (62.00)^2 + \frac{1.07_1 \times 10^{-5}}{3} (62.00)^3 - \frac{1.5_0 \times 10^{-8}}{4} (62.00)^4 \right)$$

$$= (48.5_0 + 79.6 - 76.3 + 45.9_2 - 11.3) - (36.6 + 21.0 - 5.3_4 + 0.850_8 - 0.0554) = 33.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$$

Fourth term.

$$\frac{\Delta_{fus} H}{T} = \frac{2.30 \times 10^3 \text{ J} \cdot \text{mole}^{-1}}{234.308 \text{ K}} = 9.81_6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$$

Fifth term.

$$\int_{234.308}^{298.15} \frac{C_p(\text{liquid})}{T} dT = \int_{234.308}^{298.15} \frac{32.4_8}{T} - 0.024_8 + 3.7_7 \times 10^{-5} T - 1.8_7 \times 10^{-8} T^2 dT$$

$$= \left(32.4_8 \ln T - 0.024_8 T + \frac{3.7_7 \times 10^{-5}}{2} T^2 - \frac{1.8_7 \times 10^{-8}}{3} T^3 \right) \Bigg|_{234.308}^{298.15}$$

$$= \left(32.4_8 \ln(298.15) - 0.024_8 (298.15) + \frac{3.7_7 \times 10^{-5}}{2} (298.15)^2 - \frac{1.8_7 \times 10^{-8}}{3} (298.15)^3 \right)$$

$$- \left(32.4_8 \ln(234.308) - 0.024_8 (234.308) + \frac{3.7_7 \times 10^{-5}}{2} (234.308)^2 - \frac{1.8_7 \times 10^{-8}}{3} (234.308)^3 \right)$$

$$= (185.0 - 7.3_9 + 1.6_7 - 0.16_{52}) - (177.2 - 5.8_1 + 1.0_3 - 0.080_1) = 7.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$$

The total of all four terms is $S(\text{Hg}, l)$ at 298.15 K, which is $76. \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$. This value is in agreement with the accepted value of $76.02 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$.

If one takes the given data, divides by T and then integrates in LoggerPro the value of the integral portion of the entropy expression is $66.16 \text{ J}^1 \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$. When this is added to the fourth term (from the melting of solid mercury) given above one obtains a value for $S(\text{Hg}, l)$ at 298.15 K of $75.98 \text{ J}^1 \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$.

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.

We can integrate the definition of the heat capacity, $C_p = \left(\frac{\partial H}{\partial T}\right)_p$, to give

$\Delta H = \int C_p dT$, where ΔH is the change in the enthalpy due to the temperature change. Substituting in the equation for the heat capacity of liquid mercury gives the following. Please note that I am omitting the units here for the sake of clarity, in the first three equations the units will come out to be J/mole. In the fourth equation the units are kJ/mole.

$$\Delta H = \int_{234.308}^{629.73} 32.5 - 0.0248T + 3.8 \times 10^{-5} T^2 - 1.8 \times 10^{-8} T^3 dT .$$

$$\Delta H = \left(32.5T - \frac{0.0248}{2} T^2 + \frac{3.8 \times 10^{-5}}{3} T^3 - \frac{1.8 \times 10^{-8}}{4} T^4 \right) \Bigg|_{234.308}^{629.73}$$

$$\Delta H = \left(32.5(629.73) - \frac{0.0248}{2} (629.73)^2 + \frac{3.8 \times 10^{-5}}{3} (629.73)^3 - \frac{1.8 \times 10^{-8}}{4} (629.73)^4 \right) - \left(32.5(234.308) - \frac{0.0248}{2} (234.308)^2 + \frac{3.8 \times 10^{-5}}{3} (234.308)^3 - \frac{1.8 \times 10^{-8}}{4} (234.308)^4 \right)$$

$$\Delta H = (20.4_6 - 4.91_7 + 3.1_6 - 0.70_7) - (7.61_5 - 0.680_7 + 0.16_2 - 0.013_{56}) = +10.9 \text{ kJ/mole}$$

Note that performing this integration in LoggerPro on the data set gives +10.8 kJ/mole.

This means that the enthalpy increases by ~10 kJ/mole for liquid mercury from its melting point to its boiling point. This means that if we defined $\Delta_f H^0$ (Hg, l) as 0 at the melting point it would be +10.9 kJ/mole at the boiling point, a not insignificant change!

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?

Substitute 298.15 K into your best-fit expression for the heat capacity as a function of temperature data.

$$C_{p,m} = 32.5 - 0.0248T + 3.8 \times 10^{-5} T^2 - 1.8 \times 10^{-8} T^3$$

$$C_{p,m} = 32.5 \frac{\text{J}}{\text{K} \cdot \text{mole}} - \left(0.0248 \frac{\text{J}}{\text{K}^2 \cdot \text{mole}} \right) (298.15 \text{ K}) +$$

$$\left(3.8 \times 10^{-5} \frac{\text{J}}{\text{K}^3 \cdot \text{mole}} \right) (298.15 \text{ K})^2 - \left(1.8 \times 10^{-8} \frac{\text{J}}{\text{K}^3 \cdot \text{mole}} \right) (298.15 \text{ K})^3$$

$$C_{p,m} = 32.5 \frac{\text{J}}{\text{K} \cdot \text{mole}} - \left(7.39_4 \frac{\text{J}}{\text{K} \cdot \text{mole}} \right) + \left(3.3_7 \frac{\text{J}}{\text{K} \cdot \text{mole}} \right) - \left(0.47_7 \frac{\text{J}}{\text{K} \cdot \text{mole}} \right)$$

$$C_{p,m} = 28.0 \frac{\text{J}}{\text{K} \cdot \text{mole}}$$

The calculated value of $S(298.15)$ from our best fit line of the $C_{p,m}$ as a function of temperature data is the same as the accepted value ($27.983 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$) within the limits of the significant figures.

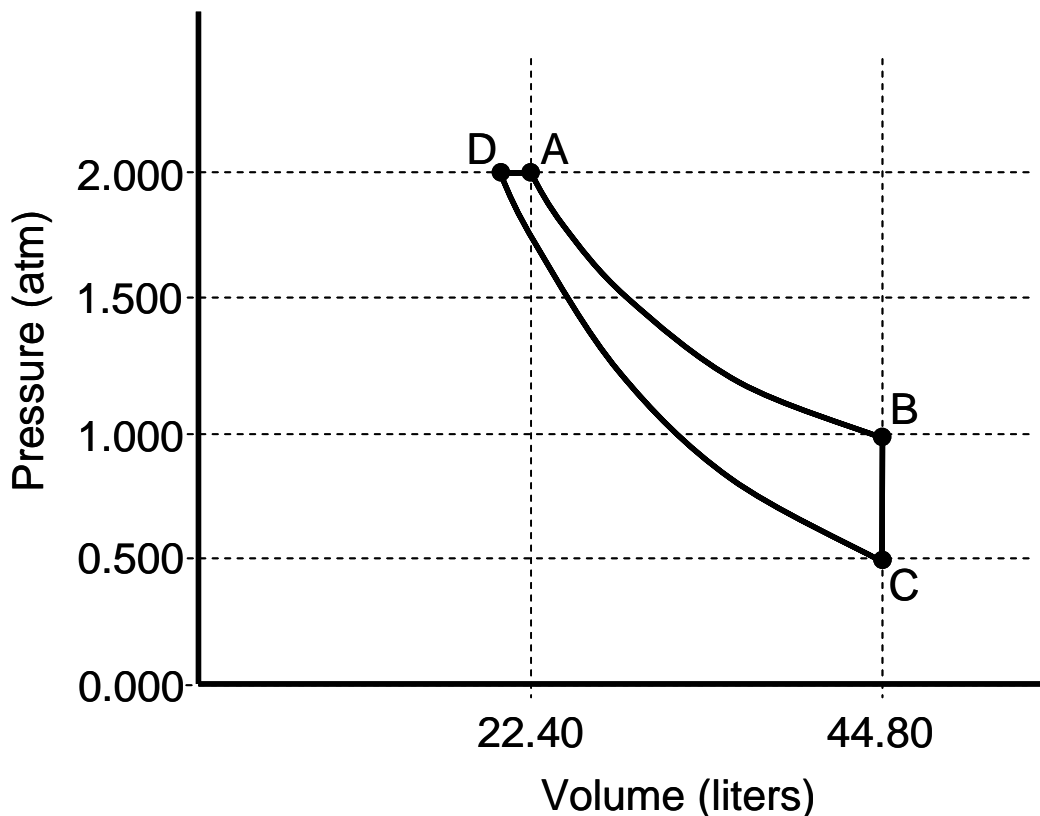
e. (7 Points) Calculate how much heat is required to heat 1.000 mole of liquid Hg from its melting point to liquid Hg at its boiling point. Assume that $C_{p,m}$ is constant and independent of temperature (use the value of $C_{p,m}$ at 298.15 K). Compare your answer here to the one in part *c*. Does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

We start with $C_{p,m} = \left(\frac{\partial H}{\partial T} \right)_p$ and integrate assuming that $C_{p,m}$ is independent of T to

give $\Delta H = nC_{p,m}\Delta T$. Substituting $C_{p,m} = 28.0 \frac{\text{J}}{\text{K} \cdot \text{mole}}$ and $n = 1.000$ mole into this expression gives $\Delta H = nC_{p,m}\Delta T = (1.000 \text{ mole})(28.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1})(629.73 - 234.308 \text{ K}) = +11.1 \text{ kJ}$.

If we had not assumed that $C_{p,m}$ is independent of T we would have gotten the same answer as in part *c*, +10.9 kJ. By assuming that $C_{p,m}$ is independent of T , we introduce an error of ~1% into our calculations, which is tolerable in many cases.

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)	ΔU (kJ)	ΔS ($\text{J}\cdot\text{K}^{-1}$)	ΔH (kJ)
a \rightarrow b	isothermal	+3.15	-3.15	0	+1.44	0
b \rightarrow c	isochoric	-3.42	0	-3.42	-2.18	-5.70
c \rightarrow d	adiabatic	0	+2.5	+2.5	0	+4.2
d \rightarrow a	isobaric	+1.5	-0.59	+0.88	+0.720	+1.5
Cycle		+1.2	-1.2	0	0	0

Note that, because of significant figure restrictions on some calculations, some of the quantities that should sum to 0 may not be exactly 0.

We know several of the entries in the table already. Since step a \rightarrow b is an isothermal expansion of an ideal gas, $\Delta U = 0$ and $q = -w$ (from the First Law). Step b \rightarrow c is isochoric ($\Delta V = 0$), so $w = 0$ and $q = \Delta U$. Since c \rightarrow d is adiabatic, $q = 0$, so $\Delta S = 0$ and $\Delta U = w$. The last step is isobaric so $q = \Delta H$, by the definition of ΔH . And finally, we know that $\Delta U = \Delta H = \Delta S = 0$ for the cycle.

It is handy to collect p and V at each point in a table along with the product pV . We can also determine T using $pV = nRT$ in the form $T = \frac{pV}{nR}$.

	p (atm)	V (L)	pV (L·atm)	T (K)
A	2.000	22.40	44.80	$2.18_{38} \times 10^3$
B	1.000	44.80	44.80	$2.18_{38} \times 10^3$
C	0.500	44.80	22.40	$1.08_{50} \times 10^3$
D	2.000	19.5	39.0	$1.90_{11} \times 10^3$

$$T = \frac{pV}{nR} = \frac{(2.000 \text{ atm})(22.40 \text{ L})}{(0.250 \text{ mole})(0.0820574 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mole}^{-1})} = 2.18_{38} \times 10^3 \text{ K}$$

$$T = \frac{pV}{nR} = \frac{(0.500 \text{ atm})(44.80 \text{ L})}{(0.250 \text{ mole})(0.0820574 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mole}^{-1})} = 1.08_{50} \times 10^3 \text{ K}$$

At point d we can use the fact that it is arrived at by an adiabatic compression from point c . For an adiabatic compression or expansion $p_i V_i^\gamma = p_f V_f^\gamma$, where $\gamma = \frac{C_{p,m}}{C_{v,m}}$.

For an ideal monatomic gas $C_{v,m} = \frac{3}{2}R$ and $C_{p,m} - C_{v,m} = R$ (and

$$C_{p,m} = R + C_{v,m} = \frac{5}{2}R), \text{ which means } \gamma = \frac{C_{p,m}}{C_{v,m}} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3}. \text{ We can rearrange}$$

$$p_i V_i^\gamma = p_f V_f^\gamma \text{ to } V_f = \left(\frac{p_i}{p_f} \right)^{1/\gamma} V_i \text{ and solve for the missing volume.}$$

$$V_f = \left(\frac{p_i}{p_f} \right)^{1/\gamma} V_i = \left(\frac{0.500 \text{ atm}}{2.000 \text{ atm}} \right)^{3/5} (44.80 \text{ L}) = 19.5 \text{ L}$$

Substituting this into the ideal gas law allows us to solve for T .

Step a → b.

For an isothermal reversible expansion

$$w = -nRT \ln\left(\frac{V_f}{V_i}\right) = -(0.250 \text{ mole})\left(8.31447 \frac{\text{J}}{\text{K} \cdot \text{mole}}\right)(2.18_{38} \times 10^3 \text{ K}) \ln\left(\frac{44.80 \text{ L}}{22.40 \text{ L}}\right)$$

$$w = -(4.53_9 \text{ kJ})(0.6931_4) = -3.15 \text{ kJ}$$

And so $q = +3.15 \text{ kJ}$.

The definition of entropy is $dS = \frac{dq_{rev}}{T}$, which we may integrate to $\Delta S = \frac{q_{rev}}{T}$.

$$\Delta S = \frac{q_{rev}}{T} = \frac{+3.14_6 \times 10^3 \text{ J}}{2.18_{38} \times 10^3 \text{ K}} = +1.44 \text{ J} \cdot \text{K}^{-1}$$

From the definition of H we may write $\Delta H = \Delta U + \Delta(pV)$, but since the product pV doesn't change we may conclude that $\Delta H = \Delta U = 0$.

Step b → c.

For an isochoric change in pressure all we need to know is how the temperature changes because ΔU for an ideal gas depends only on T . Integration of the

expression $C_V = \left(\frac{\partial U}{\partial T}\right)_V$, assuming that C_V is independent of T gives $\Delta U = C_V \Delta T$.

$$\Delta U = nC_{V,m} \Delta T = \left(\frac{3}{2}\right)(0.250 \text{ mole})\left(8.31447 \frac{\text{J}}{\text{K} \cdot \text{mole}}\right)(1.08_{50} \times 10^3 - 2.18_{38} \times 10^3 \text{ K})$$

$$\Delta U = \left(3.11_7 \frac{\text{J}}{\text{K}}\right)(-1.09_{88} \times 10^3 \text{ K}) = -3.42 \text{ kJ}$$

To calculate ΔH , we may use $\Delta H = \Delta U + \Delta(pV)$, but this time $\Delta(pV) = -22.40 \text{ L} \cdot \text{atm}$, which gives

$$\Delta H = -3.42 \text{ kJ} - 22.40 \text{ L} \cdot \text{atm} \left(\frac{0.1013325 \text{ kJ}}{1 \text{ L} \cdot \text{atm}}\right) = -3.42 - 2.269_6 \text{ kJ} = -5.70 \text{ kJ}$$

To determine ΔS use the equation $S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{nC_{V,m}}{T} dT$ because there is a temperature change at constant V . Rearranging and integrating (assuming $C_{V,m}$ is independent of T) gives $\Delta S = S(T_f) - S(T_i) = nC_{V,m} \ln\left(\frac{T_f}{T_i}\right)$. Substituting in the known values gives

$$\Delta S = nC_{V,m} \ln\left(\frac{T_f}{T_i}\right) = (0.250 \text{ mole}) \left(\frac{3}{2} (8.31447 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}) \right) \ln\left(\frac{1.08_{50} \times 10^3 \text{ K}}{2.18_{38} \times 10^3 \text{ K}}\right)$$

$$\Delta S = (3.11_7 \text{ J} \cdot \text{K}^{-1}) \ln(0.496_8) = (3.11_7 \text{ J} \cdot \text{K}^{-1}) (-0.699_4) = -2.18 \text{ J} \cdot \text{K}^{-1}$$

Step c \rightarrow *d*.

For an ideal gas the change in the internal energy depends only on T , so we can once again use the expression $\Delta U = C_V \Delta T$ (assuming C_V is independent of T).

$$\Delta U = nC_{V,m} \Delta T = \left(\frac{3}{2}\right) (0.250 \text{ mole}) \left(8.31447 \frac{\text{J}}{\text{K} \cdot \text{mole}}\right) (1.90_{11} \times 10^3 - 1.08_{50} \times 10^3 \text{ K})$$

$$\Delta U = \left(3.11_7 \frac{\text{J}}{\text{K}}\right) (8.16_1 \times 10^2 \text{ K}) = +2.5_4 \text{ kJ}$$

We can, once again, convert from ΔU to ΔH using $\Delta H = \Delta U + \Delta(pV)$, but this time $\Delta(pV) = +16.6 \text{ L} \cdot \text{atm}$.

$$\Delta H = +2.5_4 \text{ kJ} + 16.6 \text{ L} \cdot \text{atm} \left(\frac{0.101325 \text{ kJ}}{1 \text{ L} \cdot \text{atm}}\right) = +2.5_4 \text{ kJ} + 1.68_1 \text{ kJ} = +4.2 \text{ kJ}$$

Step d \rightarrow *a*

To obtain ΔU we proceed as before.

$$\Delta U = nC_{V,m} \Delta T = \left(\frac{3}{2}\right) (0.250 \text{ mole}) \left(8.31447 \frac{\text{J}}{\text{K} \cdot \text{mole}}\right) (2.18_{38} \times 10^3 - 1.90_{11} \times 10^3 \text{ K})$$

$$\Delta U = \left(3.11_7 \frac{\text{J}}{\text{K}}\right) (2.8_{27} \times 10^2 \text{ K}) = +0.88 \text{ kJ}$$

Since this step is at constant pressure we can use $C_{p,m} = \left(\frac{\partial H}{\partial T}\right)_p$ and recognize that at constant pressure $q = \Delta H$. Assuming $C_{p,m}$ is independent of T and integrating gives $\Delta H = q = nC_{p,m}\Delta T$. And therefore,

$$q = nC_{p,m}\Delta T = \left(\frac{5}{2}\right)(0.250 \text{ mole})\left(8.31447 \frac{\text{J}}{\text{K} \cdot \text{mole}}\right)(2.18_{38} \times 10^3 - 1.90_{11} \times 10^3 \text{ K})$$

$$\Delta H = q = \left(5.19_6 \frac{\text{J}}{\text{K}}\right)(2.8_{27} \times 10^2 \text{ K}) = +1.4_6 \text{ kJ}$$

Work may be obtained from the definition of work ($dw = -pdV$).

$$w = -p\Delta V = -(2.000 \text{ atm})(22.40 - 19.5 \text{ L})\left(0.101325 \frac{\text{J}}{\text{L} \cdot \text{atm}}\right) = -0.59 \text{ kJ}$$

The entropy change may be calculated from $S(T_f) = S(T_i) + \int_{T_i}^{T_f} \frac{C_p}{T} dT$ because there is a temperature change at constant p . Proceeding as before, we obtain

$$\Delta S = nC_{p,m} \ln\left(\frac{T_f}{T_i}\right) \text{ and so}$$

$$\Delta S = nC_{p,m} \ln\left(\frac{T_f}{T_i}\right) = (0.250 \text{ mole})\left(\frac{5}{2}\left(8.31447 \text{ J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}\right)\right) \ln\left(\frac{2.18_{38} \times 10^3 \text{ K}}{1.90_{11} \times 10^3 \text{ K}}\right)$$

$$\Delta S = (5.19_6 \text{ J} \cdot \text{K}^{-1}) \ln(1.14_8) = +0.720 \text{ J} \cdot \text{K}^{-1}$$

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.

The water will undergo a two-step process. In the first step it will be heated to 100.00 °C and then in the second step converted completely to steam at that temperature. The heat required to do the entire process will be the sum of the heats of each step (as required by the First Law).

Since we are only heating the water in the first step, we will use

$$q_1 = n_{\text{H}_2\text{O}} C_{p,m}(\text{H}_2\text{O}, l) \Delta T_{\text{H}_2\text{O}} \quad \text{(from integrating } C_{p,m} = \left(\frac{\partial H}{\partial T} \right)_p \text{ assuming that } C_{p,m} \text{ is}$$

independent of T and remembering that $q = \Delta H$ at constant p). In this equation $n_{\text{H}_2\text{O}}$ equals the moles of water, $C_{p,m}(\text{H}_2\text{O}, l)$ is the molar constant pressure heat capacity of water and $\Delta T_{\text{H}_2\text{O}}$ in the temperature change for the water.

For the vaporization step $q_2 = n_{\text{H}_2\text{O}} \Delta_{\text{vap}} H(\text{H}_2\text{O}, l)$, where $n_{\text{H}_2\text{O}}$ is the moles of water vaporized and $\Delta_{\text{vap}} H(\text{H}_2\text{O}, l)$ the enthalpy of vaporization of water.

The heat given off during the burning of methane will be $q_3 = n_{\text{CH}_4} \Delta_{\text{comb}} H(\text{CH}_4, \text{g})$, where n_{CH_4} is the moles of CH_4 burned and $\Delta_{\text{comb}} H(\text{CH}_4, \text{g})$ is the enthalpy of combustion for CH_4 .

The First Law requires that $-q_3 = q_1 + q_2$. So, we can write

$$-n_{\text{CH}_4} \Delta_{\text{comb}} H(\text{CH}_4, \text{g}) = n_{\text{H}_2\text{O}} C_{p,m}(\text{H}_2\text{O}, l) \Delta T_{\text{H}_2\text{O}} + n_{\text{H}_2\text{O}} \Delta_{\text{vap}} H(\text{H}_2\text{O}, l)$$

$$n_{\text{CH}_4} = - \frac{n_{\text{H}_2\text{O}} (C_{p,m}(\text{H}_2\text{O}, l) \Delta T_{\text{H}_2\text{O}} + \Delta_{\text{vap}} H(\text{H}_2\text{O}, l))}{\Delta_{\text{comb}} H(\text{CH}_4, \text{g})}$$

Substituting the known values gives

$$n_{\text{CH}_4} = - \frac{(1.000 \times 10^3 \text{ g}) \left(\frac{1 \text{ mole}}{18.01528 \text{ g}} \right) \left(\left(75.291 \frac{\text{J}}{\text{K} \cdot \text{mole}} \right) (+100.00 \text{ K}) + \left(40.7 \frac{\text{kJ}}{\text{mole}} \right) \right)}{-890. \frac{\text{kJ}}{\text{mole}}}$$

$$n_{\text{CH}_4} = \frac{(55.508_4 \text{ mole}) \left(\left(7.5291 \frac{\text{kJ}}{\text{mole}} \right) + \left(40.7 \frac{\text{kJ}}{\text{mole}} \right) \right)}{890. \frac{\text{kJ}}{\text{mole}}}$$

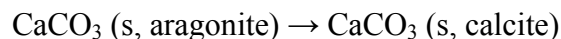
$$n_{\text{CH}_4} = \frac{(55.508_4 \text{ mole}) \left(48.2_2 \frac{\text{kJ}}{\text{mole}} \right)}{890. \frac{\text{kJ}}{\text{mole}}} = \frac{2.67_7 \times 10^3 \text{ kJ}}{890. \frac{\text{kJ}}{\text{mole}}}$$

$$n_{\text{CH}_4} = 3.01 \text{ mole}$$

So, one must burn 3.01 mole (48.3 g) of CH₄ to heat liquid water at its melting point to its boiling point and convert it completely to steam at that temperature.

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 CaCO₃ which exists in two solid forms called calcite and aragonite. Using data from your text, and making any necessary assumptions, determine which form of CaCO₃ is the more stable under standard conditions.

To determine which form is more stable we must set up a process that takes one to the other (i. e., a chemical reaction).



Now calculate ΔG^0 for this reaction.

$$\Delta G^0 = (1 \text{ mole}) \Delta_f G^0 (\text{s, calcite}) - (1 \text{ mole}) \Delta_f G^0 (\text{s, aragonite})$$

$$\Delta G^0 = (1 \text{ mole}) (-1128.8 \text{ kJ/mole}) - (1 \text{ mole}) (-1127.8 \text{ kJ/mole})$$

$$\Delta G^0 = -1128.8 \text{ kJ} + 1127.8 \text{ kJ} = -1.0 \text{ kJ}$$

Since this process is spontaneous in the direction written (i. e., takes place without input of work), we may conclude that calcite is the more stable form of CaCO₃ (s).

b. (6 Points) Is it possible by changing temperature alone, to change which form of 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.

When a process changes from being spontaneous in one direction to being spontaneous in the other direction ΔG must equal 0 (when a function changes sign it must go through 0). At constant pressure, and assuming that ΔH and ΔS are independent of temperature, we may write $\Delta G = \Delta H - T\Delta S$. For the conversion of aragonite to calcite $\Delta H = +0.2$ kJ and $\Delta S = +4.2$ kJ, as shown below.

$$\Delta H = (1 \text{ mole}) \Delta_f H^0 (\text{CaCO}_3, \text{ calcite}) - (1 \text{ mole}) \Delta_f H^0 (\text{CaCO}_3, \text{ aragonite})$$

$$\Delta H = (1 \text{ mole}) (-1206.9 \text{ kJ/mole}) - (1 \text{ mole}) (-1207.1 \text{ kJ/mole})$$

$$\Delta H = (-1206.9 \text{ kJ}) - (-1207.1 \text{ kJ}) = +0.2 \text{ kJ}$$

$$\Delta S = (1 \text{ mole}) S^0 (\text{CaCO}_3, \text{ calcite}) - (1 \text{ mole}) S^0 (\text{CaCO}_3, \text{ aragonite})$$

$$\Delta S = (1 \text{ mole}) (92.9 \text{ J/K}\cdot\text{mole}) - (1 \text{ mole}) (88.7 \text{ J/K}\cdot\text{mole})$$

$$\Delta S = (92.9 \text{ J/K}) - (88.7 \text{ J/K}) = +4.2 \text{ J/K}$$

If aragonite were to become more stable, ΔG for the process that we wrote in part a would need to change sign and there would exist a temperature where $\Delta G = 0$ and therefore $\Delta H = T\Delta S$ and $T = \frac{\Delta H}{\Delta S}$. Since ΔH and ΔS are both positive numbers and T must also be positive, then there must exist a temperature at which aragonite would be the more thermodynamically stable form of CaCO_3 . This may be calculated, assuming that ΔH and ΔS are independent of temperature (which, in this case, probably isn't valid).

$$T = \frac{\Delta H}{\Delta S} = \frac{+0.2 \times 10^3 \text{ J}}{+4.2 \text{ J/K}} = 47.6 \text{ K}$$