

Answer each question in the space provided. Answer questions so the grader can READILY understand your work. You may use **only** the "Student Handbook," a calculator, and a straight edge.

1. (10 points) Using data from your Handbook, calculate the molar enthalpy change in heating solid lead (Pb) from 25°C to its melting point of 327.4°C, maintaining the pressure at 1 bar.

This is a straightforward question. One integrates the constant-pressure heat capacity of the material between the two temperatures to find the change. From Table 2.2 of the Handbook, the heat capacity of solid lead is:

$$C_{pm}(T) = \left[c_1 + c_2 T + \frac{c_4}{T^2} \right] J K^{-1} mol^{-1}.$$

Integration of this form gives:

$$\begin{aligned} \Delta H_m &= \int_{T_1}^{T_2} \left[c_1 + c_2 T + \frac{c_4}{T^2} \right] dT \\ &= c_1(T_2 - T_1) + \frac{c_2}{2}(T_2^2 - T_1^2) - c_4 \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \end{aligned}$$

Substitution of the appropriate values of the coefficients for lead gives the result sought:

$$\Delta H_m = \left\{ 22.13(600.55 - 298.15) + \frac{11.72 \times 10^{-3}}{2}(600.55^2 - 298.15^2) - 0.96 \times 10^5 \left(\frac{1}{600.55} - \frac{1}{298.15} \right) \right\} J mol^{-1}$$

Evaluation of these terms gives:

$$\Delta H_m = \{6692 + 1593 + 162\} J mol^{-1} = 8447 J mol^{-1}$$

**DO NOT WRITE
IN THIS SPACE**

1 _____ /10

2 _____ /15

3 _____ /15

4 _____ /15

5 _____ /15

6 _____ /10

7 _____ /10

8 _____ /10

SUBTOTAL

/100

EXTRA CREDIT

9 _____ /5

TOTAL PTS

2. (15 points) Below are the steps in a Carnot cycle. Considering the working fluid to be an **ideal gas**, indicate which quantities in each step are zero by putting a **0** in the box. For quantities that are not zero, put **NZ** in the box. (Every box should have some answer in it.)

Quantity →	ΔU	q	w
(1) Isothermal absorption of heat from the reservoir at T_u	0	NZ	NZ
(2) Adiabatic expansion until the temperature is T_l	NZ	0	NZ
(3) Isothermal release of heat at T_l	0	NZ	NZ
(4) Adiabatic compression to raise the temperature to T_u	NZ	0	NZ

In each adiabatic step, the heat transferred must be zero, by definition.

In isothermal steps, the change in internal energy must be zero because the fluid is an ideal gas. In steps in which the temperature changes, there must be a nonzero change in the internal energy.

Because the sum of work and heat transferred in a step must equal the change in internal energy, the work in each process must be nonzero.

3. (15 points) The vapor pressure of CH_3Cl between -47°C and -10°C can be represented by the equation

$$\ln\left(\frac{P}{\text{pascal}}\right) = -\frac{2646\text{ K}}{T} + 22.155.$$

(a) What is the standard molar enthalpy of vaporization of CH_3Cl ?

By the definition of equation (4.20) in your Handbook, $\frac{d \ln P}{d(1/T)} = -\frac{\Delta_v H}{R}$. Taking the derivative of the right-hand side of the above equation gives:

$$-\frac{\Delta_v H}{R} = -2646\text{ K}.$$

Using the proper value of the gas constant, one may assess the molar enthalpy of vaporization:

$$\begin{aligned}\Delta_v H &= 2646\text{ K} \times 8.31451\text{ J K}^{-1}\text{ mol}^{-1} \\ &= 22.00\text{ kJ mol}^{-1}\end{aligned}$$

(b) What is the normal boiling point of CH_3Cl ?

The normal boiling point is the temperature at which the vapor pressure is precisely 1 atmosphere (= 101325 Pa). Hence, substitution into the equation above gives:

$$\ln(101325) = -\frac{2646\text{ K}}{T_b} + 22.155$$

Rearranging and solving for the boiling temperature gives:

$$T_b = 248.9\text{ K}$$

(c) What is the standard molar entropy of vaporization of CH_3Cl ?

The standard entropy of vaporization is given by

$$\Delta_v S = \frac{\Delta_v H}{T_b} = \frac{22.00\text{ kJ mol}^{-1}}{248.9\text{ K}} = 88.39\text{ J K}^{-1}\text{ mol}^{-1}$$

4. (10 points) Assuming that, at 298.15 K, oxygen may be considered to be an ideal gas, calculate the third-law entropy of oxygen at 5 bar and 298.15 K.

For an ideal gas, one may use equation (3.32) in the Handbook, with the last term equal to zero, or one may derive the following equation by integration of one of the working equations on Table 3.1:

$$\Delta S_m = - \int_{P^\theta}^P \frac{R}{P} dP = -R \ln\left(\frac{P}{P^\theta}\right).$$

Hence, the entropy at a particular pressure is:

$$S_m(T, P) = S^\theta(T) - R \ln\left(\frac{P}{P^\theta}\right).$$

The standard entropy at 298.15 K is found in Table 3.2 of your Handbook. Thus, one may determine the entropy at 5 bar:

$$\begin{aligned} S_m(298.15 \text{ K}, 5 \text{ bar}) &= S^\theta(298.15 \text{ K}) - 8.31451 \text{ J K}^{-1} \text{ mol}^{-1} \ln\left(\frac{5 \text{ bar}}{1 \text{ bar}}\right) \\ &= 205.138 \text{ J K}^{-1} \text{ mol}^{-1} - 13.381 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 191.757 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

5. (15 points) Identify these derivatives in terms of measurable quantities such as P, T, V, l and f (in an elastic system), A and γ (in a surface system) and their derivatives with respect to each other. [NOTE: In this question, A_H is used to represent the Helmholtz energy, to distinguish it from surface area, A.]

$$\left(\frac{\partial G}{\partial T}\right)_P = -S, \text{ from the equation for } dG \text{ and the definition of a partial derivative}$$

$$\left(\frac{\partial A_H}{\partial V}\right)_T = -P, \text{ from the equation for } dA_H \text{ and the definition of a partial derivative}$$

$$\left(\frac{\partial G}{\partial V}\right)_T = V\left(\frac{\partial P}{\partial V}\right)_T, \text{ by transforming the equation in Table 3.1 for } dG \text{ to eliminate terms in } dP.$$

$$\left(\frac{\partial U}{\partial A}\right)_{S,V} = \gamma, \text{ from the equation for } dU \text{ and the definition of a partial derivative}$$

$$\left(\frac{\partial S}{\partial l}\right)_{T,V} = -\left(\frac{\partial f}{\partial T}\right)_{l,V} \quad \text{See below.}$$

The last derivative is found by some transformations and Maxwell identities. Consider the first law for an elastic system.

$$dU = TdS - PdV + fdl.$$

Now, create the Helmholtz energy:

$$dA = dU - d(TS) = -SdT - PdV + fdl$$

By the Maxwell identity:

$$\left(\frac{\partial}{\partial l}\left(\frac{\partial A}{\partial T}\right)_{l,V}\right)_{T,V} = \left(\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial l}\right)_{T,V}\right)_{l,V}.$$

Now, identify the partial derivatives.

$$\left(\frac{\partial}{\partial l}(-S)\right)_{T,V} = \left(\frac{\partial}{\partial T}(f)\right)_{l,V}$$

Rearrangement gives the result above.

6. (10 points) Assume that air is exactly 79 mol % nitrogen and 21 mol% oxygen. Calculate the entropy of mixing to produce a mol of air at a pressure of 1 bar. [HINT: You may consider the two gases to be ideal under these conditions.]

This is a straightforward application of equation (3.15) in your Handbook.

$$\Delta_{mix}S = -R(X_A \ln X_A + X_B \ln X_B).$$

Since there are only two components, one substitutes the mole fractions into this equation to give:

$$\begin{aligned}\Delta_{mix}S &= -8.31451 J K^{-1} mol^{-1} (0.79 \ln 0.79 + 0.21 \ln 0.21) \\ &= 4.27 J K^{-1} mol^{-1}\end{aligned}$$

7. (10 points) When the reaction $Fe_2N(s) + \frac{3}{2}H_2(g) \leftrightarrow 2Fe(s) + NH_3(g)$ is equilibrated at a total pressure of 1 bar and 700 K, $P_{NH_3} / P_{H_2} = 2.165$. (a) Calculate K_p for this reaction.

K_p is found by noting that one can determine the pressures of ammonia and hydrogen independently, since the ratio is 2.165 and the sum of the two pressures must be 1 bar.

$$P_{H_2} = \frac{1}{3.165} \text{bar} = 0.3160 \text{bar}$$

By difference, the remainder must be ammonia:

$$P_{NH_3} = 1 \text{bar} - 0.3160 \text{bar} = 0.6840 \text{bar}$$

With these pressures, one can calculate K_p :

$$K_p = \frac{0.6840 \text{bar}}{(0.3160 \text{bar})^{3/2}} = 3.851 \text{bar}^{-1/2}$$

(b) Assuming that both gases can be treated as ideal under the conditions of the reaction, what is the standard Gibbs energy of reaction at 700 K?

Under ideal conditions, with pressures reported in bars, $K_p = K_a \text{bar}^{-1/2}$. So, one may use the value calculated in part (a) to determine the standard Gibbs energy at 700 K using this equation.

$$\Delta G^\theta(T) = -RT \ln K_a$$

Substitution gives

$$\begin{aligned} \Delta G^\theta(700 \text{K}) &= -8.31451 \text{J K}^{-1} \text{mol}^{-1} (700 \text{K}) \ln 3.851 \\ &= -7.848 \text{kJ mol}^{-1} \end{aligned}$$

8. (10 points) For each statement in column A, give the letter of the best match from column B. There is only one best match.

A	B
In a spontaneous process under constant-T and constant-P conditions, the change in Gibbs free energy is always (i) ≤ 0 .	a) $dS = \frac{dq_{rev}}{T}$
At a first-order phase transition, the (f) enthalpy is discontinuous.	b) = 0
The third law of thermodynamics states that (d) the entropy of a perfect crystalline solid is a constant, defined to be 0, at 0K.	c) Internal energy
The Boltzmann factor in the Maxwell-Boltzmann distribution function is (g) $\frac{e^{-\beta u_k}}{\sum_j e^{-\beta u_j}}$	d) The entropy of a perfect crystalline solid is a constant, defined to be 0, at 0 K.
In a system such as a rubber band the differential change in the Helmholtz energy at constant temperature and volume is given by (m) $dA = fdl$	e) ≥ 0
	f) Enthalpy
	g) $\frac{e^{-\beta u_k}}{\sum_j e^{-\beta u_j}}$
	h) z
	i) ≤ 0
	k) $\frac{A}{n}$, where n is the number of moles
	l) Heat capacity
	m) $dA = fdl$
	n) Always equal to 1.

9. (5 points, extra credit) (a) Using a Maxwell relation, determine $\left(\frac{\partial C_{V_m}}{\partial V_m}\right)_T$. Show a complete and accurate derivation.

Let us start with the definition of the heat capacity at constant volume: $C_{V_m} = \left(\frac{\partial U_m}{\partial T}\right)_V$. According to the problem, one is to find the derivative of this quantity with respect to volume. That is, the focus should be:

$$\left(\frac{\partial C_{V_m}}{\partial V_m}\right)_T = \left(\frac{\partial}{\partial V_m}\left(\frac{\partial U_m}{\partial T}\right)_{V_m}\right)_T.$$

By the Maxwell relation, one may show that the order of integration is not important, so that

$$\left(\frac{\partial C_{V_m}}{\partial V_m}\right)_T = \left(\frac{\partial}{\partial V_m}\left(\frac{\partial U_m}{\partial T}\right)_{V_m}\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U_m}{\partial V_m}\right)_T\right)_{V_m}.$$

By the first working equation on Table 3.1, one can identify that

$$\left(\frac{\partial U_m}{\partial V_m}\right)_T = \left(T\left(\frac{\partial P}{\partial T}\right)_{V_m} - P\right)_{V_m}.$$

By substitution, one has

$$\left(\frac{\partial C_{V_m}}{\partial V_m}\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U_m}{\partial V_m}\right)_T\right)_{V_m} = \left(\frac{\partial}{\partial T}\left(T\left(\frac{\partial P}{\partial T}\right)_{V_m} - P\right)\right)_{V_m}$$

Distribution of the derivative over the function in parentheses gives

$$\left(\frac{\partial C_{V_m}}{\partial V_m}\right)_T = \left(\frac{\partial P}{\partial T}\right)_{V_m} + T\left(\frac{\partial^2 P}{\partial T^2}\right)_{V_m} - \left(\frac{\partial P}{\partial T}\right)_{V_m} = T\left(\frac{\partial^2 P}{\partial T^2}\right)_{V_m}$$

(b) Calculate $\left(\frac{\partial C_{V_m}}{\partial V_m}\right)_T$ for a van der Waals gas.

According to the derivation of part (a), one must determine the second derivative of pressure with respect to temperature.

$$\left(\frac{\partial P}{\partial T}\right)_{V_m} = \left(\frac{\partial}{\partial T}\left[\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right]\right)_{V_m} = \frac{R}{V_m - b}.$$

The second derivative is found easily from this:

$$\left(\frac{\partial^2 P}{\partial T^2}\right)_{V_m} = \left(\frac{\partial}{\partial T}\left[\frac{R}{V_m - b}\right]\right)_{V_m} = 0.$$

Since this is zero, the derivative of the heat capacity must also be zero.

$$\left(\frac{\partial C_{V_m}}{\partial V_m}\right)_T = 0$$

For a van der Waals gas, the heat capacity at constant volume does not depend on the volume, an important result.