Problem Set #1

This problem set deals with the general introductory material presented in Chapter 1. The purpose of this chapter is to familiarize you with some key concepts of Thermodynamics and Statistical Mechanics: These are the concepts of entropy $S$ and thermodynamic temperature $T$, the First, Second and Third Laws, the concepts of state functions and state variables, and finally the so called fundamental equations of Thermodynamics, as embodied in the explicit expressions

$$S = S(E, V, N)$$ for the entropy $S$
$$E = E(S, V, N)$$ for the energy $E$
$$F = F(T, V, N)$$ for the Helmholtz free energy $H$
$$G = G(T, p, N)$$ for the Gibbs free energy $G$

Depending on the degree of your previous exposure to these matters, this first problem assignment may appear easy or very hard. In any case, your mastery of this material will pay off handsomely later.

Problem 1: The Information Contents of the Equation of State

The equation of state expresses a relation between pressure $p$, volume $V$, and temperature $T$ in a homogenous, one-phase system. We consider here the case of a gas (of a single chemical species, or else a non-reactive gas mixture). Assuming one mole of this material, we have

for an ideal gas:  
$$pV = RT$$

(1)

for a Van der Waals gas:  
$$p + \frac{a}{V^2}(V - b) = RT$$

(2)

where $R$ is the universal gas constant, and $a$, $b$ are the van der Waals parameters, assumed to be constants. As we go along, you will establish the physical interpretation of these parameters. It follows from the equations of state that if two of the three variables $T$, $V$, $p$ are given, the value of the third is determined.

The goal in this problem is to obtain expressions for the energy $E$ of the system, in the form of a statement such as

$$E(T, V) = \text{some specific function of } T \text{ and } V$$
1A: The Ideal Gas Case.

In this case, it is known experimentally that the energy is a function of the temperature $T$ only: $E = E(T)$, so that $(\partial E/\partial V)_T = 0$. You will show that this information is in fact already contained in the equation of state. To demonstrate this, one needs the basic expression for the energy change in terms of heat and work: (Notes section 1.1)

$$dE = dQ - dW = T\,dS - p\,dV$$ (3)

This is the differential form of an expression $E = E(S, V)$ for the energy. Since the problem is to find the dependence of $E$ on $T$ and $V$, we must first view the entropy $S$ an a function of $T$ and $V$, giving:

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$ (4)

**Question 1**: Show that the physical interpretation of the quantity $T\left(\frac{\partial S}{\partial T}\right)_V$ is the molar heat capacity at constant volume, $C_V$.

Inserting (4) into equation (3), you find

$$dE = T\left(\frac{\partial S}{\partial T}\right)_V dT + \left\{ T\left(\frac{\partial S}{\partial V}\right)_T - p \right\} dV$$ (5)

**Question 2**: To this you may now apply the Maxwell relation

$$\frac{\partial}{\partial V} \left(\frac{\partial E}{\partial T}\right)_V = \frac{\partial}{\partial T} \left(\frac{\partial E}{\partial V}\right)_T$$ (6)

Show that this gives you the relation:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$$ (7)

**Question 3**: This leaves you with the expression

$$dE = C_v dT + \left\{ T\left(\frac{\partial p}{\partial T}\right)_V - p \right\} dV$$ (8)

Show that by the ideal gas equation of state, this reduces to:

$$dE(T, V) = C_v dT$$ (9)

**Question 4**: Now one could assume that the heat capacity $C_V$ might still depend both on $T$ and $V$. Equation (9) however tells you that $C_v$ can depend on $T$ only. Show why this is so. So finally one has, for the ideal gas, the result that

$$dE = C_v(T) dT$$
1B: The Van der Waals Gas.
In this part, you will carry out the corresponding steps, with the goal of finding an explicit expression for the differential form \( dE(T,V) \). It is clear that equations (3) to (8) remain valid, since no special property of the system was invoked. In eq.(8) however, the term:

\[
T \left( \frac{\partial p}{\partial T} \right)_V - p
\]

will not be zero for the Van der Waals gas.

**Question 5**: Show that in this case, one has

\[
\left( \frac{\partial p}{\partial T} \right)_V = \frac{R}{V - b}
\]

**Question 6**: Show that the expression for the energy differential \( dE(T,V) \) will now be:

\[
dE(T,V) = C_V dT + \frac{a}{V^2} dV
\]

**Question 7**: Show that if the parameter \( a \) is truly a constant, and hence independent of \( T \), the heat capacity \( C_V \) remains independent of \( V \), and will be a function of \( T \) only.

**Question 8**: Assume that the Van der Waals equation is valid only in the domain \( T \geq T_0, V \geq V_0 \). Let \( E(T_0,V_0) = E_0 \). Find an expression for \( E(T,V) - E_0 \), for \( (T,V) > (T_0,V_0) \).

**Question 9**: Using eq. (2) as well as the result obtained in Question 8, give a physical interpretation of the parameters \( a \) and \( b \).

**Problem 2: Properties of the Entropy (S)**

In section (1.2) of the notes, this quantity is introduced from the perspective of statistical mechanics. Notice that from this perspective, the entropy is naturally viewed as a pure number (called \( S^* \) in the notes); historically, as introduced by Clausius in 1856 in the context of articulating the second law, the entropy has the dimension of \((\text{energy/}K)\), and is called \( S \). One has \( S = kS^* \), \( k \) being the Boltzmann constant: \( k = R/N_0 = 1.38 \times 10^{-16} \, \text{erg/K} \).

**Question 1**: In eq. (1.2-15) you are given the expression \( S(E,V,N) \) for the entropy of a monoatomic ideal gas (for a more interesting gas like oxygen, there are additional terms, revealed in section 1.5.5b). Convert this expression into a function of \((T,V,N)\) using the relation

\[
E = \frac{3}{2} NkT
\]

**Question 2**: Using the ideal gas law, \( pV = NkT \), you can also write \( S \) as a function of \( T \), \( p \), and \( N \). This will have the form:

\[
S(T, p, N) = N \left[ \ln \left( \frac{P_F}{P} \right) + \frac{5}{2} \right]
\]
Obtain an expression for the "Fermi pressure" \( p_F \), and estimate its magnitude, (in multiples of atmospheric pressure) for a gas like oxygen and body temperature \( T = 310 \text{ K} \). To do this, you need the values

\[
\begin{align*}
  h &= 6.65 \times 10^{-27} \text{ erg sec}, \quad m = 5 \times 10^{-23} \text{ grams} \\
  1 \text{ erg} &= 1 \text{ gm cm}^2/\text{sec}^2, \quad 1 \text{ atm} = 10^6 \text{ erg/cm}^3
\end{align*}
\]

You will see that this pressure is enormously large; its value will play a role when you will study the binding of oxygen to Hemoglobin.

**Problem 3: The Entropy of Mixing**

In this problem you will bridge a conceptual gap engendered by the difference between the thermodynamic (Clausius) and the statistical mechanical definitions of the entropy. In Thermodynamics, the entropy difference \( \Delta S \) between two equilibrium states (1) and (2) is given by

\[
S(2) - S(1) = \int_1^2 \frac{dQ_{\text{rev}}}{T} \tag{3}
\]

We now apply this to the entropy of mixing, which is the increase \( \Delta S \) in entropy occurring when two (chemically) distinct substances, previously kept in separate volumes \( V_a \) and \( V_b \), are allowed to mix, jointly occupying a common volume \( V = V_a + V_b \).

For simplicity, let the materials be ideal gases, initially kept at a common pressure \( p \) and common temperature \( T \). The initial entropy is then

\[
S_m = N_a k \left\{ \frac{5}{2} \ln \frac{V_a}{N_a V_{F_a}} + \frac{5}{2} \right\} + N_b k \left\{ \frac{5}{2} \ln \frac{V_b}{N_b V_{F_b}} + \frac{5}{2} \right\} \tag{4}
\]

where \( V_{F_a} \) and \( V_{F_b} \) indicate Fermi volumes for the gases a and b.

Assume that \( T_a = T_b = T \), and that \( V_a/N_a = V_b/N_b \), so that also \( p_a = p_b \).

**Question 1**: From a Statistical Mechanical perspective, removing the wall separating the two compartments allows the atoms of each gas now to occupy the entire volume \( V = V_a + V_b \). The entropy will then have a final value:

\[
S_{\text{fin}} = N_a k \left\{ \frac{5}{2} \ln \frac{V}{N_a V_{F_a}} + \frac{5}{2} \right\} + N_b k \left\{ \frac{5}{2} \ln \frac{V}{N_b V_{F_b}} + \frac{5}{2} \right\} = S_m + \Delta S_{\text{mix}} \tag{5}
\]

Show that this entropy of mixing, \( \Delta S_{\text{mix}} \), may be written as

\[
\Delta S_{\text{mix}} = -Nk \left\{ x_a \ln x_a + x_b \ln x_b \right\} \text{ where } x_{a,b} = \frac{N_{a,b}}{N_a + N_b} \tag{6}
\]

It is quite a different proposition to obtain an expression for \( \Delta S_{\text{mix}} \) from a purely thermodynamic perspective, based on eq. (3) above. The key point is now to carry out this mixing in a reversible way. This is done by means of two semi-permeable pistons, one piston being permeable to the molecules of gas a, the other to the molecules of gas b. Initially both pistons are adjacent and form the divider defining volumes \( V_a \) and \( V_b \).
Now the two pistons are allowed to be slowly pushed out by the two gases, against an external force just matching the gas pressure on the pistons. In that process the system does work, $\Delta W'$ which we count as a negative contribution, $\Delta W = -\Delta W'$, to the system's energy. During this process, the temperature $T$ is kept constant, by allowing heat inflow from a "heat bath" surrounding the system.

**Question 2**: Show that $\Delta W'$ is given by

$$\Delta W' = N_a kT \int_{V_a}^{V_f} \frac{dV}{V} + N_b kT \int_{V_b}^{V_f} \frac{dV}{V} \quad (7)$$

**Question 3**: Evaluate the integrals, so as to get a closed expression for $\Delta W'$.

**Question 4**: Since we deal with an ideal gas, the energy $E$ of the joint system depends only on the temperature $T$, which we kept constant, by allowing heat to flow into the system during the mixing process. So one has

$$\Delta E = E_f - E_m = \Delta Q + \Delta W = \Delta Q - \Delta W' = 0 \quad (8)$$

This gives you the value of $\Delta Q_{rev}$, the heat input into the system during this reversible mixing process. Show that indeed one has

$$\Delta S = S_f - S_m = \frac{\Delta Q_{rev}}{T} = \frac{\Delta W'}{T} = 0 \quad (9)$$

**Problem 4: The Chemical Potential**

This concept plays a crucial role in formulating reaction and phase equilibria. In each situation, one deals with a multicomponent system, and the possibility of the transfer of particles, i.e. reshuffling particle numbers. All this is elaborated in section 1.5 of the notes for Chapter 1. In this problem, you will look at a few simple situations.

**Case A: Phase equilibria**

Examples are equilibria between a liquid and its vapor, or a liquid and its solid form, etc. In considering such equilibria, one generally deals with a so-called open system, where pressure and temperature are externally imposed; the proper fundamental relation to invoke is then the Gibbs Free Energy

$$G(T,p,N_1,N_2) = G_1(T,p,N_1) + G_2(T,p,N_2) \quad (1)$$

$N_1$ and $N_2$ referring to the number of molecules in phases 1 and 2, respectively.

The equilibrium between phases 1 and 2 is then characterized by the condition that the free energy $G$ be stationary under a transfer of molecules from one phase to the other:

$$G(T,p,N_1+\delta N,N_2-\delta N) = G(T,p,N_1,N_2) \quad (2)$$

**Question 1**: Show that this leads to the equilibrium condition $\mu_1 = \mu_2$, where

$$\mu_1 = \left( \frac{\partial G}{\partial N_1} \right)_{T,p,N_2} \quad \text{and} \quad \mu_2 = \left( \frac{\partial G}{\partial N_2} \right)_{T,p,N_1} \quad (3)$$
Question 2: The coexistence of two phases defines a curve in T-p space. Obtain a differential equation for this coexistence curve:

\[ \frac{dp}{dT} = \text{rhs}, \]

by expressing the rhs by means of suitable partial derivatives of \( \mu_1 \) and \( \mu_2 \).

Question 3: How many phases of a single chemical substance may coexist?

Case B: The Simplest Reaction Equilibrium
This occurs when a substance (such as a protein, e.g. Hemoglobin) exists in two distinct 'tautomeric' forms, arising from two different subunit geometries. What is the relative abundance of the two forms, here called "a" and "b"?

Here the crucial point is that the Gibbs free energy \( G(T,p,N_a,N_b) \) is fundamentally given by \( G = E + pV - TS \), and therefore contains a term \(-T \Delta S_{\text{mix}}\), which depends jointly on \( N_a \) and \( N_b \). So \( G \) will have the form (with \( x_{a,b} = N_{a,b}/(N_a+N_b) \))

\[
G(T,p,N_a,N_b) = G_a(T,p,N_a) + G_b(T,p,N_b) + N_a kT \ln x_a + N_b kT \ln x_b \tag{4}
\]

Question 4: What are the expressions for the chemical potentials \( \mu_a \) and \( \mu_b \)? You may use the notation:

\[ \mu_a^0 = \frac{\partial G_a}{\partial N_a} \] and take this as a given; (same for "b").

Question 5: Show that the expression for \( G(T,p,N_a,N_b) \) may be written in the form

\[ G = \mu_a N_a + \mu_b N_b \]

Question 6: Make use of the equilibrium condition to obtain expressions for \( x_a \) and \( x_b = (1-x_a) \) in terms of \( \mu_a^0 \) and \( \mu_b^0 \).