Exam 1

Physical Chemistry
Fall 2005
100 pts

Please verify that your name is
Fall 2005
is the back of the last page

Please do your own work, relax and take your time.
Remember, this is only a test.

The following information may be useful:

\[ 1 \text{ m}^3 = 1000 \text{ L} = 1000 \text{ dm}^3 \]

\[ N! = \left( \frac{N}{e} \right)^N \]

\[ \int \frac{dx}{x} = \ln x \]

\[ \int dx = x \]

Note that you should choose to do EITHER problem 1 or problem 2, not both!
Also, anytime I ask you to explain, be very clear and complete. These questions will be graded carefully.

1) For each of the sections below, assume you have some number of fair six-sided dice.

(a) (4 pts) Make a sketch of a plot of the probability distribution for rolling one die. (i.e. put probability on the y-axis and the numbers 1-6 on the x-axis, then plot your distribution.) Note that I expect you to be quantitative about your values for both the x- and y-axes.
(b) (8 pts) Now, let’s say you have three dice. Make a new plot of the probability distribution for the sum of the values of the three dice. (i.e. if you rolled a 3 and a 5 and a 5 your sum would be 13.) Again, be quantitative regarding both the x- and y- axes. (I don’t expect you to get the shape exactly right, but the max and min values of the distribution should be correct.)

(c) (6 pts) Finally, let’s say you have 100 dice. Make another plot of the probability distribution for the sum of the values of 100 dice. Still be quantitative about the x-axis, but now provide just order-of-magnitude values for the y-axis. DO NOT TRY TO CALCULATE ANYTHING DIFFICULT!
2) (18 pts) Imagine two sets of lattices and particles. The first has $A$ lattice sites with $b$ particles ($b < A$). The second has $Z$ lattice sites with $y$ particles ($y < Z$). **Prove that entropy is extensive.** You may assume that $A$, $b$, $Z$ and $y$ are all economically large. Note that if you should ever want to calculate the entropy of the unified $AZby$ system, it still has a partition separating the two halves.
3) The Carnot cycle represents the most efficient (heat) engine that can operate between two heat baths. Let’s say our two heat baths are at $T_1$ and $T_3$ (you’ll see why in a second). We are going to conduct a four-step thermodynamic cycle, ending up where we started. Note that all four steps are performed quasi-statically A.K.A. reversibly.

- Process 1) We’ll start our engine at point A where it is in thermal contact with the heat bath that is at $T_1$. Now we’ll go through an isothermal expansion to some new volume, $V_B$. The engine is now at point B. (i.e. $V_B > V_A$ and $T_A = T_B = T_1$).
- Process 2) Now we disconnect the engine from the heat bath and expand adiabatically until the engine reaches $T_3$. This is point C. ($V_C > V_B$)
- Process 3) With the system now in thermal contact with the $T_3$ heat bath, our engine undergoes an isothermal compression to point D. ($V_D < V_C$)
- Process 4) Once again, we disconnect from the heat bath. This time we compress adiabatically until we return to point A. ($V_A < V_D$)

(a) (5 pts) Make a P-V plot of the Carnot cycle. Don’t worry about getting all of the shapes exactly right. This is really just to get all of the above information organized into something visual for you. Make the plot large because you’ll be adding more stuff to it as we go along. Label points A, B, C, D, processes 1, 2, 3, 4 and which steps are isothermal and which are adiabatic.

Now let’s get quantitative. Let $T_1 = 500$ K and $T_3 = 300$ K. Let’s also say we’ve got 1 mole of some ideal monatomic gas ($C_p = \frac{5}{2} R$) as our working substance in the engine (don’t say I’m not nice). And, let $V_A = 5L$ and $V_B = 10$ L.
(b) (39 pts) Using the values given above, determine $q$, $w$, $\Delta S$, $\Delta U$, and $\Delta H$ for each of the four processes as well as for the total cycle. (You have 2½ pages of paper for this.)
There is an old adage about needing to remember history so that one doesn’t repeat it. In that spirit I remind you of the following political cartoon from the first term of the second Bush presidency:

still #3 part b)
still #3 part b)
(c) (2 pts) Indicate the total work done for the complete Carnot cycle on your sketch in part (a).

4) One simple model for describing gas behavior is the hard-sphere model.

\[ p(V - nb) = nRT \]

(a) (12 pts) Given that \( dU = TdS - pdV \), derive the dependence of internal energy on volume at constant temperature for a hard-sphere gas. You may take any fundamental thermodynamic equation as a given. Anything else that is needed to complete this problem must be derived to receive full credit.
(b) (5 pts) Based on the hard-sphere energy, explain why your answer to part (a) looks as it does.

(c) (2 pts) Which gas is most accurately described by the hard-sphere model?
   a. HCl
   b. N₂
   c. CO₂
   d. H₂O

(d) (5 pts) Explain your answer to part c.
5) Suppose we have a bunch of particles, let’s call them Goetzes. We know that Goetzes can only exist at certain energies:

\[ E_j = 0, k_B, 2k_B, 4k_B, 8k_B, 16k_B \ldots \quad \text{for } j = 0, 1, 2, 3, 4, 5 \ldots \]

a) (8 pts) Calculate the ratio of the number of Goetz particles in the \( j = 4 \) state to the number in the \( j = 0 \) state at temperatures 1 K, 10 K, and 100 K.

b) (4 pts) Can this ratio ever be greater than 1? Explain your answer.