

Chemistry 163C Problem Set #4  
Not Due, solutions will be posted Tuesday, 4/29

- 1) Consider a two level system where the ground state is doubly degenerate and the excited state of energy  $\epsilon$  is three fold degenerate. Develop expressions for the internal energy  $U$  and evaluate  $U$  at  $T = 0$  and  $T \rightarrow \infty$ . How do you interpret your high  $T$  results?
- 2) In class we worked out the internal energy for rotation of a diatomic molecule. Repeat this calculation for a polyatomic (in the high  $T$  limit). Does the temperature dependence reflect what you expect from the equipartition theorem? Next, determine the constant volume heat capacity (use formula 15.32 from the text). From your result, what is the actual numerical value for the heat capacity of water in the gas phase? Do you expect a different result for ozone?
- 3) In class, we determined the internal energy  $U$  for vibration of a diatomic molecule and developed the expression 15.27 in the text. However, this calculation neglected zero point energy. Repeat the calculation for  $U$  but using the full expression for  $q$  that includes the zero point energy, given by equation 14.41 in the text. How do you interpret your answer?

From Engel & Reid 3<sup>rd</sup> Edition,  
And....

Chapter 14, Problems: 35, 44  
Chapter 15, Problems: 1, 3, 12, 13