Physical Chemistry Cumulative Exam
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1. (25 pts) This problem is a simple application of the first and second laws of thermodynamics. A system has a temperature independent heat capacity C. The system is initially at a temperature T_i. The system is connected to a heat reservoir which has a constant temperature of T_c where $T_c < T_i$. The system and reservoir can exchange heat with each other but not with the surroundings. The system's energy will obviously decrease as it becomes cooler by transferring heat to the reservoir. Find the maximum work the system can deliver to the surroundings as it is cooled to the temperature of the reservoir. Remember that $C = T(\partial S/\partial T) = (dQ/dT)$. Also, remember that energy and entropy are extensive quantities and that the maximum work is obtained from a reversible process.

2. (25 pts) The compressibility of a material is a measure of how much the volume changes in response to a change in pressure. Explain which quantity should be larger, the isothermal compressibility, $\kappa_T = -(1/V)(\partial V/\partial P)_T$, or the adiabatic compressibility, $\kappa_S = -(1/V)(\partial V/\partial P)_S$. Your answer should display physical insight. No derivations or equations are necessary.

3. (25 pts) This problem concerns phase equilibria.

a) (15 pts) Is a glass of ice water (a glass containing solid and liquid H_2O in equilibrium) colder at an ocean resort or at a mountain resort? Explain your answer. (Hint: It may be useful to refer to the Clapeyron equation.)

b) (10 pts) If the glass contained water, alcohol and ice (solid water) in equilibrium instead, would the temperature necessarily be different at the two places? If not, what would be different? Give a brief explanation for your answers.

4. (25 pts) The performance of heat engines and refrigerators can be modeled as a Carnot cycle. In a Carnot cycle the system undergoes 1) an isothermal expansion while in contact with a thermal reservoir at temperature T_h, 2) an adiabatic expansion while thermally isolated, 3) an isothermal compression while in contact with a thermal reservoir at temperature T_c, and 4) an adiabatic compression while thermally isolated. At the end of the cycle, the system has returned t its initial state. Suppose we chose an *ideal* monatomic gas for our system. For such a system $E = (3/2)nRT$ which implies $dE = (3/2)nRdT$.

a) (10 pts) Give expressions, in terms of volume and temperature, for the work and heat added to the system and the change in energy of the system for each of the four steps of the cycle.

b) (5 pts) Give the total energy change of the system after completing the four steps.

c) (5 pts) Give the ratio of the net work the system can deliver to the surroundings to the heat added to the system during the isothermal expansion step.

d) (5 pts) Give an expression for the maximum efficiency of a heat engine modeled as a Carnot cycle.