Name and Surname: Student ID: Department:

- 1. Describe the following concepts(do not use equations, use words) (21 points, 3 points each):
 - Ergodic Hypothesis Microcanonical Ensemble Grand Canonical Ensemble Distribution function Le Chatelier principle Closed system Subsystem
- 2. Consider a closed system consisting of N non-interacting spins. The Hamiltonian is given by

$$H = -k \sum_{i=1}^{N} \sigma_z^i$$

where k is some constant. If the system has energy E, what is its temperature? (20 points)

- 3. Derive the expression for the entropy of the non-interacting ideal gas. (20 points)(5 additional bonus points if you use the canonical ensemble, 10 additional bonus points if you use the grand canonical ensemble)
- 4. Consider a mixture consisting of two different kinds of molecules, molecule A and molecule B. These molecules can undergo the reaction $2A \leftrightarrow 3B + energy$ where the energy released is ϵ . Let n_A be the number of A molecules per unit volume and n_B be the number of Bmolecules per unit volume. Assume that the molecules are distributed uniformly. The A molecules can be treated to form a subsystem of the whole system, similarly for B molecules. In this problem we will neglect the internal structure of the molecules, and hence treat them as point like particles. This will limit the approach to temperatures

 $T \ll \epsilon \ (50 \text{ points})$

(If you could not solve the previous problem, use the expression

$$S = N \ln \frac{CT^{\frac{3}{2}}}{N}$$

where C is some constant)

a)(10 points) The total number of molecules and the energy available for thermalization is no longer conserved, since the reaction changes the number of molecules and is endothermic. What are the new conserved quantities? (Hint: if the reaction would have been $2O_3 \leftrightarrow 3O_2$, it would not be the total number of molecules but the total number of atoms that is conserved)

b)(5 points) Show that in equilibrium, the temperature of both of the subsystems (that formed by the A molecules, and that formed by the B molecules) are equal.

c)(10 points) Show that in equilibrium

$$2\mu_A = 3\mu_B - \epsilon$$

where μ_A and μ_B are the chemical potentials of the A and B molecules respectively.

d)(5 points) Write down the total entropy of the system.

e)(10 points) By equating the derivative of the total entropy to zero, derive a relation for the particle densities of the A and B type molecules, in equilibrium (Let the equilibrium temperature be denoted by T_{eq} , and sketch the general behavior of n_B^3/n_A^2)

f)(10 points) Suppose that the system that was in equilibrium is heated. Show explicitly that the number of B molecules decreases as the system reaches equilibrium, consistent with Le Chatelier's Principle. (Do not just use Le Chatelier's principle. You are asked to confirm Le Chatelier's principle for a specific case)

You can use the following formulas/definitions without deriving them:

$$dE = TdS - PdV + \mu dN$$

$$dF = -SdT - PdV + \mu dN$$

$$dW = TdS + VdP + \mu dN$$

$$d\Phi = -SdT + VdP + \mu dN$$

$$F = E - ST; \quad W = E + PV; \quad \Phi = E - ST + PV$$
$$S = \ln \Delta \Gamma(E); \quad \Delta \Gamma(E) = \Delta E \frac{\partial}{\partial E} \Gamma(E)$$
$$\ln N! \simeq N \ln N - N$$

(1)

For anything else, you need to derive it.