
Time yourself carefully – do not spend most of your time on a single question. Remember, you can take up to 3 hours. Give as much written explanation as possible of your reasoning, and write clearly and legibly.

Bonding. (50 points)

1. (10 points) What are the quantum numbers that describe the eigenfunctions of an electron in a hydrogen atom ? How are these quantum numbers called, what do they refer to, and what are the possible values that they can take ? Why do we use these quantum numbers in the case of a hydrogen atom, or in general for the case of a central potential ?

2. (10 points) What are the orbitals involved in the bonding between the two carbon atoms in a molecule of ethane (C_2H_6), of ethene (also known as ethylene, C_2H_4), and of ethyne (also known as acetylene, C_2H_2) ? Which molecule will have the shortest distance between the carbons ? And which molecule will require more energy to break the bond between the carbons ?

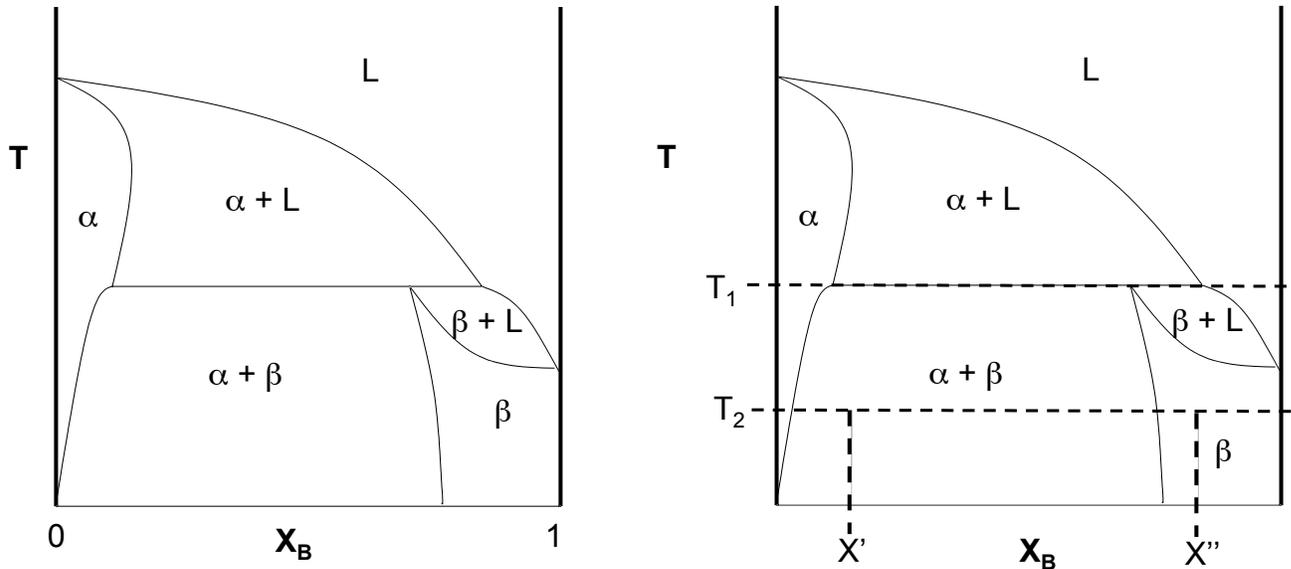
3. (10 points) What are the molecular orbitals of a homonuclear diatomic molecule ? Choose one among the second row elements (i.e. Li_2 or Be_2 or B_2 or C_2 or N_2 or O_2 or F_2 or Ne_2). What would be the Hamiltonian for this molecule, in atomic units ? Also, plot the total energy of the molecule as a function of the distance between the nuclei: what determines the equilibrium distance ?

4. (10 points) Describe the method of “linear combinations of atomic orbitals” and its application to the study of bonding in molecules. What is its relation to the variational principle ? Actually, what is the variational principle ?

5. (10 points) What is the expectation value for the distance from the nucleus of an electron in a hydrogen atom, when it is in a 1s state ? (Note: in atomic units, and using spherical coordinates, $|\psi_{1s}\rangle = \frac{1}{\sqrt{\pi}} e^{-r}$; also, $\int_0^\infty r^n e^{-ar} dr = \frac{1}{a^{n+1}} n!$, where n is an integer, a is a real positive number, and $n!$ is n factorial, i.e. $n*(n-1)*(n-2)*...*2*1$, that is to say that $1!=1$, $2!=2$, $3!=6$, $4!=24$, $5!=120$ and so on...).

Thermodynamics. (50 points)

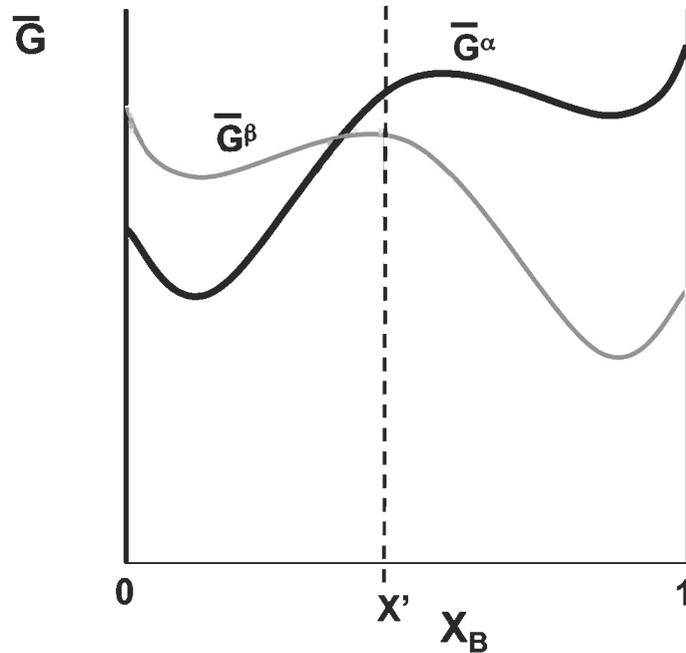
6. Shown below on the left is a binary phase diagram, and on the right the same diagram with annotation. Use these diagrams to answer the questions below:



- a. (3 points) On the left-hand diagram, mark the invariant point(s) and write the equilibrium that exists at each in the space below.
- b. (4 points) **For temperature T_2 , identify the phases present, the composition of the phases, and the phase fraction of each phase present at the composition X' and at the composition X'' .** (Identify additional points on the diagram as needed.)

- c. (4 points) What is the difference between the phase rule for a single component T/P diagram and the phase rule for a binary T/ X_B phase diagram? Explain your answer with 1-2 sentences.
- d. (4 points) In the space below, sketch a reasonable set of molar free energy vs. composition curves for each phase of the binary system at the temperature marked T_1 above.

7. Shown below is a free energy vs. composition diagram for a binary system that has two different solid phases α and β , each of which behaves as a regular solution. Use this diagram to answer the questions below:



Composition bar:

- a. (6 points) **For the composition marked X' above:**
- Mark the free energy of the stable state of the system on the diagram above. If the stable state of the system is a multi-phase equilibrium, mark the partial molar free energies of each phase present.
 - Minimization of the Gibbs free energy at constant temperature and pressure for a closed system occurs if the chemical potential of A is the same in every phase present, and if the chemical potential of B is the same in each phase. Show on the graph how this condition is met for the stable phases at this composition and temperature.
- b. (4 points) Suppose the β phase did not exist in this system. Would homogeneous α phase with a composition X' transform to a phase separated state by nucleation and growth or spinodal decomposition? Explain your answer.

8. A system of N distinguishable molecules that each have 3 possible energy states (with energies $-\epsilon$, 0 , and $+\epsilon$) is equilibrated at a temperature T .

a. (6 points) What is the partition function of the **entire system** of N molecules?

b. (6 points) Show that the ratio $\frac{P_{\epsilon}}{P_{-\epsilon}}$, the probability to find one molecule of the system in the $E = \epsilon$ state over the probability of one molecule residing in the $E = -\epsilon$ state can be determined without knowledge of the partition function, and calculate this ratio.

c. (7 points) Show that the free energy of this system becomes a linear function of T at very high temperatures.

9. (6 points) In our work on binary solution phase behavior, we showed that **some** degree of mixing (homogeneous solution formation on addition of a small amount of the component B to pure A and vice versa) is **always** favored if the components form a regular solution- even though the two components may be very chemically incompatible (i.e., they have a very large interaction parameter Ω). Mixing in this situation is driven by a favorable entropy change. Using arguments based on the statistical mechanical definition of entropy, explain in a few sentences why entropy favors mixing. (You may invoke a lattice model description of the binary solution to help with your explanation).