BONDING

1. (35 points) What is the expectation value for the potential energy of an electron in the 1s ground state of the hydrogen atom ? Derive explicitly and explain all the steps in obtaining your result (Table 16.3 has the wavefunctions for the hydrogenoid atom. Hydrogen corresponds to Z=1, and a in that table is 1 Bohr=.529177 Å; if r is expressed in atomic units, a=1. Appendix C.2 can help with the integrals).

2. (15 points) Show graphically and analytically that the 1s and 2s wavefunctions of the electron in the hydrogen atom are orthogonal: $\langle \psi_{1s} | \psi_{2s} \rangle = 0$. This constraint forces the 2s electrons in an atom to be, on average, further away from the nucleus than the 1s electrons. What are the expectation values for the distance from the nucleus of these two states ?

THERMODYNAMICS

1. **Analyzing binary phase diagrams**. Shown on the following page is a hypothetical phase diagram (Phase diagram 1) for a closed binary system (call the two components generically A and B). The system behaves as a ***regular solution in the solid state***, and an ***ideal solution in the liquid state***. Note that the qualitative shape of the molar free energy of the regular solution $\overline{G}^{RS}$ curve vs. composition is similar to the shape of the molar free energy change on mixing in the regular solution vs. composition $\left(\Delta\overline{G}^{mix,RS} = \overline{G}^{RS} - \overline{G}^{heter}\right)$. Answer the following questions about the given phase diagram:

    a. Using the diagram and the given information, construct qualitatively reasonable curves for the molar free energies of the solution vs. composition (X_B) for each phase at the temperatures denoted T_1 and T_2 –you can use the 'frames' provided below or sketch it on another sheet of paper. Mark the identity of each free energy curve you draw.

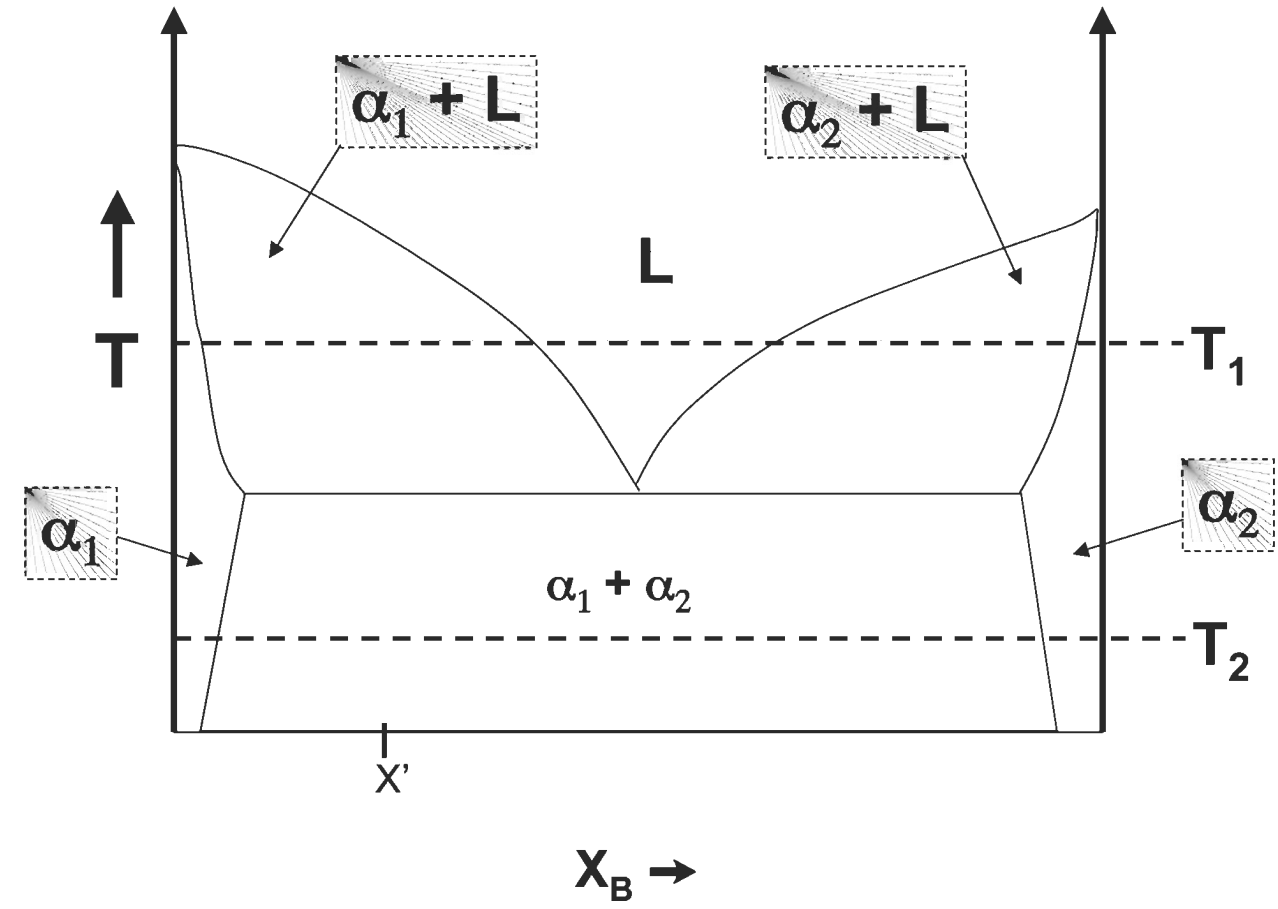
    b. On the free energy diagrams you have sketched, draw in any common tangents that are present (qualitatively). Along the X_B axis, mark the compositions that bound the ends of each common tangent with a number or letter designation. Finally, mark these same letters/numbers (from both free energy graphs) along the X_B axis of the phase diagram, to show where those compositions lie on the phase diagram. Use vertical dashed lines to mark where these compositions intersect with features on the phase diagram.

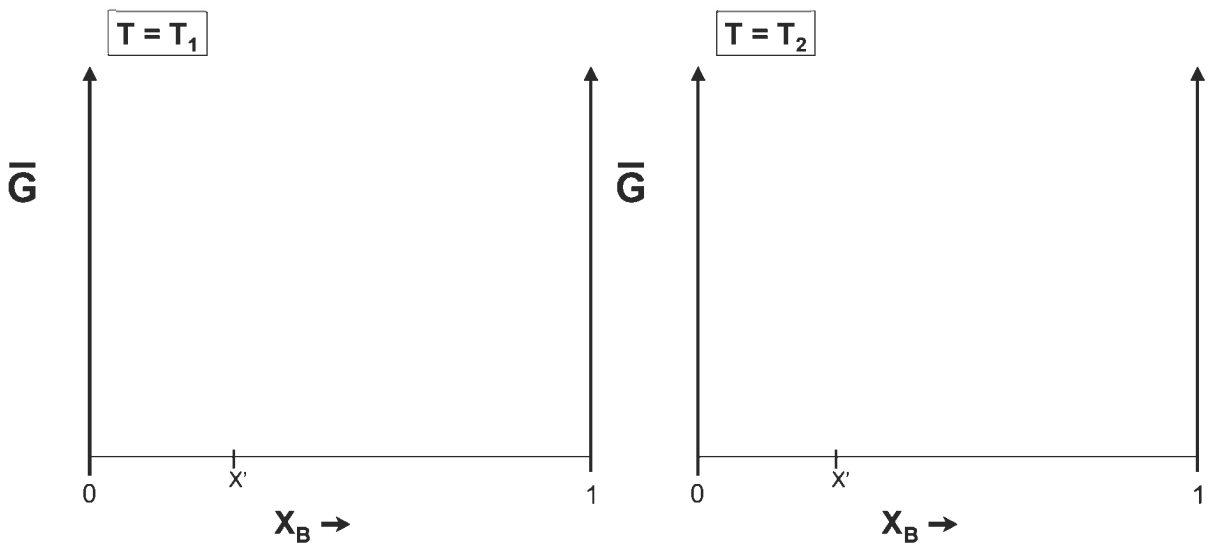
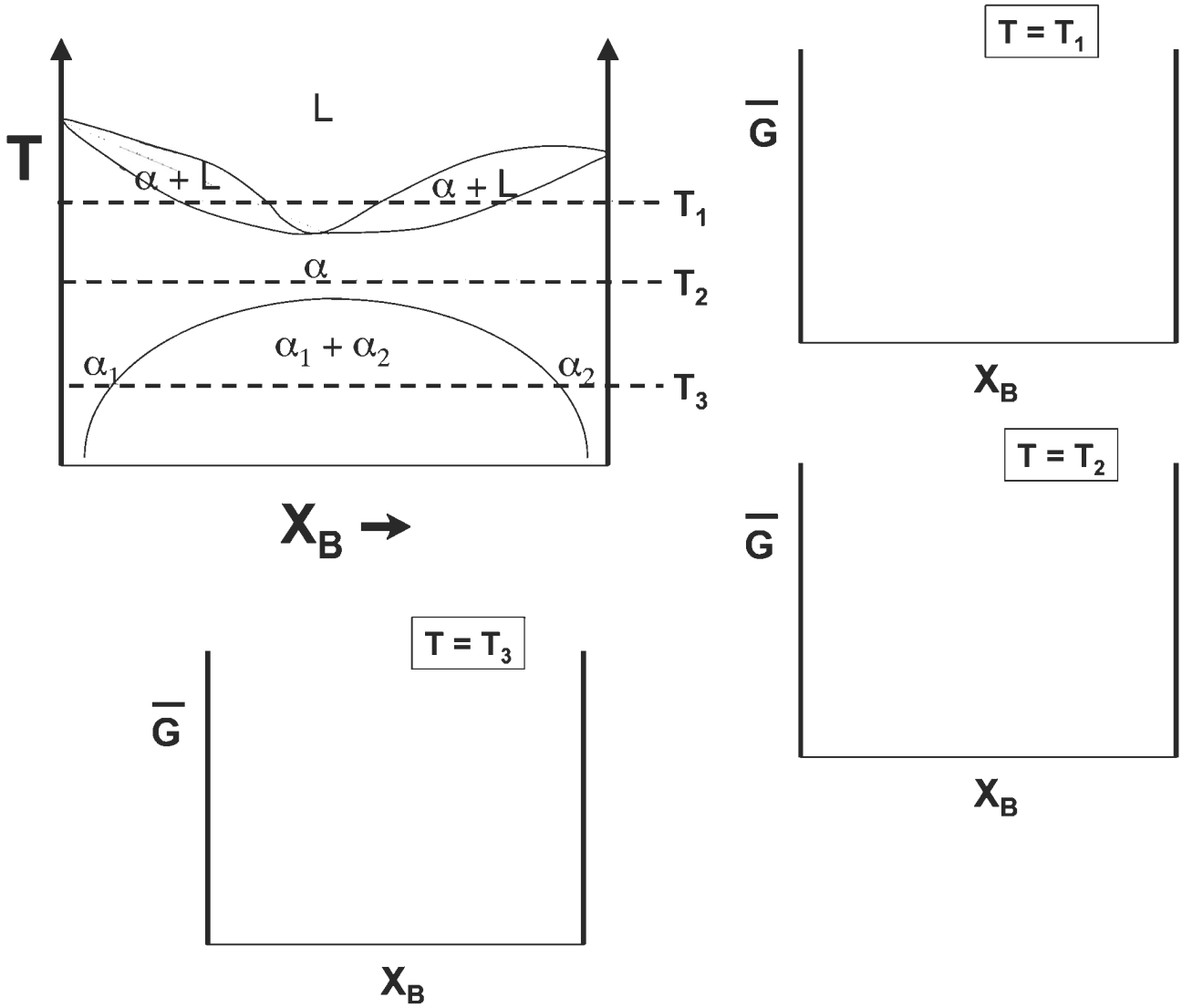
    c. Write an expression for the phase fraction of each phase present at composition X' at temperature T_1, in terms of the composition points you marked on the phase diagram in part (b).

    d. Mark on your free energy diagram for temperature T_1 the free energy change that occurs if liquid with composition X' transforms to the stable state.

    e. Now, let's look at phase diagram 2 on page 4. This system also has regular solution behavior in the solid state and ideal solution behavior in the liquid state. Use your analyses of phase diagram 1 and your understanding of how the regular solution mixing free energy varies with temperature to help you predict what the free energy curves at temperatures T_1, T_2, and T_3 must look like (qualitatively) to obtain this phase diagram.

PHASE DIAGRAM 1





PHASE DIAGRAM 2