3.012 PS 8 : Bonding

1. Expectation value for the potential energy of the 1s ground state of the hydrogen atom

The potential energy operator of the hydrogen atom can be written as:

$$\hat{\mathcal{V}}(\hat{r}) = \mathcal{V}(r) = -\frac{e^2}{4\pi\epsilon_0 r} \tag{1}$$

From Table 16.3. (Mortimer), the normalized wavefunction of the ground state is (Z=1):

$$\psi_{10} = \psi_{1s} = \frac{1}{\pi^{\frac{1}{2}} a^{\frac{3}{2}}} e^{-\frac{r}{a}} \tag{2}$$

In atomic units, the preceding expressions can be rewritten as follows:

$$\mathcal{V}(r) = -\frac{1}{r} \tag{3}$$

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} e^{-r} \tag{4}$$

($\frac{e^2}{4\pi\epsilon_0 a}$=1 $hartree$=1 a.u.=27.21 eV; a=1 $bohr$=1 a.u.=0.5292 $\times$ 10^{-10} m)

Consequently, in atomic units, the expectation value for the potential energy of an electron in the 1s ground state is:

$$\langle\psi_{1s}| -\frac{1}{r}|\psi_{1s}\rangle = \int_{r=0}^{r=\infty} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} (\frac{1}{\sqrt{\pi}} e^{-r})^* \times (-\frac{1}{r}\frac{1}{\sqrt{\pi}} e^{-r}) r^2 sin(\theta) dr d\theta d\phi \tag{5}$$

$$\langle\psi_{1s}| -\frac{1}{r}|\psi_{1s}\rangle = -\frac{1}{\pi}(\int_{r=0}^{r=\infty} re^{-2r} dr)(\int_{\theta=0}^{\theta=\pi} sin(\theta) d\theta)(\int_{\phi=0}^{\phi=2\pi} d\phi) \tag{6}$$

$$\langle\psi_{1s}| -\frac{1}{r}|\psi_{1s}\rangle = -\frac{1}{\pi}(\int_{r=0}^{r=\infty} re^{-2r} dr)(2)(2\pi) \tag{7}$$

Moreover, from Appendix C.2. (Mortimer):

$$\int_{r=0}^{r=\infty} re^{-2r} dr = \frac{1!}{2^{1+1}} = \frac{1}{4} \tag{8}$$

As a result:

$$\langle\psi_{1s}| -\frac{1}{r}|\psi_{1s}\rangle = -\frac{1}{\pi}(\frac{1}{4})(2)(2\pi) \tag{9}$$

$$\underline{\langle\psi_{1s}| -\frac{1}{r}|\psi_{1s}\rangle = -1 \ hartree = -27.21 \ eV} \tag{10}$$

[the expectation value of the potential energy $\langle\psi_{1s}|-\frac{1}{r}|\psi_{1s}\rangle = -1$ *hartree* is twice the expectation value of the total energy $\langle\psi_{1s}|\mathcal{H}|\psi_{1s}\rangle = -\frac{1}{2}$ *hartree*; this result is known as the "virial theorem"]

2. 1s and 2s states of the hydrogen atom

a. To show that the 1s and 2s wavefunctions are orthogonal, we have to show that:

$$\langle\psi_{1s}|\psi_{2s}\rangle = \int_{r=0}^{r=\infty}\int_{\theta=0}^{\theta=\pi}\int_{\phi=0}^{\phi=2\pi}\psi_{1s}\psi_{2s}r^2sin(\theta)drd\theta d\phi = 0 \qquad (11)$$

$$\langle\psi_{1s}|\psi_{2s}\rangle = 4\pi\int_{r=0}^{r=\infty}\psi_{1s}(r)\psi_{2s}(r)r^2dr = 0 \qquad (12)$$

Let us calculate $\int_{r=0}^{r=\infty}\psi_{1s}(r)\psi_{2s}(r)r^2dr$:

$$\int_{r=0}^{r=\infty}\psi_{1s}(r)\psi_{2s}(r)r^2dr = \int_{r=0}^{r=\infty}\frac{1}{\sqrt{\pi}}e^{-r}\times\frac{2-r}{4\sqrt{2\pi}}e^{-\frac{r}{2}}r^2dr \qquad (13)$$

$$(14)$$

(from Table 16.3)

$$\int_{r=0}^{r=\infty}\psi_{1s}(r)\psi_{2s}(r)r^2dr = A\int_{r=0}^{r=\infty}(2-r)e^{-\frac{3r}{2}}r^2dr$$

$$(A = \frac{1}{4\pi\sqrt{2}})$$

$$\int_{r=0}^{r=\infty}\psi_{1s}(r)\psi_{2s}(r)r^2dr = A(2\int_{r=0}^{r=\infty}r^2e^{-\frac{3r}{2}}dr - \int_{r=0}^{r=\infty}r^3e^{-\frac{3r}{2}}dr)$$

$$\int_{r=0}^{r=\infty}\psi_{1s}(r)\psi_{2s}(r)r^2dr = A(2\frac{2!}{(3/2)^3} - \frac{3!}{(3/2)^4}) \quad (from\ Appendix\ C.2.)$$

$$\int_{r=0}^{r=\infty}\psi_{1s}(r)\psi_{2s}(r)r^2dr = A\frac{2!}{(3/2)^3}(2 - \frac{3}{3/2})$$

$$\underline{\int_{r=0}^{r=\infty}\psi_{1s}(r)\psi_{2s}(r)r^2dr = 0} \qquad (15)$$

(note: one can also show that the two integrals are equal by carrying out an integration by parts: $\int_{r=0}^{r=\infty}r^2e^{-\frac{3r}{2}}dr = 0 - \int_{r=0}^{r=\infty}\frac{r^3}{3}(-\frac{3}{2})e^{-\frac{3r}{2}}dr)$

Graphically, the preceding result means that the curve of the function $r^2\psi_{1s}(r)\psi_{2s}(r)$ is such that the area denoted "+" is equal and opposite to the area denoted "-".
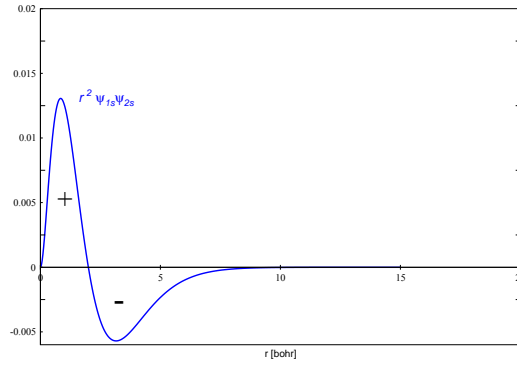
This requirement has two main consequences:
- there exists a node in the graph of $\psi_{2s}(r)$, around which the function changes its sign;
- $\psi_{2s}(r)$ is less localized around the origin $r = 0$ than $\psi_{1s}(r)$ (otherwise the negative part of the integral of $r^2\psi_{1s}(r)\psi_{2s}(r)$ would not composate its positive part).

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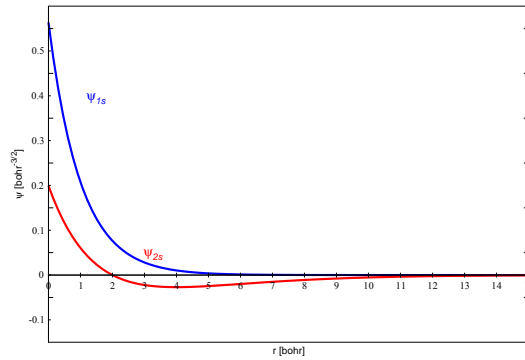
b. The expectation value for the distance from the nucleus of the 1s state can be calculated as follows:

$$\langle \psi_{1s} | \hat{r} | \psi_{1s} \rangle = \langle \psi_{1s} | r | \psi_{1s} \rangle = \int_{r=0}^{r=\infty} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} (\frac{1}{\pi^{\frac{1}{2}}} e^{-r})^* \times (r \frac{1}{\pi^{\frac{1}{2}}} e^{-r}) r^2 sin(\theta) dr d\theta d\phi \tag{16}$$

$$\langle \psi_{1s} | r | \psi_{1s} \rangle = \frac{4\pi}{\pi} \int_{r=0}^{r=\infty} r^3 e^{-2r} dr = 4\frac{3!}{2^4} \tag{17}$$

$$\underline{\langle \psi_{1s} | r | \psi_{1s} \rangle = 1.5 \ bohr} \tag{18}$$

[The most probable distance from the nucleus corresponding to the 1s state is the radius r_m where the 1s radial distribution function (cf. Mortimer P. 593-594) is maximum. By solving the equation $\frac{d}{dr} r^2 \psi_{1s}^2 = 0$, we obtain $r_m = 1 \ bohr$. The most problable distance r_m is lower that the expectation value $\langle \psi_{1s} | r | \psi_{1s} \rangle$ because the function $r^2 \psi_{1s}^2(r)$ is not equally distributed around its maximum (due to the exponential tail).]

Similarly, from the expression of ψ_{2s}:

$$\langle \psi_{2s} | \hat{r} | \psi_{2s} \rangle = \frac{4\pi}{(4\sqrt{2\pi})^2} \int_{r=0}^{r=\infty} r(2-r)^2 e^{-\frac{2r}{2}} r^2 dr \tag{19}$$

$$\langle \psi_{2s} | r | \psi_{2s} \rangle = \frac{4\pi}{32\pi} [4 \int_{r=0}^{r=\infty} r^3 e^{-r} dr - 4 \int_{r=0}^{r=\infty} r^4 e^{-r} dr + \int_{r=0}^{r=\infty} r^5 e^{-r} dr] \tag{20}$$

$$\langle \psi_{2s} | r | \psi_{2s} \rangle = \frac{1}{8} [4\frac{3!}{1^4} - 4\frac{4!}{1^5} + \frac{5!}{1^6}] = \frac{1}{8} [8 \times 3 - 8 \times 12 + 8 \times 15] \tag{21}$$

$$\underline{\langle \psi_{2s} | r | \psi_{2s} \rangle = 6 \ bohr} \tag{22}$$

As expected $\langle \psi_{2s} | r | \psi_{2s} \rangle > \langle \psi_{1s} | r | \psi_{1s} \rangle$.

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.

      See diagrams below.

   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.

      See diagrams below.

   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).

      The phase fractions for the point (X', T_1) are obtained by applying the lever rule to the tie line running from X_1 to X_2 at temperature T_1:

      $$f^{\alpha_1} = \frac{\overline{X}'\,\overline{X}_2}{\overline{X}_1\overline{X}_2} = \frac{\left(X_2 - X'\right)}{\left(X_2 - X_1\right)}$$

      $$f^{L} = \frac{\overline{X}_1\overline{X}'}{\overline{X}_1\overline{X}_2} = \frac{\left(X'-X_1\right)}{\left(X_2 - X_1\right)}$$

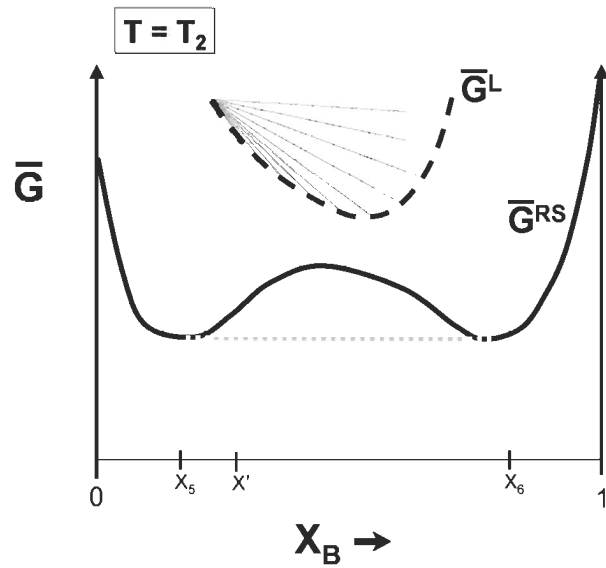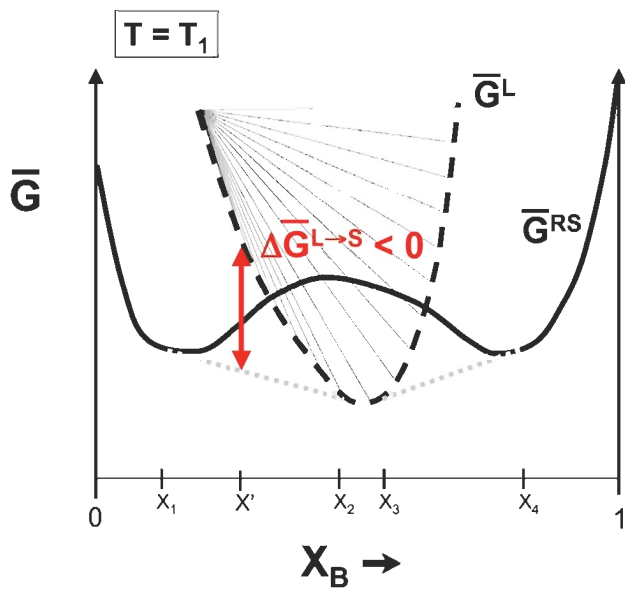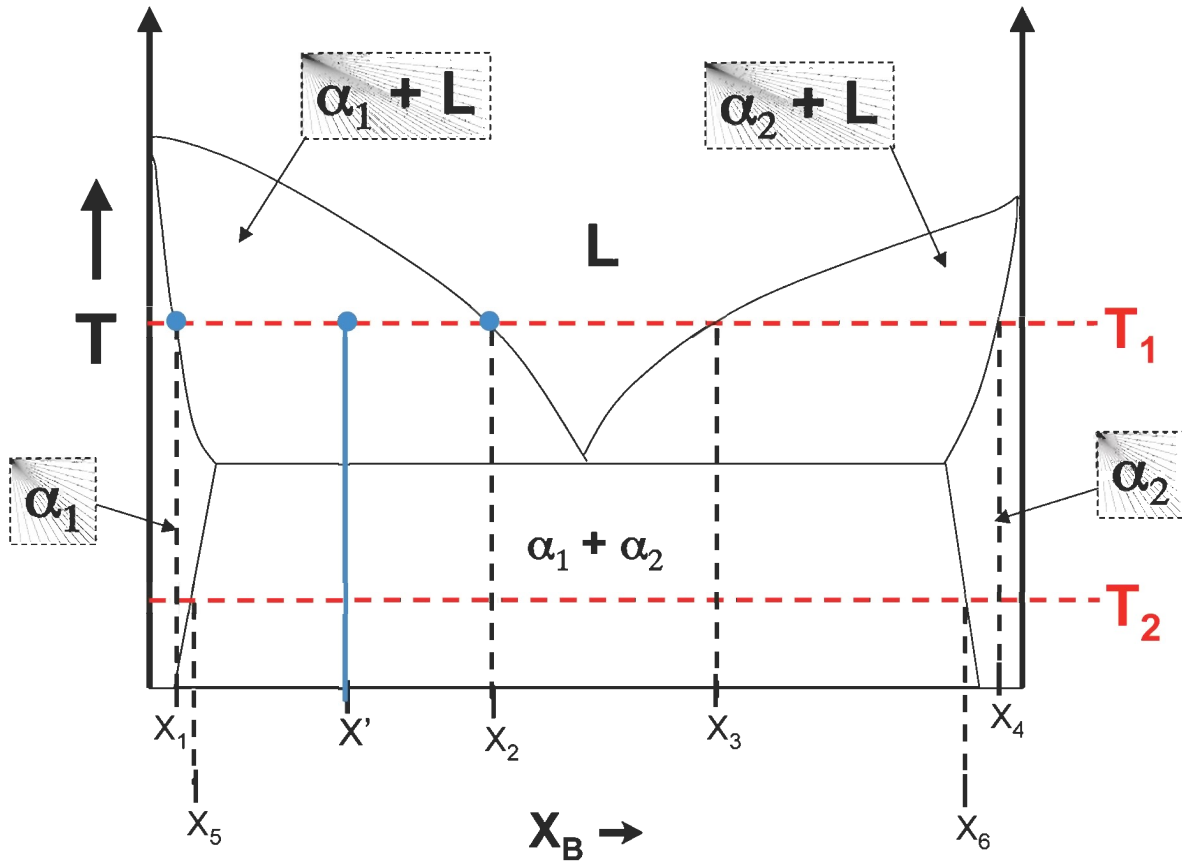   (where the X's with bars are meant to represent line segments).

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.
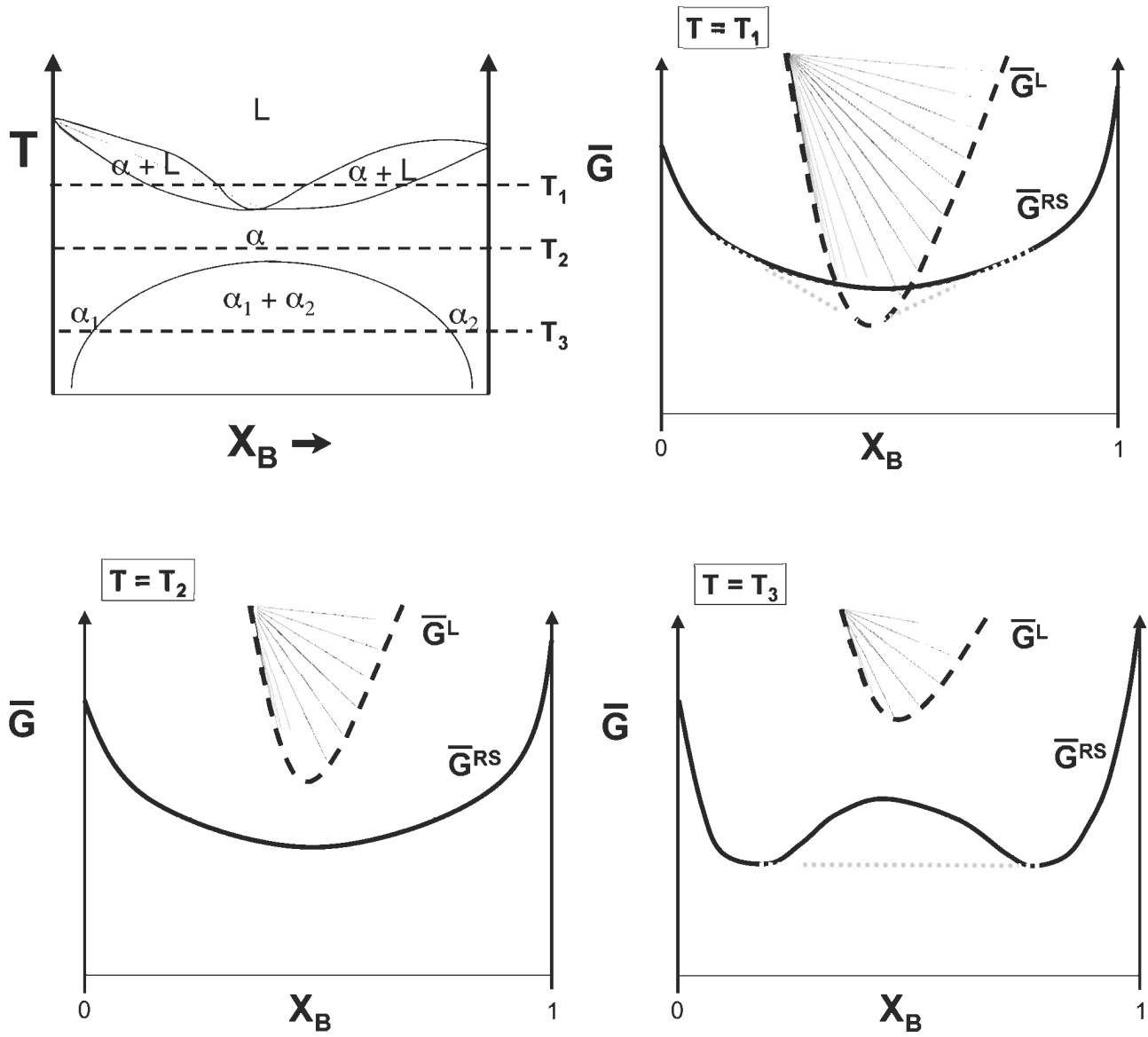

See diagram below.

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.

The diagrams are shown below. We see that this completely different phase diagram arises from a rather simple conceptual change in the free energy behavior of the material: The liquid free energy curve 'passes through' the regular solution free energy curve as temperature drops *before* the regular solution phase separates at the critical temperature (i.e., the liquid solidifies to solid α at a temperature above the critical temperature of the solid α solution). In this situation, a eutectic diagram does not form.

$\alpha_1 + L$

$\alpha_2 + L$

L

T_1

α_1

$\alpha_1 + \alpha_2$

α_2

T_2

X_1 X' X_2 X_3 X_4

X_5 X_6

$X_B \rightarrow$

$T = T_1$

$\overline{G}$

$\overline{G}^L$

$\overline{G}^{RS}$

$\Delta\overline{G}^{L \rightarrow S} < 0$

0 X_1 X' X_2 X_3 X_4 1

$X_B \rightarrow$

$T = T_2$

$\overline{G}$

$\overline{G}^L$

$\overline{G}^{RS}$

0 X_5 X' X_6 1

$X_B \rightarrow$

PHASE DIAGRAM 2

$T = T_1$

$T = T_2$

$T = T_3$

what: