

## Key and guide to exam #2

### Chemistry 341, (01:160:341), Fall 2014 Physical Chemistry of Biochemical Systems

Use the hints below to get you started on problems you had trouble with on the first exam. You should arrange to meet with me if you still don't understand how to do the problems.

**Problem 1** See Example 4.8 on p. 122 for a worked-out explanation.

**Problem 2** Just as in the first example we did in class, there are four states,  $P, P_\alpha, P_\beta, P_{\alpha\beta}$ . Hence,  $Q = 1 + K[L] + cK[L] + cK^2[L]^2$ , the sum of the relative probabilities (or populations, or concentrations) of the four states. Use Eq. (1) in the notes on binding to compute  $f$  by differentiating  $Q$  with respect to  $[L]$ . For part (c), see Eq. 12 in the notes on the Boltzmann distribution.

**Problem 3** This is example 4.16 in the text (at a different temperature). Note the important distinction between  $\Delta G^\circ$  and  $\Delta G$ ; also note that you must express concentrations in M, not  $\mu\text{M}$ .

**Problem 4** See p. 137 in the text.

**Problem 5** The mole fraction of solute "B" in solution is given by  $x_B = p_{v,B}/k_B$  (header to Table 6.1), which is  $(0.78 \text{ bar}/84,000 \text{ bar}) = 9.3 \times 10^{-6}$  for  $\text{N}_2$ . Now we need to convert this mole fraction to a concentration. Note that the number of moles of gas in solution is much less than the number of moles of water, so that  $x_B \approx n_B/n_{\text{wat}}$ . Hence, the concentration of  $\text{N}_2$ , in mol/L, is  $c_B = (n_B/n_{\text{wat}})(55.5 \text{ mol wat}/1 \text{ L}) = (9.3 \times 10^{-6})(55.5) = 5.2 \times 10^{-4} \text{ mol/L}$ . (It's helpful to remember that the concentration of water is 55.5 M; if you forgot this, you can compute it as  $(1000 \text{ g/L})(1 \text{ mol}/18 \text{ g})$ ). Note also that this calculation was part of homework problem 6.4.

**Problem 6** Start with Eq. 3 in the notes on the Boltzmann distribution. Plug in  $p_i = (\exp[-E_i/kT])/Q$ . The resulting expression looks a bit messy, and is not easy to simplify. As  $B \rightarrow 0$ , all three states have the same energy (zero), and hence all three have the same probability,  $1/3$ . Plugging these probabilities into Eq. 3 gives  $S = k \ln 3 = 9.13 \text{ J mol}^{-1} \text{ K}^{-1}$ . As  $B \rightarrow \infty$ , only one state (that with  $m=-1$ ) is occupied (i.e. has a non-zero probability). Then  $S = (1) \ln(1) = 0$ , as might be expected for any single-level system, where there is no randomness, and hence zero entropy.