Study guide for exam #1

Chemistry 341, Fall 2013
Physical Chemistry of Biochemical Systems

1 Key concepts and equations

For the following, you should understand the concepts, know (have memorized) the key equations, understand what all the symbols mean, and be able to explain the equations in words and to appreciate their context. Please pay close attention to the *Summary* and the *Mathematics Needed* sections at the end of the chapters.

1.1 Chapter 5: Statistical foundations of biophysical chemistry

- Boltzmann distribution: $p_i = \exp(-\beta E_i)/Q$, where $\beta = 1/k_B T$
- Partition function: $Q = \sum_i g_i \exp(-\beta E_i)$
- Entropy: $S = -k_B \sum_i p_i (\ln p_i)$; note that this is a more general expression than Eq. 5.38 in your text
- Average number of ligands bound: $\nu = (d \ln Q / d \ln S)$, where $S = K[A]$; same formula, with a different interpretation of S, for conformational changes like helix-coil transitions.

1.2 Chapter 9: Kinetics: Rates of chemical reactions

- differences between differential and integrated rate laws
- rate law for first order decay: $[A](t) = [A](0) \exp(-k_r t)$
- half life for a non-reversible first-order reaction: $t_{1/2} = (\ln 2)/k_r$
- Arrhenius equation: $k_r = \exp(-E_a/RT)$
- relation of equiibrium and rate constants: $K = k_r/k_r'$
- relaxation times: $x = x_0 \exp(-t/\tau)$; $\tau^{-1} = k_r + k_r'$
- transition state theory (Eyring equation): $k = (k_B T/h) \exp(-\beta \Delta G^{\ddagger})$

1.3 Chapter 10: Enzyme kinetics

- Michaelis-Menten kinetics: initial rate $v_0 = V_{max}[S]/(K_M + [S])$, where $V_{max} = k_2[E]_0$
- Form of a Lineweaver-Burke plot

2 Sample exam questions

1. Explain (define in words) each of the symbols in the above expressions; explain their limitations (what they assume)

2. The anesthetic phenobarbitol metabolizes following first-order kinetics, with a half-life of 4.5 hours. For an initial dose of 450 mg, how much remains after 2 hours?

3. What are the units of k_r for zeroth, first, second and third-order reactions?

4. A protein dimerizes $2A \leftrightarrow A_2$ with a forward rate constant (second order) of k_r and a reverse rate constant (first order) of k_r'. Show that the relaxation time is $\tau^{-1} = k_r' + 4k_r[A_{eq}]$.

5. The Michaelis-Menten mechanism is broadly applicable to many enzyme reactions, where "E" (enzyme) catalyzes the conversion of "S" (substrate) to "P" (product).

   (a) Write down this mechanism, showing rate constants for the elementary steps.

   (b) Write an expression for the Michaelis constant, K_M, in terms of the elementary rate constants identified in part *(a)*.

   (c) Experiments often measure v, the rate of production of products, as a function of substrate concentration, at a fixed concentration of total enzyme. Draw a qualitative plot of rate *vs.* substrate concentration for reactions following this mechanism.

6. Carbonic anhydrase is a zinc-based enzyme that catalyzes the conversion of carbon dioxide to carbonic acid. In one experiment with this enzyme, it was found that the concentration of CO_2 decreased from 220 mM to 56 mM in 3.4 hours. Assuming a rate law that is first-order in $[CO_2]$, what is the rate constant? (M=moles per liter).