Study guide for exam #2

Chemistry 488, Spring 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. For chapters 5-8, please pay close attention to the *Checklist of key concepts* and the *Checklist of key equations*.

1.1 Chapter 5

- transfer across a membrane: $\Delta G_m = RT\ln(a_{in}/a_{out}) + zF\Delta\phi$
- Nernst equation: $E_{cell} = E^{\ominus}_{cell} - (RT/\nu F)\ln Q$
- dependence of cell potential on pH: $E = E' - \frac{\nu_{H+} RT\ln 10}{\nu_e F} \times pH$
- know how to combine half-reactions into balanced full reactions, and how to obtain cell potentials and equilibrium constants

1.2 Chapter 6

- 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: $k_r = \exp(-E_a/RT)$

1.3 Chapter 7

- relation of equiibrium and rate constants: $K = k_r/k_r'$
- relaxation times: $x = x_0\exp(-t/\tau);\ \tau^{-1} = k_r + k_r'$

1.4 Chapter 8

- Fick's first and second laws: $J = -D(dc/dx)$; $\partial c/\partial t = D(\partial^2 c/\partial x^2)$
- Diffusion constant temperature dependence: $D = D_0 \exp(-E_a/RT)$
- Ion mobility: $u = ez/6\pi\eta a$
- Stokes-Einstein relation: $D = kT/(6\pi\eta a)$
- 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. Does $FADH_2$ have a tendency to reduce coenzyme Q at pH 7? (Use values in Table 5.2).
3. What is the equilibrium constant for the reaction in example 2 at pH 7? at pH 4?
4. Cytochrome c oxidase accepts electrons from reduced cytochrome c (Fe^{+2}cyt c) and transmits them to molecular oxygen, forming water. Write a balanced reaction for this process, and estimate $E^{\oplus}_{cell}$. Does lowering the pH promote or inhibit the reaction? (Use data in Table 5.2)
5. 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?
6. What are the units of k_r for zeroth, first, second and third-order reactions?
7. 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 $\tau^{-1} = k_r' + 4k_r[A_{eq}]$.
8. 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.