Exam #2 NAME________________________

Chemistry 342, (01:160:342), Spring 2012
Physical Chemistry of Biochemical Systems

Some constants: R=8.314 J $K^{-1}mol^{-1}$; F=9.648 $\times 10^4$ C mol^{-1}. Also note (I hope you already know this!) that 1 V = 1 J C^{-1}.

1. Explain (define in words) each of the symbols in the following expressions; please be brief!

   (a) $-\nu F E_{cell} = \Delta_r G$; (b) $k_r = A\exp(-E_a/RT)$; (c) $\tau^{-1} = (k_r + k_r')$

2. Glutathione is sometimes used as a reducing agent, both in living systems and in biochemical experiments. Here we consider whether glutathione is capable of reducing a disulfide bond (cystine) to two cysteine amino acids. (Refer to the table on the back of the exam.)

   (a) write a balanced reaction for the reduction of cystine by glutathione as a sum of the two relevant half-reactions.
   (b) What is the biological standard cell potential for this reaction? What is the corresponding value of $\Delta_r G^{\oplus}$?
   (c) Would it be easier for glutathione to carry out this reduction if one went to lower pH? Explain your answer.

3. The standard hydrogen electrode, for the reaction $2H^+ + 2e^- \rightarrow H_2$ is defined to have a standard cell potential of zero at pH 0. What is its cell potential at pH 7?

4. The anesthetic phenobarbitol metabolizes following first-order kinetics, with a half-life of 4.5 hours. For an initial dose of 300 mg, how much remains after 2 hours?

5. The rate constant for a second-order reaction is $1.78 \times 10^{-4} M^{-1}s^{-1}$ at 292 K, and is 1.38×10^{-3} $M^{-1}s^{-1}$ at 310 K. What is the activation energy?

6. Consider the following reaction mechanism, with an intermediate "A"

$$\begin{aligned} A_2 &\longleftrightarrow A + A \quad (fast) \\ A + B &\rightarrow P \quad (slow) \end{aligned}$$

   Denote the forward and reverse rate constants for the fast step as k_a and k_a', respectively, and the rate constant for the slow step as k_b.

   (a) What is the equilibrium constant for the fast equilibrium? Write your answer in terms of the rate constants defined above.
   (b) What is the differential rate law for the formation of P? You may make the pre-equilibrium assumption for the fast step. What is the overall order of the reaction?
   (c) Write an expression for the effective rate constant in terms of k_a, k_a' and k_b.

7. Cytochrome *c* oxidase pumps protons across the mitochondrial membrane, such that the pH on the outside is three units lower than the inside.

   (a) How much free energy is needed at 298 K to pump protons against such a concentration gradient?
   (b) What is the equilibrium membrane potential that this correponds to?

Biological standard potentials, $E^{\oplus}$ at 298.15 K, in electrochemical order:

Reduction half-reaction	$E^{\bullet}$/V
$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O$	+0.81
$NO_3^- + 2\,H^+ + 2\,e^- \rightarrow NO_2^- + H_2O$	+0.42
Fe^{3+}(cyt *f*) + $e^- \rightarrow Fe^{2+}$ (cyt *f*)	+0.36
Cu^{2+}(plastocyanin) + $e^- \rightarrow Cu^+$(plastocyanin)	+0.35
Cu^{2+}(azurin) + $e^- \rightarrow Cu^+$(azurin)	+0.30
$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2$	+0.30
Fe^{3+}(cyt c_{551}) + $e^- \rightarrow Fe^{2+}$ (cyt c_{551})	+0.29
Fe^{3+}(cyt *c*) + $\rightarrow Fe^{2+}$ (cyt *c*)	+0.25
Fe^{3+}(cyt *b*) + $e^- \rightarrow Fe^{2+}$ (cyt *b*)	+0.08
Dehydroascorbic acid + $2\,H^+ + 2\,e^- \rightarrow$ ascorbic acid	+0.08
Coenzyme Q + $2\,H^+ + 2\,e^- \rightarrow$ coenzyme QH_2	+0.04
Fumarate^{2-} + $2\,H^+ + 2\,e^- \rightarrow$ succinate^{2-}	+0.03
Vitamin K_1(ox) + $2\,H^+ + 2\,e^- \rightarrow$ vitamin K_1(red)	−0.05
Oxaloacetate^{2-} + $2\,H^+ + 2\,e^- \rightarrow$ malate^{2-}	−0.17
Pyruvate$^-$ + $2\,H^+ + 2\,e^- \rightarrow$ lactate$^-$	−0.18
Ethanal + $2\,H^+ + 2\,e^- \rightarrow$ ethanol	−0.20
Riboflavin(ox) + $2\,H^+ + 2\,e^- \rightarrow$ riboflavin (red)	−0.21
FAD + $2\,H^+ + 2\,e^- \rightarrow FADH_2$	−0.22
Glutathione (ox) + $2\,H^+ + 2\,e^- \rightarrow$ glutathione (red)	−0.23
Lipoic acid (ox) + $2\,H^+ + 2\,e^- \rightarrow$ lipoic acid (red)	−0.29
$NAD^+ + H^+ + 2\,e^- \rightarrow NADH$	−0.32
Cystine + $2\,H^+ + 2\,e^- \rightarrow$ 2 cysteine	−0.34
Acetyl − CoA + $2\,H^+ + 2\,e^- \rightarrow$ ethanal + CoA	−0.41
$2H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$	−0.42
Ferredoxin (ox) + $e^- \rightarrow$ ferredoxin (red)	−0.43
$O_2 + e^- \rightarrow O_2^-$	−0.4