Final Exam 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}; c (speed of light) = 3.00 $\times$ 10^8 m/s; h (Planck's constant) = 6.63 $\times 10^{-34}$ J s; $4\pi\varepsilon_0$= 1.11 $\times$ $10^{-10}C^2/(Jm)$. 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

   (a) $\lambda = h/p$

   (b) $\Delta S = q_{rev}/T$

   (c) $G = n_A\mu_A + n_B\mu_B$

   (d) $E_{cell} = E^{\ominus}_{cell} - (RT/\nu F)\ln Q$

   (e) $D = kT/(6\pi\eta a)$

2. Write down Fick's first and second laws of diffusion; identify each symbol.

3. Orange light has a wavelength of 620 nm. What is its frequency? How much energy does it have in wavenumbers (cm^{-1})?

4. At 1 C, the vapor pressure of pure water is 0.0064 atmospheres. What is $\Delta_{vap}G^{\ominus}$ at this temperature? Note that $\Delta_{vap}G^{\ominus} \equiv \mu^{\ominus}$(gas) $- \mu^{\ominus}$(liquid) . Show your work.

5. Phenol, C_6H_5OH, is a very weak acid, with a pK_a of 9.89. What is the pH of a 0.65 M solution of phenol in water?

6. Draw a skectch of an differential scanning calorimeter, identifying all the parts. What does this measure?

7. Does $FADH_2$ have the ability to reduce coenzyme Q at pH 7? (Use values in Table at the end of the exam.) Show your reasoning, including a balanced equation for this reaction and a calculation of its cell potential.

8. Consider the following acid-catalyzed reaction mechanism

$$A^- + H^+ \longleftrightarrow AH \quad (fast)$$
$$AH + B \rightarrow BH^+ + A^- \quad (slow)$$

   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 BH^+? You may make the pre-equilibrium assumption for the fast step. Write the differential rate law in terms of $[A^-]$, $[H^+]$ and $[B]$. 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.

9. A certain protein pumps protons across a membrane, such that the pH on the outside is two 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?

10. Consider the H_2^+ molecule, where the two protons (hydrogen nuclei) can be considered as fixed points. Let R be the distance between the two protons, r_1 be the distance of the electron from nucleus "1" and r_2 be the distance of the electron from nucleus "2". Write the Schrodinger equation for the motion of the electron in this system; identify the parts of the equation that refer to the kinetic, potential and total energies of the system. [The potential energy part should be expressed in terms of the electron charge e, and the three distances described above.]

11. 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.

12. What is the potential energy between two electrons that are 1 nm apart? Express your answer in J/mol.

13. Give a brief definition or equation of the following terms, identifying any symbols that you use:

    (a) selection rules for quantum transitions

    (b) Beer-Lambert law for absorption of light

    (c) Arrhenius equation for the temperature dependence of rate constants

    (d) Half life for a first order reaction

    (e) Phosphorescence

(exam continues on the next page)

14. Consider a problem of the combination of two orbitals: if $\psi = c_A \psi_A + c_B \psi_B$, then one gets the following simultaneous equations:

$$\begin{aligned} (H_{AA} - ES_{AA})c_A + (H_{AB} - ES_{AB})c_B &= 0 \\ (H_{BA} - ES_{BA})c_A + (H_{BB} - ES_{BB})c_B &= 0 \end{aligned}$$

The equation for the allowed values of E:

$$\det \begin{vmatrix} H_{AA} - ES_{AA} & H_{AB} - ES_{AB} \\ H_{BA} - ES_{BA} & H_{BB} - ES_{BB} \end{vmatrix} = 0$$

In the Huckel approximation, one assumes that $H_{AA} = H_{BB} = \alpha$; $H_{AB} = H_{BA} = \beta$; $S_{AA} = S_{BB} = 1$; and $S_{AB} = S_{BA} = 0$.

(a) Using these assumptions, show that the allowed values for the energy are $E = \alpha \pm \beta$.

(b) Next, instead of assuming that $S_{AB} = S_{BA} = 0$, assume instead that $S_{AB} = S_{BA} = S$, where S is some known non-zero number (called an *overlap integral*). Write an expression for the allowed energy levels with this new assumption. (Warning: the answer is a bit complicated: show your work and simplify as much as you can. A fully complete answer will have no square roots.)

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

Reduction half-reaction	$E^{\oplus}$/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