Chemistry 130 A Final Exam Typos & Hints Dec. 14, 1999
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Unfortunately there are some typographical errors in the fianl exam that I did not spot until after the copies were run off.

Pg. 2, Prob. 2(d) Second equation at right should read

I_2 (g) + Br_2 (g) -> 2 IBr (g)

Pg. 5, Prob. 4. Arrows are missing in the acid dissociation equations

H_3PO_4 <==> H^+ + $H_2PO_4^-$
$H_2PO_4^-$ <==> H^+ + HPO_4^{2-}
HPO_4^{2-} <==> H^+ + PO_4^{-3}

Part (b) Assume a volume of 1 liter.

Pg. 7, Prob. 5(c). The equation on lines 4 and 5 should read

$$v_o = \left[\frac{d([Allo]/[Ile])}{dt}\right]_o \cong k_1$$

is a good approximation for [Allo]/[Ile] < 0.5.

Hint:
There are (at least) two ways to approach this problem.

1. Using calculus, re-write v in terms of d[Allo]/dt and d[Ile]/dt and proceed to evaluate the resulting expression based on the stated mechanism for the reaction and during the initial phase when [Allo]/[Ile] is small.

2. Start with the mechanism and develop an expression for [Allo]/[Ile] as a function of time based on the solution to the first-order kinetic equation, keeping in mind that [Allo] + [Ile] = constant. Then take the first derivative in the limit of relatively short times.

Chemistry 130A	Final Examination	Dec. 14, 1999	3 hours	1
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Prof. K. Sauer Total Credit - 250 points	SHOW YOUR WORK		Open textbook and class notes	4 5 6
			Exam Total	
			Course Grade	

1. (Credit 20 + 20)

The reaction of A to form B in aqueous solution has the following rate expression:

$$-\frac{d[A]}{dt} = k[A](1 + k'[OH^-])$$

Hydroxide is neither formed nor consumed by the reaction.

a) Propose a mechanism that is consistent with the experimental rate expression. Relate the rate constants in your expression to k and k′.

b) From the pH dependence of the reaction, k′ was found to be $5.0 \times 10^4 M^{-1}$. In a pH 10.0 buffer, it took 10 min for a 0.050 M solution of A to decrease to 0.025 M. Calculate the value of k, including its units.

2. (10 each) For each of the statements at the left, circle the best answer from the list at the right. Briefly indicate your reasoning and state important assumptions.

a) Lowest standard chemical potential of NaCl at 25°C. Solubility of NaCl in water is > 5 M at 25°C.	Pure solid. Standard state in water solution. Saturated solution in water. Supersaturated solution in water.
b) Greatest amount of work done during expansion of ideal gas at 10 atm, 298 K and 1L to 5L.	Against P_{op} = 2 atm. Reversible, isothermal. Reversible, adiabatic. Against P_{op} = 1 atm.
c) Largest fraction of gaseous molecules with speed greater than 1000 m/sec.	He at 300K. H_2 at 350K. N_2 at 300K. C_2H_4 at 350K.
d) Greatest entropy increase at 298K.	$2ClF(g) \rightarrow Cl_2(g) + F_2(g)$. $I_2(g) + Br_2(g) \rightarrow$ ~~2ibr~~ 2IBr(g). $2IBr(g) \rightarrow I_2(s) + Br_2(g)$. $IBr(g) + ClF(g) \rightarrow ICl(g) + FBr(g)$.

3. (Credit 10 each)

At the neuro-muscular junction, a nerve impulse results in the release of acetylcholine (AcCh) into the junction, which in turn depolarizes the postsynaptic membrane. Each impulse results in the release of some 10^4 AcCh molecules from synaptic vesicles. These released molecules must then be destroyed rapidly so that the polarized state of the postsynaptic membrane can be restored and ready for the next nerve impulse. Synapses can transmit up to 1000 impulses/sec. Acetylcholine is hydrolyzed by the membrane-bound enzyme acetylcholinesterase by the reaction

$$\underset{\text{acetylcholine}}{\text{AcCh}} + H_2O \xrightleftharpoons{\text{AcChase}} \underset{\text{acetate}}{\text{Ac}^-} + \text{Ch} + H^+ \quad \text{choline} = [\text{HO-CH}_2\text{CH}_2\overset{+}{\text{N}}(\text{CH}_3)_3]$$

a) A solution containing 1.8×10^{-5}M AcCh was treated with an AcChase enzyme preparation and found to exhibit an initial velocity $\upsilon_0 = 5 \times 10^{-6}$M sec^{-1}. Further studies showed that, for this enzyme preparation, $V_{max} = 3 \times 10^{-5}$M sec^{-1} at high AcCh concentration. Calculate a value for the Michaelis constant, K_M, for acetylcholinesterase.

b) Using the irreversible enzyme inhibitor (and nerve poison!) di-iso-propylphosphofluoridate (DFP), which binds in a 1:1 stoichiometry to the active site of AcChase, the concentration of the enzyme used in the studies of part (a) was found to be 2×10^{-9}M. What is the value for k_{cat} for AcChase?

c) Is the turnover time for the enzyme compatible with its role in mediating normal nerve signal transduction? Explain your reasoning.

4. (Credit 28 + 8)

You want to make a pH 7.5 buffer using NaOH and phosphoric acid. The sum of the concentrations of all phosphoric acid species is 0.100M. Assume ideal solution behavior. The equilibrium constants for concentrations given in mol L^{-1} for the following equilibria at 298K are

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \qquad K_1 = 7.1 \times 10^{-3}$$
$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \qquad K_2 = 6.2 \times 10^{-8}$$
$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \qquad K_3 = 4.5 \times 10^{-13}$$

a) Calculate the concentrations of all species in the pH 7.5 buffer at 298K.

$[H_3PO_4] =$

$[H_2PO_4^-] =$

$[HPO_4^{2-}] =$

$[PO_4^{3-}] =$

$[H^+] =$

$[OH^-] =$

$[Na^+] =$

b) How many moles of solid NaOH would be required to increase the pH of this buffer to 7.6 at 298K?

5. (Credit 14 + 10 + 15 + 15)

Prof. G. H. Miller and his students at the University of Colorado have studied emu and ostrich eggshells to determine both the age of archeological samples back to 1000 ka (1,000,000 years before present) and the average temperature of the climate in which the materials have been preserved. Protein residues are quantitatively retained in the eggshells; however, the amino acid L-isoleucine (Ile) undergoes epimerization to D-alloisoleucine (Allo) with a rate that depends on temperature. No Allo is present in modern eggshell protein. The reaction has been shown to exhibit reversible first-order kinetics

$$\text{Ile} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Allo}$$

The temperature dependence was studied in simulated high-temperature experiments in the laboratory, from which the following values were obtained

$k_1 = 211\ a^{-1}$ at 161°C

and $k_1 = 2.05\ a^{-1}$ at 110°C

a) Use the above data to calculate an Arrhenius activation energy for k_1 for the Ile → Allo conversion.

b) When the Ile → Allo reaction is balanced by the reverse reaction at long times, the [Allo]/[Ile] ratio reaches 1.30. Calculate k_{-1} at 110° and 161°C.

c) Miller, et al. [Science (1990) **248**, 60-64] plotted values of the ratio [Allo]/[Ile] against time to obtain a value of k_1 from the slope. Using the relevant kinetic expressions for the first-order reversible mechanism, show that the initial rate

$$\upsilon_0 = \left[\frac{d([Allo]/[~~Iso~~\ Ile])}{dt}\right]_0 \cong k_1 \ \ ~~\frac{[Allo]}{[Iso]}~~$$

is a good approximation for $\frac{[Allo]}{[~~Iso~~\ Ile]} < 0.5$.

[Hint: You may wish to use the relation $e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots$ where $-1 < x < 1$.]

d) A sample of ostrich eggshell from the Apollo 11 cave in Namibia was dated at 9.3 ka using ^{14}C measurements, which are not temperature-dependent. Analysis showed that the [Allo]/[Ile] ratio for the eggshell protein was 0.144. Use these measurements together with the previous information to calculate the average temperature of the Apollo 11 cave during the past 10,000 years. State any important assumptions that you make.

6. (Credit 10 each)

a) Use nearest-neighbor values (Table 4.3) for the thermodynamics of DNA double-strand helix formation to calculate ΔG° at 298K for the complementary hexanucleotides

5′GCATCG-3′
●●●●●●
3′-CGTAGC-5′

b) Calculate f, the fraction of single strands in the helix at equilibrium at 298K for a solution where the initial concentration of each single strand is 1.0×10^{-4}M in aqueous buffer.

c) Calculate the osmotic pressure (in torr) of the solution of part (b) when measured against the aqueous buffer without the DNA.

d) Do you expect the osmotic pressure to increase, decrease or remain unchanged upon increasing the temperature to 303K? Explain your reasoning.