Columbia University in the City of New York
New York, N.Y. 10027

Chemistry C2407x		**1999**
Second Exam		**George Flynn**
November 4, 1999	**Total Points: 150**	**75 Minutes**

Answer Key

All questions are NOT weighted equally. I have attempted to order the questions from the least difficult to the most difficult, but "beauty is in the eye of the beholder", so skip around to find the problems that are easiest for you. Good luck!

Please print your name in the boxes provided and sign where indicated. Tear off this sheet and pass it to the right for the proctors to pick up.

Print your last name:
Print your first name:

Signature:____

Columbia University in the City of New York
New York, N.Y. 10027

Chemistry C2407x **1999**
Second Exam **George Flynn**
November 4, 1999 **Total Points: 150** **75 Minutes**

All questions are NOT weighted equally. I have attempted to order the questions from the least difficult to the most difficult, but "beauty is in the eye of the beholder", so skip around to find the problems that are easiest for you. Good luck!

Please print your name in the boxes provided.

Print your last name:

Print your first name:

Do not write anything else on this page. Answer the questions in the spaces provided on the following pages.

1a	**3a**
1b	**3b**
1c	**3c**
	3d
	4a
2a	**4b**
2b	**4c**
2c	**4d**

Print your name here:

Problem 1: (25 points) [Oxtoby Problem 10.27] Aspirin is acetylsalicylic acid ($HC_9H_7O_4$), for which K_a is $3.0\text{x}10^{-4}$. The molecular weight of acetylsalicylic acid is 180.16 gm/mole. A solution is made by dissolving 0.65 g of acetylsalicylic acid in water and diluting to 50.0 mL.

a)(5 points) What is the (initial) concentration of acetylsalicylic acid in solution before it ionizes and transfers a proton to water? Show all reasoning clearly.

MW = 180.16 g/mole 0.65 g sample

 # moles = 0.65 / 180.16 = 3.61×10^{-3} moles

$[HC_9H_7O_4]_o = 3.61 \times 10^{-3}$ moles / 0.050 liters

$[HC_9H_7O_4]_o = 7.22 \times 10^{-2}$ moles/liter

$[HC_9H_7O_4]_o = 7.22 \times 10^{-2}$ M

b)(15 points) Calculate the $[H_3O^+]$ at equilibrium for this solution. (The usual approximate solution gives too large an error to be an acceptable result, so proceed accordingly.) Show all reasoning clearly.

$HC_9H_7O_4 + H_2O = H_3O^+ + C_9H_7O_4^-$

Neglect H_3O^+ from $H_2O + H_2O = H_3O^+ + OH^-$

$HC_9H_7O_4 + H_2O = H_3O^+ + C_9H_7O_4^-$

C_o-x x x

C_o = 0.0722 M (part a)

$K_a = [H_3O^+][C_9H_7O_4^-] / [HC_9H_7O_4] = 3.0\times10^{-4}$

$K_a = (x)(x) / (C_o - x) = 3.0\times10^{-4}$

Since $K_a << 1$, $x << C_o$ → approximate solution

$x^2/C_o \approx 3.0 \times 10^{-4}$

$x^2 = (0.0722)(3.0\times10^{-4}) = 21.66\times10^{-6}$

$x = [H_3O^+] = 4.65\times10^{-3}$ M (Note that x is about 6% of C_o)

Exact solution: $x^2 + (3.0\times10^{-4})x - (.0722)(3.0\times10^{-4}) = 0$

$2x = -(3.0\times10^{-4}) \pm [(3.0\times10^{-4})^2 + 4(.0722)(3.0\times10^{-4})]^{1/2}$

$x = [H_3O^+] = 4.51\times10^{-3}$ M

Print your name here:

c)(5 points) Calculate the pH of the solution in part (b). Show all reasoning clearly.

pH = $-\log_{10}[H_3O^+]$
pH = $-\log_{10}(4.65\times10^{-3})$ (approximate result)
pH = 2.33
pH = $-\log_{10}(4.51\times10^{-3})$ (exact result)
pH = 2.35

Print your name here:

Problem 2: (35 points) [Oxtoby Problem 13.46] The conversion of dissolved carbon dioxide in blood to HCO_3^- and H_3O^+ is catalyzed by the enzyme carbonic anhydrase. The reaction is:

$$CO_2 + 2\,H_2O \rightarrow HCO_3^- + H_3O^+$$

When catalyzed by carbonic anhydrase, this reaction obeys Michaelis-Menten kinetics (all elementary steps):

$$\mathbf{E+CO_2 \xrightarrow{k_1} ECO_2 \qquad E + CO_2 \xleftarrow[k_{-1}]{} ECO_2}$$

$$\mathbf{ECO_2 + 2\,H_2O \xrightarrow{k_2'} E + HCO_3^- + H_3O^+} \quad \textbf{(Product} \equiv \mathbf{P = [HCO_3^-])}$$

The Michaelis-Menten constants for this enzyme and substrate are $K_m = 8\times10^{-5}$ mol L^{-1} and $k_2 = 6\times10^5\ s^{-1}$.

a)(15 points) Using the above elementary steps for the reaction mechanism, **derive** (as done in the homework solution for this problem) an expression for dP/dt in terms of the total enzyme concentration $[E_0]$, the concentration of carbon dioxide $[CO_2]$ and the constants k_2 and K_m. Be sure to indicate how K_m and k_2 depend on the elementary rate constants k_1, k_{-1}, and k_2 . Show all reasoning clearly.

$d[P]/dt = k_2'[H_2O]^2[ECO_2]$

Usually, $[H_2O] >>> [E], [ECO_2]$, etc., and remains constant,

so $k_2'[H_2O]^2 \equiv k_2 \rightarrow$

$d[P]/dt = k_2'[H_2O]^2[ECO_2] = k_2[ECO_2]$

$d[ECO_2]/dt = k_1[E][CO_2] - (k_{-1} + k_2'[H_2O]^2)[ECO_2] = 0$

$d[ECO_2]/dt = k_1[E][CO_2] - (k_{-1} + k_2)[ECO_2] = 0$

$[E_0] = [E] + [ECO_2]$

$k_1[E_0][CO_2] - k_1[ECO_2][CO_2] - (k_{-1} + k_2)[ECO_2] = 0$

$[ECO_2] = k_1[E_0][CO_2] \,/\, \{k_1[CO_2] + (k_{-1} + k_2)\}$

$[ECO_2] = [E_0] \,/\, \{1 + (k_{-1} + k_2) / k_1[CO_2]\}$

$d[P]/dt = k_2'[H_2O]^2[ECO_2] = k_2[ECO_2]$

$$\mathbf{d[P]/dt = k_2[E_0] \,/\, \left\{1+\frac{k_{-1}+k_2}{k_1}\frac{1}{[CO_2]}\right\}}$$

This is exactly the M-M result with $k_2[E_0] = V_{max}$

and $(k_{-1} + k_2) / k_1 = k_m$ with $[CO_2] = [S]$ and $k_2'[H_2O]^2 \equiv k_2$

Print your name here:

b)(10 points) Calculate the maximum rate of reaction of carbon dioxide if the total enzyme concentration is 5×10^{-6} M.. Show all reasoning clearly.

Given $k_m = 8\times10^{-5}$ mole/liter and $k_2 = 6\times10^{5}\ s^{-1}$
If $[E_0] = 5\times10^{-6}$ M
$d[P]/dt|_{max}$ = limit $[CO_2] \rightarrow \infty = k_2[E_0]$ (see part a above)
$V_{max} = (6\times10^{+5}\,s^{-1})(5\times10^{-6}M) = 3.0$ mole/liter–s

c)(10 points) Calculate the carbon dioxide concentration at which the reaction rate reaches 30% of its maximum value calculated in part **b** where the total enzyme concentration is 5×10^{-6} M. Show all reasoning clearly.

$d[P]/dt = 0.3\ V_{max}$
$d[P]/dt = V_{max}\ /\ (1 + k_m/[CO_2])$
$d[P]/dt = 0.3\ V_{max} = V_{max}\ /\ (1+ k_m/[CO_2]_{0.3})$
$1+ k_m/[CO_2]_{0.3} = 1/0.3$
$k_m/[CO_2]_{0.3} = (1/0.3) - 1 = (1 - 0.3)/0.3 = 7/3$
$[CO_2]_{0.3} = k_m\ (3/7)$
$[CO_2]_{0.3} = \{(8\times10^{-5})$ mole/liter$\}\ 3/7$
$[CO_2]_{0.3} = 3.43\times10^{-5}$ mole/liter

Print your name here:

Problem 3: (55 Points)[Much in common with Oxtoby problems 10.45, 10.49, 10.54 and 10.55 and the titration recitation exercise.]A solution is prepared by adding 0.25 moles of acetic acid, CH_3COOH, to enough water to make precisely 1.00 liters of solution. The pH of the solution is found to be 2.68.

a) (10 points) Determine K_a, the acid ionization constant, for acetic acid. Show all reasoning and calculations clearly!

$CH_3COOH + H_2O = CH_3COO^- + H_3O^+$

0.25 – x	**x**	**x**

Here moles and concentration are the same since V=1 liter

Have ignored H_3O^+ from $H_2O+H_2O = H_3O^+ + OH^-$

$K_a=[CH_3COO^-][H_3O^+]/[CH_3COOH]$

$K_a= (x)(x)/(.25-x)$

But $x = [H_3O^+] = 10^{-2.68}$ is given (pH = 2.68)!

$K_a= (10^{-2.68})(10^{-2.68})/(.25-10^{-2.68})$

$K_a = 1.76\times10^{-5}$

To this one liter of solution is added 0.100 moles of solid sodium hydroxide (NaOH), a strong base. The volume of the solution does not change.

b)(20 points) What is the pH of this new solution? Show all reasoning and calculations clearly!

$CH_3COOH + OH^- = CH_3COO^- + H_2O$

0.25	**0.1**		**Initial**
0.15	**≈ 0**	**0.10**	**Intermediate**
0.15+x	**x**	**0.10-x**	**Final**

Here moles and concentration are the same since V=1 liter

$K_b=[CH_3COOH][OH^-]/[CH_3COO^-]$

But this is a buffer with large concentration of weak acid CH_3COOH and its conjugate base CH_3COO^-, so x<<0.10

$K_b= (0.15+x)(x)/(.10-x)\approx (0.15)(x)/(.10)$

$x = K_b(0.10)/(0.15)$

$K_b= K_w/K_a$ (free formula sheet)

$K_a = 1.76\times10^{-5}$ From part (a) and $K_w = 10^{-14}$

So $K_b = K_w/K_a = 10^{-14}/(1.76\times10^{-5})$

$K_b = 5.68\times10^{-10}$

$x = K_b(0.10)/(0.15) = [5.68\times10^{-10}(0.10)]/(0.15)$

$x = [OH^-] = 3.79\times10^{-10}$

pOH = 9.42

pH = 14-pOH

pH = 4.58

To this one liter of solution is added another 0.150 moles of solid sodium hydroxide (NaOH), a strong base. The volume of the solution still does not change.

c)(15 points) What is the pH of this new solution? Show all reasoning and calculations clearly!

$CH_3COOH + OH^- = CH_3COO^- + H_2O$

0.15	**0.15**	**0.10**	**Initial**
≈ 0	≈ 0	**0.25**	**Intermediate**
x	**x**	**0.25-x**	**Final**

Here moles and concentration are the same since V=1 liter

$K_b = [CH_3COOH][OH^-]/[CH_3COO^-]$

$K_b = (x)(x)/(.25-x) \approx (x)(x)/(.25)$ $\{x << .25\}$

$x^2 = K_b(0.25)$

But from part (b) we have $K_b = 5.68\times10^{-10}$

$x = [OH^-] = 1.19\times10^{-5}$

pOH = 4.92

pH = 14 – pOH

pH = 9.08

To this one liter of solution is added another 0.001 moles of solid sodium hydroxide (NaOH), a strong base. The volume of the solution still does not change.

Print your name here:

d)(10 points) What is the pH of this new solution? Show all reasoning and calculations clearly!

CH_3COOH +	OH^- =	CH_3COO^- + H_2O	
1.19×10^{-5}	1.19×10^{-5}	0.25	**Initial**
1.19×10^{-5}	$1.19\times10^{-5}+0.001$	0.25	**Intermediate**
$1.19\times10^{-5}-x$	$1.19\times10^{-5}+0.001-x$	$0.25+x$	**Final**

Here moles and concentration are the same since V=1 liter

However, $x << 0.001$ since max $x = 1.19\times10^{-5}$, so

$0.001 \cong [OH^-]$

pOH= 3.0

pH = 14-pOH

pH = 11

Print your name here:

Problem 4: (35 Points)[A lot in common with the derivation of the Lindemann unimolecular decomposition model described in class.] Simple photochemical reactions can be described by the following elementary kinetic steps which are *nearly* identical to the Lindemann unimolecular reaction scheme discussed in class:

(1) $A+h\nu \rightarrow A^*$

(2) $A^*+A \rightarrow A+A$ Rate constant k_2

(3) $A^* \rightarrow$ Products Rate constant k_3

The first step in this scheme may be thought of as a collision between an A molecule and a photon of energy hν. Such an elementary kinetic process occurs at a rate or velocity (for just this one step) $v_1=k_1I_0[A]$, where I_0 is the constant intensity of the light shining on the reaction mixture, and k_1 is the kinetic rate constant for this process. A* is an “activated complex” which can either be deactivated by a collision with unexcited A in step (2), or go on to product in step (3). [The collisional activation of A to form A* by a collision of two unactivated A molecules, a core assumption of the Lindemann model, may be ignored here.]

a)(5 Points) Write a differential rate equation for the rate of change of the intermediate species [A*] using this kinetic scheme. Show all reasoning clearly.

$d[A^*]/dt = k_1I_0[A] - k_2[A][A^*] - k_3[A^*]$

First term is creation using light

Second term is destruction through second order quenching

Third term is destruction via unimolecular product production

b)(10 points) Making appropriate approximations solve the equation in part (a) above for [A*]. Show reasoning clearly!

$d[A^*]/dt = k_1I_0[A] - k_2[A][A^*] - k_3[A^*]$

$d[A^*]/dt = 0$, steady state approximation

$0 = k_1I_0[A] - k_2[A][A^*] - k_3[A^*]$

$k_1I_0[A] = \{k_2[A] + k_3\}[A^*]$

$k_1I_0[A]/\{k_2[A] + k_3\} = [A^*]$

Print your name here:

c)(10 points) Under what conditions would the result of part (b) above lead to a rate equation for the appearance of product, dP/dt, which is independent of the concentration of A? Show all work clearly, especially the equation for dP/dt under these conditions!

$dP/dt = k_3[A^*]$

$k_1I_0[A]/\{k_2[A] + k_3\} = [A^*]$ (part b)

$dP/dt = k_3\ k_1I_0[A]/\{k_2[A] + k_3\}$

When $k_2[A] >> k_3$

$dP/dt = k_3\ k_1I_0[A]\ /\{\ k_2[A]\} = k_3\ k_1I_0/k_2$, independent of [A]

d)(10 points) The quantum yield, φ, for such a photochemical reaction is defined as the fraction of photons absorbed that lead to reaction (product formation). Alternatively, φ can be defined equivalently as the number of product molecules formed per second (i.e. dP/dt) divided by the number of photons absorbed per second (v_1 for the first step of the above elementary scheme). Find an expression for φ in terms of rate constants and [A] using the information given at the beginning of this problem and the results of part (b). Under what conditions does φ→1? Show all work clearly!

Photons absorbed per second = $v_1 = k_1I_0[A]$

$dP/dt = k_3\ k_1I_0[A]/\{k_2[A] + k_3\}$ (part c above)

$\phi = [dP/dt]/k_1I_0[A] = [k_3\ k_1I_0[A]/\{k_2[A] + k_3\}]/k_1I_0[A]$

$\phi = [dP/dt]/k_1I_0[A] = k_3/\{k_2[A] + k_3\}$

$k_2[A] << k_3 \rightarrow$

$\phi = [dP/dt]/k_1I_0[A] \rightarrow k_3/\{k_3\} = 1$

The End