

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

Chemistry C2407x
Second Exam
October 29, 1998

Total Points: 150

1998
George Flynn
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: _____

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

1a

2d

1b

2e

1c

3a

1d

3b

1e

4a

2a

4b

2b

4c

2c

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Problem 1: (50 points) [Oxtoxy Problems 10.28 and 10.35]

Vitamin C is ascorbic acid ($\text{HC}_6\text{H}_7\text{O}_6$), for which K_a is 8.0×10^{-5} . The molecular weight of ascorbic acid is 176.126 gm/mole. A 500-mg tablet of pure vitamin C is dissolved in water and diluted to 100.0 mL.

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

$$\text{MW} = 176.126 \text{ g/mole} \quad 500 \text{ mg sample} = 0.500 \text{ g}$$

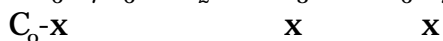
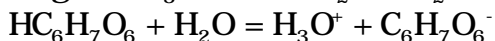
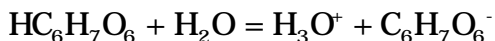
$$\# \text{ moles} = 0.500 / 176.126 = 2.84 \times 10^{-3} \text{ moles}$$

$$[\text{HC}_6\text{H}_7\text{O}_6]_0 = 2.84 \times 10^{-3} \text{ moles} / 0.100 \text{ liters}$$

$$[\text{HC}_6\text{H}_7\text{O}_6]_0 = 2.84 \times 10^{-2} \text{ moles/liter}$$

$$[\text{HC}_6\text{H}_7\text{O}_6]_0 = 2.84 \times 10^{-2} \text{ M}$$

b) (15 points) Calculate the $[\text{H}_3\text{O}^+]$ at equilibrium for this solution. Show all reasoning clearly.



$$\text{C}_0 = 0.0284 \text{ M (part a)}$$

$$K_a = [\text{H}_3\text{O}^+][\text{C}_6\text{H}_7\text{O}_6^-] / [\text{HC}_6\text{H}_7\text{O}_6] = 8.0 \times 10^{-5}$$

$$K_a = (x)(x) / (\text{C}_0 - x) = 8.0 \times 10^{-5}$$

Since $K_a \ll 1$, $x \ll \text{C}_0$

$$x^2 / \text{C}_0 = 8.0 \times 10^{-5}$$

$$x^2 = (0.0284)(8.0 \times 10^{-5}) = 2.27 \times 10^{-6}$$

$$x = [\text{H}_3\text{O}^+] = 1.51 \times 10^{-3} \text{ M}$$

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

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log_{10}(1.51 \times 10^{-3})$$

$$\text{pH} = 2.82$$

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Morphine is a weak base for which K_b is 8.0×10^{-7} . 0.0400 mole of morphine is dissolved in water and diluted to 600 mL.

d) (15 points) Calculate the $[\text{OH}^-]$ at equilibrium for this solution. Show all reasoning clearly.

$$\begin{aligned} \text{M} + \text{H}_2\text{O} &= \text{MH}^+ + \text{OH}^- \\ \text{C}_o - x & \qquad \qquad \qquad x & \qquad \qquad x \\ (\text{neglects } \text{OH}^- \text{ from } \text{H}_2\text{O} + \text{H}_2\text{O} = \text{H}_3\text{O}^+ + \text{OH}^-) \\ [\text{M}]_o = \text{C}_o &= (0.0400) / (0.600 \text{ liters}) = 0.06667 \text{ M} \\ K_b = [\text{MH}^+][\text{OH}^-] / [\text{M}] &= 8.0 \times 10^{-7} \\ (x)(x) / (\text{C}_o - x) &= 8.0 \times 10^{-7} \\ K_b \ll 1 \quad x \ll \text{C}_o & \\ x^2 = \text{C}_o(8.0 \times 10^{-7}) & \\ x^2 = (0.06667)(8.0 \times 10^{-7}) &= 5.334 \times 10^{-8} \\ x = [\text{OH}^-] &= 2.31 \times 10^{-4} \end{aligned}$$

e) (10 points) Calculate the pH of the solution in part (d), assuming that the temperature is 25°C . Show all reasoning clearly.

$$\begin{aligned} [\text{H}_3\text{O}^+][\text{OH}^-] &= K_w \\ [\text{H}_3\text{O}^+][\text{OH}^-] &= 10^{-14} \text{ (} 25^\circ \text{C)} \\ [\text{OH}^-] &= 2.31 \times 10^{-4} \text{ (part d)} \\ [\text{H}_3\text{O}^+][2.31 \times 10^{-4}] &= 10^{-14} \\ [\text{H}_3\text{O}^+] &= 4.33 \times 10^{-11} \\ \text{pH} &= -\log_{10}[\text{H}_3\text{O}^+] \\ \text{pH} &= 10.36 \end{aligned}$$

Problem 2: (55 Points) [Much in common with Oxtoby problems 13.7, 13.35 and 13.39] The following data are measured for the reaction of A with B:

T=300 K:

A(mol/L)	B(mol/L)	Initial Rate(mol/L-s)
2.3×10^{-4}	3.1×10^{-5}	5.20×10^{-4}
4.6×10^{-4}	6.2×10^{-5}	4.16×10^{-3}
9.2×10^{-4}	6.2×10^{-5}	1.66×10^{-2}

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T=310 K:

A(mol/L)	B(mol/L)	Initial Rate(mol/L-s)
2.3×10^{-4}	3.1×10^{-5}	1.04×10^{-3}

a) (10 points) Determine the order of the reaction with respect to species A. Show all reasoning clearly.

$$R_i = k[A]_o^n [B]_o^m$$

$$\text{Row 2: } R_i(2) = k(4.6 \times 10^{-4})^n (6.2 \times 10^{-5})^m = 4.16 \times 10^{-3}$$

$$\text{Row 3: } R_i(3) = k(9.2 \times 10^{-4})^n (6.2 \times 10^{-5})^m = 1.66 \times 10^{-2}$$

Take ratio of equations for Rows 2 & 3:

$$\frac{k(4.6 \times 10^{-4})^n (6.2 \times 10^{-5})^m}{k(9.2 \times 10^{-4})^n (6.2 \times 10^{-5})^m} = \frac{4.16 \times 10^{-3}}{1.66 \times 10^{-2}}$$

$$\frac{4.6 \times 10^{-4} \quad^n}{9.2 \times 10^{-4}} = \frac{4.16 \times 10^{-3}}{1.66 \times 10^{-2}} = 0.2506$$

$$\frac{4.6 \times 10^{-4} \quad^n}{9.2 \times 10^{-4}} = \frac{4.16 \times 10^{-3}}{1.66 \times 10^{-2}} = 0.2506$$

$$(1/2)^n = 0.2506$$

$$(2/1)^n = 3.990$$

$$n=2$$

b) (10 points) Determine the order of the reaction with respect to species B. Show all reasoning clearly.

$$R_i = k[A]_o^2 [B]_o^m$$

$$\text{Row 1: } k(2.3 \times 10^{-4})^2 (3.1 \times 10^{-5})^m = 5.2 \times 10^{-4}$$

$$\text{Row 2: } k(4.6 \times 10^{-4})^2 (6.2 \times 10^{-5})^m = 4.16 \times 10^{-3}$$

Take ratio of equations for Rows 1 & 2:

$$\frac{k(2.3 \times 10^{-4})^2 (3.1 \times 10^{-5})^m}{k(4.6 \times 10^{-4})^2 (6.2 \times 10^{-5})^m} = \frac{5.20 \times 10^{-4}}{4.16 \times 10^{-3}}$$

$$\frac{k(2.3 \times 10^{-4})^2 (3.1 \times 10^{-5})^m}{k(4.6 \times 10^{-4})^2 (6.2 \times 10^{-5})^m} = \frac{5.20 \times 10^{-4}}{4.16 \times 10^{-3}}$$

$$(2.3/4.6)^2 (3.1/6.2)^m = 0.125$$

$$(1/2)^2 (1/2)^m = 0.125$$

$$(1/2)^m = 4(0.125) = 0.500$$

$$(0.5)^m = 0.5$$

$$m=1$$

Print your name here:

c) (10 points) Determine the kinetic rate constant (including units!) for the reaction of A with B at T=300 K. Show all reasoning clearly.

Can use any row of T = 300 K data

$$R_i = k[A]_o^2[B]_o$$

$$\text{Row 1: } 5.20 \times 10^{-4} \text{ Ms}^{-1} = k(2.3 \times 10^{-4} \text{ M})^2(3.1 \times 10^{-5} \text{ M})$$

$$k = [(5.20 \times 10^{-4}) / (2.3 \times 10^{-4})^2(3.1 \times 10^{-5})](\text{Ms}^{-1}) / \text{M}^2\text{M}$$

$$k = 3.17 \times 10^8 \text{ M}^{-2}\text{s}^{-1}$$

d) (10 points) Determine the kinetic rate constant (including units!) for the reaction of A with B at T=310 K. Show all reasoning clearly.

Only 1 set of data at T = 310 K

$$R_i = k[A]_o^2[B]_o$$

$$1.04 \times 10^{-3} \text{ Ms}^{-1} = k(2.3 \times 10^{-4})^2(3.1 \times 10^{-5})\text{M}^2\text{M}$$

$$k = [(1.04 \times 10^{-3} \text{ Ms}^{-1}) / (2.3 \times 10^{-4} \text{ M})^2(3.1 \times 10^{-5} \text{ M})]$$

$$k = 6.34 \times 10^{-8} \text{ M}^{-2}\text{s}^{-1}$$

e) (15 points) Determine the activation energy for the reaction. Show all reasoning clearly.

$$k = Ae^{-E_a / RT}$$

Simplest assumption: A indep of T

$$k(310) / k(300) = Ae^{-E_a/R(310)} / Ae^{-E_a/R(300)}$$

$$k(310) / k(300) = e^{-E_a/R(310)} / e^{-E_a/R(300)}$$

$$\ln[k(310)/k(300)] = -E_a(1/310R) + E_a(1/300R)$$

$$\text{From c,d } \ln[k(310) / k(300)] = \ln[(6.34 \times 10^{-8}) / (3.17 \times 10^8)]$$

$$\ln[k(310) / k(300)] = \ln 2 = (E_a/R)(1/300 - 1/310)$$

$$\ln 2 = (E_a/R)(1.075 \times 10^{-4} \text{ deg}^{-1})$$

$$R = 8.314 \text{ joules / mole-deg}$$

$$E_a = [R \ln 2] / [1.075 \times 10^{-4} \text{ deg}^{-1}]$$

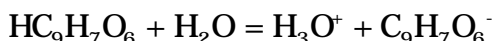
$$E_a = (0.693)(8.314) / (1.075 \times 10^{-4}) \text{ joules / mole}$$

$$E_a = 53594 \text{ joules / mole}$$

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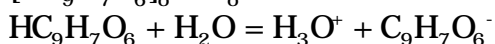
Problem 3: (25 Points) [Much in common with Oxtoby problems 10.17, 10.18, 10.27 and 10.39] The ion product of water in blood at 98.6° C is 2.4×10^{-14} . In a test of the behavior of aspirin in blood, a biochemist dissolves 0.01 moles of acetylsalicylic acid (aspirin), $\text{HC}_9\text{H}_7\text{O}_6$, in a 100 mL blood sample thermostated at 98.6° C. She measures the pH and finds it to be 3.00.

a) (10 points) Determine the acid ionization constant for aspirin in blood at 98.6° C. That is, determine K_a for the reaction:



Show all reasoning and calculations clearly!

$$[\text{HC}_9\text{H}_7\text{O}_6]_0 = C_o = 0.01 \text{ moles} / 0.100 \text{ liter} = 0.100 \text{ M}$$



$$C_o - x \qquad \qquad \qquad x \qquad \qquad x$$

$$x = [\text{H}_3\text{O}^+] = 10^{-3} \text{ (given)}$$

$$K_a = [\text{H}_3\text{O}^+][\text{C}_9\text{H}_7\text{O}_6^-] / [\text{HC}_9\text{H}_7\text{O}_6]$$

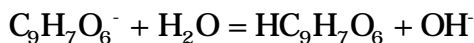
$$K_a = x^2 / (C_o - x)$$

$$\text{but } x = 10^{-3}, C_o = 0.100$$

$$K_a = (10^{-3})^2 / (0.100 - 10^{-3})$$

$$K_a = 1.010 \times 10^{-5}$$

b) (15 points) The same biochemist takes a second sample of blood and dissolves 0.0100 moles of the salt of the conjugate base of aspirin ($\text{NaC}_9\text{H}_7\text{O}_6$) in a new 100 mL blood sample also thermostated at 98.6° C. Determine the pH of this blood solution. Show all reasoning and calculations clearly!



$$C_o - x \qquad \qquad \qquad x \qquad \qquad x$$

$$C_o = 0.0100 \text{ moles} / 0.100 \text{ liters} = 0.100 \text{ M}$$

$$K_b = x^2 / (C_o - x) = [\text{HC}_9\text{H}_7\text{O}_6][\text{OH}^-] / [\text{C}_9\text{H}_7\text{O}_6^-]$$

$$K_b = \frac{[\text{HC}_9\text{H}_7\text{O}_6][\text{OH}^-][\text{H}_3\text{O}^+]}{[\text{C}_9\text{H}_7\text{O}_6^-][\text{H}_3\text{O}^+]} = \frac{K_w}{K_a}$$

$$K_a = 1.01 \times 10^{-5} \text{ (part a)}$$

$$K_w = 2.4 \times 10^{-14} \text{ (given)}$$

$$K_b = 2.4 \times 10^{-14} / 1.01 \times 10^{-5} = 2.38 \times 10^{-9}$$

$$K_b \ll 1 \quad x \ll C_o$$

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$$x^2 / C_o = K_b$$

$$x^2 = (0.100)(2.38 \times 10^{-9})$$

$$x = [\text{OH}^-] = 1.54 \times 10^{-5}$$

$$[\text{OH}^-][\text{H}_3\text{O}^+] = K_w = 2.4 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = (2.4 \times 10^{-14}) / (1.54 \times 10^{-5})$$

$$[\text{H}_3\text{O}^+] = 1.56 \times 10^{-9}$$

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = 8.81$$

Problem 4 (20 points) The graph on the next page shows data (initial rate in units of mM/min vs. substrate concentration in mM = 10^{-3} M) for the decomposition of paraoxon by organophosphorus hydrolase in foam. This is the same data Dr. Giancarlo showed you in class. Dots represent actual data points, and the solid curve through the points is the best fit line to these points. The solid straight line at the top of the graph is the asymptotic limit of the solid curve at infinite substrate concentration. Answer all of the following questions assuming the decomposition of paraoxon substrate by organophosphorus hydrolase obeys Michaelis-Menten kinetics.

a) (5 points) Determine the numerical value (including units) of the kinetic rate constant k_2 if the total enzyme concentration is 5×10^{-6} M. Show all reasoning clearly by using formulas from the free formula sheet.

For Michaelis-Menten kinetics, initial rate v is

$$v = k_2 E_o / (1 + K_m / [S])$$

$$\text{As } [S] \rightarrow \infty, K_m / [S] \rightarrow 0$$

$$\text{and } v \rightarrow v_{\max} = k_2 E_o$$

v_{\max} is the asymptotic value on the graph

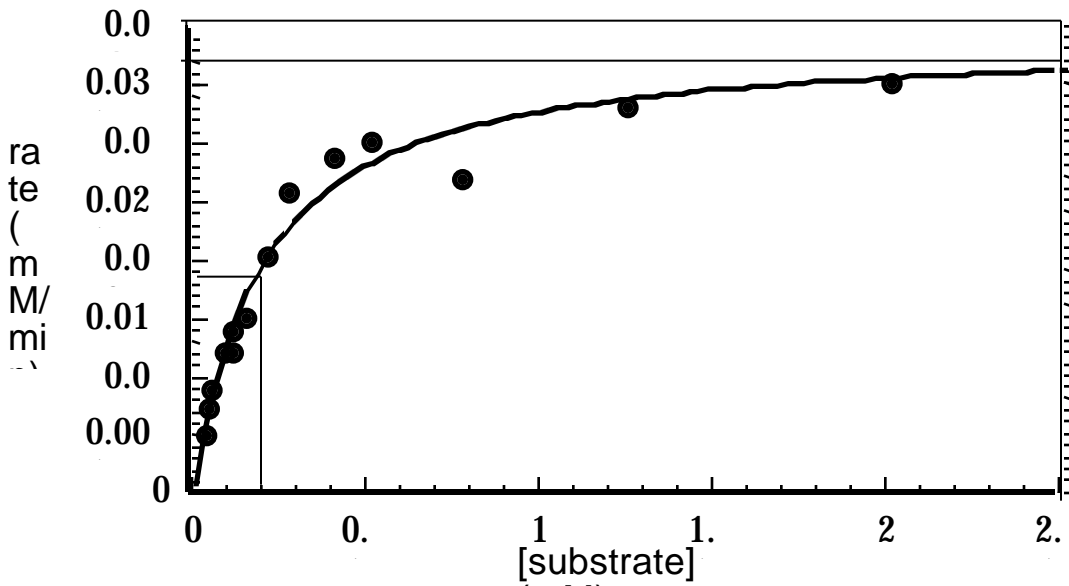
$$v_{\max} = 0.037 \text{ mM/min}$$

$$k_2 E_o = 0.037 \text{ mM/min}$$

$$E_o = 5 \times 10^{-6} \text{ M} = 5 \times 10^{-3} \text{ mM}$$

$$k_2 = (0.037 \text{ mM / min}) / (5 \times 10^{-3} \text{ mM})$$

$$k_2 = 7.4 \text{ min}^{-1}$$



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b) (5 points) What is the numerical value (including units) of K_M , the Michaelis-Menten constant for this system. Show all reasoning clearly using formulas from the free formula sheet.

$$v = v_{\max} / [1 + K_m / [S]]$$

$$v = v_{\max} / 2 \text{ when } [S] = [S]_{1/2}$$

$$\text{From graph, } v_{\max} / 2 = (0.037) / 2 = 0.0185 \text{ mM}\cdot\text{min}^{-1}$$

$$[S] = [S]_{1/2} \text{ at } v = v_{\max} / 2$$

$$\text{From graph } [S]_{1/2} = 0.2 \text{ mM}$$

$$v_{\max} / 2 = v_{\max} / [1 + (K_m / 0.2 \text{ mM})]$$

$$1 + (K_m / 0.2 \text{ mM}) = 2$$

$$K_m = 0.2 \text{ mM}$$

c) (10 points) If the total enzyme concentration is halved to $2.5 \times 10^{-6} \text{ M}$, give the numerical value (including units) for the maximum initial rate at infinite substrate concentration and the value of K_M , the Michaelis-Menten constant. Show all reasoning clearly using formulas from the free formula sheet..

$$v_{\max} = k_2 E_o$$

$$k_2 = 7.4 \text{ min}^{-1} \text{ (part a)}$$

$$E_o = 2.5 \times 10^{-6} \text{ M (given)}$$

$$v_{\max} = (7.4 \text{ min}^{-1})(2.5 \times 10^{-6} \text{ M})$$

$$v_{\max} = 1.85 \times 10^{-5} \text{ M}\cdot\text{min}^{-1} = 1.85 \times 10^{-2} \text{ mM}/\text{min}$$

$$K_m = (k_{-1} + k_2) / k_1 \text{ is independent of } E_o$$

$$K_m = 0.2 \text{ mM (part b)}$$

The End