Chemistry C2407 Problem Set 2

Solutions to Oxtoby Even Numbered Problems

Problem 13.32

Reaction Mechanism Elementary Steps:

$A \xleftarrow[k_{-1}]{} B + C$, $A \xrightarrow{k_1} B + C$, $C + D \xleftarrow[k_{-2}]{} E$, $C + D \xrightarrow{k_2} E$

$E \xrightarrow{k_3} F$

Make steady state assumption for [C], {E} and express rate of production of [F] in terms of [A], [B], [D]

$d[F] / dt = k_3[E]$

$d[E] / dt = k_2[C][D] - k_{-2}[E] - k_3[E] = 0$ (Steady State Assumption)

$[E] = k_2[D][C] / (k_{-2} + k_3)$

Since [C] is an intermediate (usually undetectable in the laboratory) used to eliminate it →

$d[C] / dt = k_1[A] - k_{-1}[B][C] - k_2[C][D] + k_{-2}[E] = 0$

To solve for [C], substitute $[E] = k_2[D][C] / (k_{-2} + k_3)$ →

$k_1[A] - k_{-1}[B][C] - k_2[D][C] + k_{-2}k_2[D][C] / (k_{-2} + k_3) = 0$

Solve for [C] →

$$[C] = \frac{\mathbf{k_1[A]}}{\mathbf{k_{-1}[B] + k_2[D] - k_2k_{-2}[D]/(k_{-2} + k_3)}}$$

$dF / dt = k_3[E] = \{k_3k_2\,[D] / (k_{-2} + k_3)\,\}[C]$

$$dF / dt = \left\{\frac{\mathbf{k_2k_3[D]}}{\mathbf{k_{-2} + k_3}}\right\}\left\{\frac{\mathbf{k_1[A]}}{\mathbf{k_{-1}[B] + k_2[D] - k_2k_{-2}[D]/(k_{-2} + k_3)}}\right\}$$

$dF / dt = k_1k_2k_3\,[A][D] / \{k_{-1}(k_{-2} + k_3)[B] + k_2(k_{-2} + k_3)[D] - k_2k_{-2}[D]\}$

but $k_2(k_{-2} + k_3)[D] - k_2k_{-2}[D] = k_3k_2[D]$

So →

$dF/dt = k_1k_2k_3[A][D] / \{k_{-1}(k_{-2} + k_3)[B] + k_2k_3[D]\}$ (Steady State Result)

For problem 25b, the first 2 steps are assumed to reach equilibrium with

$k_1[A] = k_{-1}[B][C]$ and $k_2[C][D] = k_{-2}[E]$

$dF/dt = k_3[E]$

From 1st of these, $[C] = k_1[A] / k_{-1}[B]$ while the 2nd gives

$[E] = k_2[D][C] / k_{-2}$ →

$[E] = (k_2 / k_{-2})[D]\{k_1[A] / k_{-1}[B]\}$ or →

$[E] = k_1k_2[A][D] / k_{-1}k_{-2}[B]$

$d[F]/dt = k_3[E] = k_1k_2k_3[A][D] / k_{-1}k_{-2}[B]$

The steady state expression above reduces to this when

$k_{-1}k_{-2}[B] >> k_{-1}k_3[B] + k_2k_3[D]$

This is equivalent to $k_{-2} >> k_3$ and $k_{-1}k_{-2}[B] >> k_2k_3[D]$

Problem 13.46

$CO_2 + 2\ H_2O \rightarrow HCO_3^- + H_3O^+$ when catalyzed by carbonic anhydrase, obeys Michaelis-Menten kinetics

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

$ECO_2 + 2\ H_2O \xrightarrow{k_2'} E + HCO_3^- + H_3O^+$ (Product ≡ P = $[HCO_3^-]$)

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

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

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

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

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

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

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

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

$d[P]/dt = k_2[ECO_2]$

$$d[P]/dt = k_2[E_0] \Big/ \left\{1 + \frac{\mathbf{k}_{-1} + \mathbf{k}_2}{\mathbf{k}_1} \frac{1}{[\mathbf{CO}_2]}\right\}$$

This is exactly the M-M result with $k_2[E_0] = V_{max}$ and $(k_{-1} + k_2) / k_1 = k_M$ with $[CO_2] = [S]$

Given $k_M = 8 \times 10^{-5}$ mole/liter and $k_2 = 6 \times 10^5\ s^{-1}$

a) What is V_{max} if $[E_0] = 5 \times 10^{-6}$ M

$d[P]/dt\ |_{max}$ = limit $[CO_2] \rightarrow \infty = k_2[E_0]$

$V_{max} = (6 \times 10^{+5}\ s^{-1})(5 \times 10^{-6}\ M) = 3.0$ mole/liter –s

b) At what $[CO_2]$ will $d[P]/dt = 0.3\ V_{max}$?

$d[P]/dt = V_{max} / (1 + k_M / [CO_2])$

$d[P]/dt = 0.3\ V_{max} = V_{max} / (1 + k_M / [CO_2]_{0.3})$

$1 + k_M / [CO_2]_{0.3} = 1 / 0.3$

$k_M / [CO_2]_{0.3} = 1 / 0.3 - 1 = (1 - 0.3) / 0.3 = 7 / 3$

$[CO_2]_{0.3} = k_M (3 / 7)$

$[CO_2]_{0.3} = \{(8 \times 10^{-5})$ mole/liter$\}\ 3 / 7$

$[CO_2]_{0.3} = 3.43 \times 10^{-5}$ mole/liter

Problem 10.18

pH = 7.4 = $-\log[H_3O^+]$ $[H_3O^+] = 10^{-7.4}$

$[H_3O^+] = 3.98 \times 10^{-8}$ M

$K_W = [H_3O^+][OH^-] = 2.4 \times 10^{-14}$

$[OH^-] = 2.4 \times 10^{-14} / [H_3O^+]$

$[OH^-] = 2.4 \times 10^{-14} / 3.98 \times 10^{-8}$

$[OH^-] = 6.03 \times 10^{-7}$ M

Problem 10.22

a) $C_5H_4NCOOH + H_2O\ (l) \Leftrightarrow C_5H_4NCOO^-\ (aq) + H_3O^+\ (aq)$

b) If K_a for C_5H_4NCOOH is 1.5×10^{-5}, what is K_b for

$C_5H_4NCOO^-$ (aq) +H_2O (l) ⇔C_5H_4NCOOH (aq) + OH^- (aq)

$K_b = [C_5H_4NCOOH][OH^-] / [C_5H_4NCOO^-]$

Multiply by $[H_3O^+] / [H_3O^+] \rightarrow$

$K_b = \{[C_5H_4NCOOH] / [C_5H_4NCOO^-][H_3O^+]\}\{[OH^-][H_3O^+]\}$

$K_b = (1 / K_a) K_w = K_w / K_a$

$K_b = 1.00 \times 10^{-14} / 1.5 \times 10^{-5} = 6.67 \times 10^{-10}$

c) The K_a for pyridinium ion $HC_5H_5N^+$, the conjugate acid of pyridine, C_5H_5N, (Table 10.2) is $5.6 \times 10^{-6} = K_a \rightarrow$

$K_b (C_5H_5N) = 1.0 \times 10^{-14} / 5.6 \times 10^{-6} = 1.79 \times 10^{-9}$

So $K_b (C_5H_5N) > K_b (C_5H_4NCOO^-)$

pyridine is the stronger base

Problem 10.28

Vitamin C, $HC_6H_7O_6$ has K_a 8.0×10^{-5}

? pH of a solution of a 500 mg tablet diluted to 100mL in H_2O.

Molecular weight of $HC_6H_7O_6$ is 176.126 gm/mole

500 mg = 0.5 gm = (0.5 / 176.126) moles

500 mg is 2.84×10^{-3} moles of ascorbic acid

Initial concentration is 2.84×10^{-3} moles / 0.1 liter

= 0.0284 M

$HC_6H_7O_6 + H_2O \Leftrightarrow C_6H_7O_6^- + H_3O^+$

0.0284-x x x

$K_a = [C_6H_7O_6^-][H_3O^+] / [HC_6H_7O_6] = 8.0 \times 10^{-5}$

$8.0 \times 10^{-5} = (x)(x) / (.0284 - x)$

Since $K_a << 1$ must not dissociate much $HC_6H_7O_6$

So guess x << 0.0284 →

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

$x = [H_3O^+] = 1.51 \times 10^{-3}$ M

pH = 2.82

"Exact Solution": $x^2 = (.0284 - x)\, 8.0 \times 10^{-5}$

$x^2 + 8.0 \times 10^{-5}x - 2.27 \times 10^{-6} = 0$

$2x = -8.0 \times 10^{-5} + (64 \times 10^{-10} + 4(2.27 \times 10^{-6}))^{1/2}$

$2x = -8 \times 10^{-5} + 3.01 \times 10^{-3}$

$x = [H_3O^+] = 1.47 \times 10^{-3}$, pH = 2.83

Problem 10.36

$CH_3NH_2 + H_2O \Leftrightarrow CH_3NH_3^+ + OH^-$

$K_b = 4.4 \times 10^{-4} = [CH_3NH_3^+][OH^-] / [CH_3NH_2]$

Initial concentration of CH_3NH_2 = 0.070 moles/ 0.8 liter

= 0.0875 M

$CH_3NH_2 + H_2O \Leftrightarrow CH_3NH_3^+ + OH^-$

0.0875 – x x x

$4.4 \times 10^{-4} = x^2 / (0.0875 - x)$

Approximate solution $0.0875 - x \approx .0875$

$x^2 = (0.0875)(4.4 \times 10^{-4}) = 3.85 \times 10^{-5}$

$x = [OH^-] = 6.20 \times 10^{-3}$ M

$[H_3O^+][OH^-] = K_w = 10^{-14}$

$[H_3O^+] = 10^{-14} / 6.20 \times 10^{-3} = 1.61 \times 10^{-12}$ M

$pH = -\log[H_3O^+] = 11.79$

"Exact Solution": $4.4 \times 10^{-4} = x^2 / (0.0875 - x)$

$x^2 + 4.4 \times 10^{-4}x - (.0875)(4.4 \times 10^{-4}) = 0$

$2x = -4.4 \times 10^{-4} + \{(4.4 \times 10^{-4})^2 + 4(.0875)(4.4 \times 10^{-4})\}^{1/2}$

$= -4.4 \times 10^{-4} + \{(1.54 \times 10^{-4})^{1/2}\}$

$2x = 1.198 \times 10^{-2}$ $\quad x = 5.99 \times 10^{-3}$

$[OH^-] = 5.99 \times 10^{-3}$

$[H_3O^+] = 10^{-14} / 5.99 \times 10^{-3} = 1.67 \times 10^{-12}$

$pH = 11.78$

Problem 10.46

The acid ionization of sulfanilic acid has the equilibrium law

$$\frac{[NH_2C_6H_4SO_3^-][H_3O^+]}{[NH_2C_6H_4SO_3H]} = K_a = 5.9 \times 10^{-4}$$

Initial concentrations: $[NH_2C_6H_4SO_3^-] = 0.13$ and $[NH_2C_6H_4SO_3H] = 0.20$

$NH_2C_6H_4SO_3H$	+	H_2O	=	$NH_2C_6H_4SO_3^-$	+	H_3O^+
0.20-x				0.13+x		x

a) The pH is computed by substituting 0.20 M –x for the concentration of sulfanilic acid and 0.13 M + x for the concentration of sulfanilate ion, solving for $x = [H_3O^+]$ and taking the negative logarithm. However, remember from our discussion of buffers, x<<< 0.2, 0.13. So,

$(0.13)(x)/(0.20) = 5.9 \times 10^{-4}$

Thus, $x = 9.08 \times 10^{-4}$ and the pH is 3.04.

b) Adding the HCl converts 0.040 mol of sulfanilate ion to its conjugate acid, sulfanilic acid.

$NH_2C_6H_4SO_3H$	+	H_2O	=	$NH_2C_6H_4SO_3^-$	+	H_3O^+	
0.20				0.13		.040	Initial
0.24				0.09		≈ 0	
0.24-x				0.09+x		x	Final

The concentrations of the two are 0.24 M – x and 0.09 M + x , respectively. Again remember from our discussion of buffers that x<<< .24, .09, so,

$(0.09)(x)/(0.24) = 5.9\text{x}10^{-4}$.

Thus $x = 1.57\text{x}10^{-3}$ and the pH is 2.80.

Problem 10.54

Initially, before add base, just have chloroacetic acid which dissociates to give its conjugate base:

$CH_2ClCOOH + H_2O = CH_2ClCOO^- + H_3O^+$
0.100-x x x

$$\frac{x^2}{0.1000 - x} = 1.4 \times 10^{-3}$$

but x<<<0.100:
x = 1.18×10^{-2} M = $[H_3O^+]$ pH = 1.93
(More exact if solve quadratic: x = 1.12×10^{-2} M = $[H_3O^+]$, pH = 1.95)

(b) After 5 mL of 0.100 M NaOH are added convert 0.500 millimoles of chloroacetic acid to its conjugate base and new volume is 55 mL. Original number of moles of chloroacetic acid = (50/1000)(0.1) =0.005 moles = 5 millimoles.

$CH_2ClCOOH + H_2O = CH_2ClCOO^- + H_3O^+$
.0050-.0005 .0005 ≈0 (Moles) (Action of base, NaOH)
(4.5/55) (0.5/55) ≈0 M

(4.5/55)-x (0.5/55)+x x

$$\frac{\left(\frac{5.00 \times 0.1000\text{mmol}}{55.00\text{mL}} + x\right)x}{\left(\frac{4.50\text{mmol}}{55.00\text{ mL}} - x\right)} = 1.4 \times 10^{-3}$$

$$\frac{\left(9.091 \times 10^{-3} + x\right)x}{8.182 \times 10^{-2} - x} = 1.4 \times 10^{-3}$$

$x^2 + (1.049)10^{-2}\,x - (1.145)\,10^{-4} = 0$

$x = 6.67 \times 10^{-3} = [H_3O^+]$ pH = 2.18

(Note x is significant (about 8%) compared to concentration of chloroacetic acid. Must solve quadratic!)

c) After addition of 25 mL of base, total volume is 75 mL:

$$\frac{\left(\frac{\mathbf{2.50mmol}}{\mathbf{75.00mL}}+x\right)x}{\left(\frac{\mathbf{2.50mmol}}{\mathbf{75.00mL}}-x\right)}=\mathbf{1.4\times 10^{-3}}$$

$$\frac{(\mathbf{0.0333}+x)x}{\mathbf{0.0333}-x}=\mathbf{1.4\times 10^{-3}}$$

$x = [H_3O^+] = 1.3 \times 10^{-3}$, pH = 2.89

d) After addition of 49 mL of base, total volume is 99 mL:

$$\frac{\left(\frac{\mathbf{4.90mmol}}{\mathbf{99.00mL}}+x\right)x}{\left(\frac{\mathbf{0.10mmol}}{\mathbf{99.00mL}}-x\right)}=\mathbf{1.4\times 10^{-3}}$$

$x = 2.8 \times 10^{-5} = [H_3O^+]$ pH = 4.56

e) After the addition of 49.9 mL of base, total volume is 99.9 mL:

$$\frac{\left(\frac{\mathbf{4.99mmol}}{\mathbf{99.90mL}}+x\right)x}{\left(\frac{\mathbf{0.010mmol}}{\mathbf{99.90mL}}-x\right)}=\mathbf{1.4\times 10^{-3}}$$

$x = 2.7 \times 10^{-6} = [H_3O^+]$ pH = 5.56

f) At the equivalence point, we have a 0.0500 M CH_2ClCOO^- solution because moles of chloroacetate at end point are same as moles of chloroacetic acid at the beginning (0.005 moles) but the volume is now 100mL.

$CH_2ClOO^-(aq) + H_2O(l) \Leftrightarrow CH_2ClCOOH(aq) + OH^-(aq)$

$[CH_2ClCOOH] = [OH^-] = x$

$$\frac{x^2}{0.0500 - x} = K_b = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-3}} = 7.14 \times 10^{-12}$$

$x = 6.0 \times 10^{-7} = [OH^-]$

pOH = 6.22   pH = 7.78

g) 0.10 mL NaOH beyond the equivalence point, volume is 100.10 mL.

$$\frac{(0.10\,\text{mL})(0.1000\,\text{M})}{100.10\,\text{mL}} = 1.0 \times 10^{-4}\,\text{M} = [\text{OH}^-]$$

pOH = 4.00   pH = 10.00

h) 5.00 mL NaOH beyond the equivalence point, volume is 105.0 mL.

$$\frac{(5.00\,\text{mL})(0.1000\,\text{M})}{105.00\,\text{mL}} = 4.76 \times 10^{-3}\,\text{M} = [\text{OH}^-],$$ pOH = 2.32   pH = 11.68