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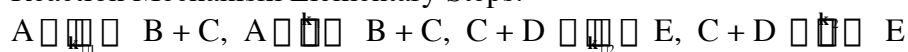
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**Problem Set 2**

**Solutions to Oxtoby Even Numbered Problems**

**Problem 13.32**

Reaction Mechanism Elementary Steps:



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

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

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

$$[E] = k_2[D][C] / (k_2 + k_3)$$

Since [C] is an intermediate (usually undetectable in the laboratory), use steady state approximation 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  $[E] = k_2[D][C] / (k_2 + k_3)$

$$k_1[A] - k_1[B][C] - k_2[D][C] + k_2k_2[D][C] / (k_2 + k_3) = 0$$

Solve for [C]

$$[C] = \frac{k_1[A]}{k_1[B] + k_2[D] + k_2k_2[D] / (k_2 + k_3)}$$

$$dF / dt = k_3[E] = \{k_3k_2[D] / (k_2 + k_3)\} [C]$$

$$dF / dt = \frac{k_2k_3[D]}{k_2 + k_3} \frac{k_1[A]}{k_1[B] + k_2[D] + k_2k_2[D] / (k_2 + k_3)}$$

$$dF / dt = k_1k_2k_3[A][D] / \{k_1(k_2 + k_3)[B] + k_2(k_2 + k_3)[D] + k_2k_2[D]\}$$

$$\text{but } k_2(k_2 + k_3)[D] + k_2k_2[D] = k_3k_2[D]$$

So

$$dF/dt = k_1k_2k_3[A][D] / \{k_1(k_2 + k_3)[B] + k_2k_3[D]\} \text{ (Steady State Result)}$$

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

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

$$dF/dt = k_3[E]$$

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

$$[E] = k_2[D][C] / k_2$$

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

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

$$d[F]/dt = k_3 [E] = k_1 k_2 k_3 [A][D] / k_{-1} k_{-2} [B]$$

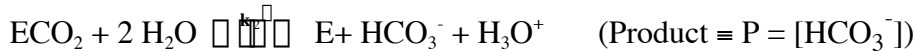
The steady state expression above reduces to this when

$$k_{-1} k_{-2} [B] \gg k_{-1} k_3 [B] + k_2 k_3 [D]$$

This is equivalent to  $k_{-2} \gg k_3$  and  $k_{-1} k_{-2} [B] \gg k_2 k_3 [D]$

### Problem 13.46

$\text{CO}_2 + 2 \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}_3\text{O}^+$  when catalyzed by carbonic anhydrase, obeys Michaelis-Menten kinetics



$$d[\text{P}]/dt = k_2 [\text{H}_2\text{O}]^2 [\text{E} \cdot \text{CO}_2]$$

Usually,  $[\text{H}_2\text{O}] \gg \gg [\text{E}], [\text{E} \cdot \text{CO}_2]$ , etc., and remains constant,

$$\text{so } k_2 [\text{H}_2\text{O}]^2 = k_2 \quad d[\text{P}]/dt = k_2 [\text{E} \cdot \text{CO}_2]$$

$$d[\text{E} \cdot \text{CO}_2]/dt = k_1 [\text{E}][\text{CO}_2] - (k_{-1} + k_2)[\text{E} \cdot \text{CO}_2] = 0$$

$$[\text{E}_0] = [\text{E}] + [\text{E} \cdot \text{CO}_2]$$

$$k_1 [\text{E}_0][\text{CO}_2] - k_1 [\text{E} \cdot \text{CO}_2][\text{CO}_2] - (k_{-1} + k_2)[\text{E} \cdot \text{CO}_2] = 0$$

$$[\text{E} \cdot \text{CO}_2] = k_1 [\text{E}_0][\text{CO}_2] / \{k_1 [\text{CO}_2] + (k_{-1} + k_2)\}$$

$$[\text{E} \cdot \text{CO}_2] = [\text{E}_0] / \{1 + (k_{-1} + k_2) / k_1 [\text{CO}_2]\}$$

$$d[\text{P}]/dt = k_2 [\text{E} \cdot \text{CO}_2]$$

$$d[\text{P}]/dt = k_2 [\text{E}_0] / \left\{ 1 + \frac{k_{-1} + k_2}{k_1 [\text{CO}_2]} \right\}$$

This is exactly the M-M result with  $k_2 [\text{E}_0] = V_{\text{max}}$

and  $(k_{-1} + k_2) / k_1 = k_M$  with  $[\text{CO}_2] = [\text{S}]$

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

a) What is  $V_{\text{max}}$  if  $[\text{E}_0] = 5 \times 10^{-6} \text{ M}$

$$d[\text{P}]/dt \Big|_{\text{max}} = \text{limit } [\text{CO}_2] \rightarrow \infty = k_2 [\text{E}_0]$$

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

b) At what  $[\text{CO}_2]$  will  $d[\text{P}]/dt = 0.3 V_{\text{max}}$ ?

$$d[\text{P}]/dt = V_{\text{max}} / (1 + k_M / [\text{CO}_2])$$

$$d[\text{P}]/dt = 0.3 V_{\text{max}} = V_{\text{max}} / (1 + k_M / [\text{CO}_2]_{0.3})$$

$$1 + k_M / [\text{CO}_2]_{0.3} = 1 / 0.3$$

$$k_M / [\text{CO}_2]_{0.3} = 1 / 0.3 - 1 = (1 - 0.3) / 0.3 = 7 / 3$$

$$[\text{CO}_2]_{0.3} = k_M (3 / 7)$$

$$[\text{CO}_2]_{0.3} = \{(8 \times 10^{-5}) \text{ mole/liter}\} 3 / 7$$

$$[\text{CO}_2]_{0.3} = 3.43 \times 10^{-5} \text{ mole/liter}$$

### Problem 10.18

$$\text{pH} = 7.4 = -\log[\text{H}_3\text{O}^+] \quad [\text{H}_3\text{O}^+] = 10^{-7.4}$$

$$[\text{H}_3\text{O}^+] = 3.98 \times 10^{-8} \text{ M}$$

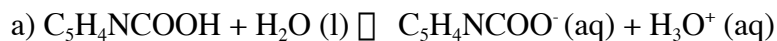
$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 2.4 \times 10^{-14}$$

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

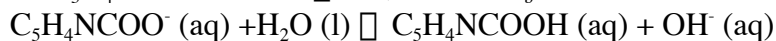
$$[\text{OH}^-] = 2.4 \times 10^{-14} / 3.98 \times 10^{-8}$$

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

### Problem 10.22



b) If  $K_a$  for  $\text{C}_5\text{H}_4\text{NCOOH}$  is  $1.5 \times 10^{-5}$ , what is  $K_b$  for



$$K_b = [\text{C}_5\text{H}_4\text{NCOOH}][\text{OH}^-] / [\text{C}_5\text{H}_4\text{NCOO}^-]$$

Multiply by  $[\text{H}_3\text{O}^+] / [\text{H}_3\text{O}^+] \rightleftharpoons$

$$K_b = \{[\text{C}_5\text{H}_4\text{NCOOH}] / [\text{C}_5\text{H}_4\text{NCOO}^-][\text{H}_3\text{O}^+]\} \{[\text{OH}^-][\text{H}_3\text{O}^+]\}$$

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

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

c) The  $K_a$  for pyridinium ion  $\text{HC}_5\text{H}_5\text{N}^+$ , the conjugate acid of pyridine,

$$\text{C}_5\text{H}_5\text{N}, (\text{Table 10.2}) \text{ is } 5.6 \times 10^{-6} = K_a \rightleftharpoons$$

$$K_b (\text{C}_5\text{H}_5\text{N}) = 1.0 \times 10^{-14} / 5.6 \times 10^{-6} = 1.79 \times 10^{-9}$$

So  $K_b (\text{C}_5\text{H}_5\text{N}) > K_b (\text{C}_5\text{H}_4\text{NCOO}^-)$

pyridine is the stronger base

### Problem 10.28

Vitamin C,  $\text{HC}_6\text{H}_7\text{O}_6$  has  $K_a$   $8.0 \times 10^{-5}$

? pH of a solution of a 500 mg tablet diluted to 100mL in  $\text{H}_2\text{O}$ .

Molecular weight of  $\text{HC}_6\text{H}_7\text{O}_6$  is 176.126 gm/mole

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

500 mg is  $2.84 \times 10^{-3}$  moles of ascorbic acid

Initial concentration is  $2.84 \times 10^{-3}$  moles / 0.1 liter

$$= 0.0284 \text{ M}$$



$$0.0284 - x \qquad \qquad \qquad x \qquad \qquad \qquad x$$

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

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

Since  $K_a \ll 1$  must not dissociate much  $\text{HC}_6\text{H}_7\text{O}_6$

So guess  $x \ll 0.0284 \rightleftharpoons$

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

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

$$\text{pH} = 2.82$$

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

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

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

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

$$x = [\text{H}_3\text{O}^+] = 1.47 \times 10^{-3}, \text{pH} = 2.83$$

**Problem 10.36**

$$K_b = 4.4 \times 10^{-4} = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

Initial concentration of  $\text{CH}_3\text{NH}_2 = 0.070 \text{ moles} / 0.8 \text{ liter}$   
 $= 0.0875 \text{ M}$



$$0.0875 - x \qquad \qquad x \qquad \qquad x$$

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

Approximate solution  $0.0875 - x \approx 0.0875$

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

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

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

$$[\text{H}_3\text{O}^+] = 10^{-14} / 6.20 \times 10^{-3} = 1.61 \times 10^{-12} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = 11.79$$

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

$$x^2 + 4.4 \times 10^{-4}x - (0.0875)(4.4 \times 10^{-4}) = 0$$

$$2x = -4.4 \times 10^{-4} + \{(4.4 \times 10^{-4})^2 + 4(0.0875)(4.4 \times 10^{-4})\}^{1/2}$$

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

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

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

$$[\text{H}_3\text{O}^+] = 10^{-14} / 5.99 \times 10^{-3} = 1.67 \times 10^{-12}$$

$$\text{pH} = 11.78$$

**Problem 10.46**

The acid ionization of sulfanilic acid has the equilibrium law

$$\frac{[\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3^-][\text{H}_3\text{O}^+]}{[\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}]} = K_a = 5.9 \times 10^{-4}$$

Initial concentrations:  $[\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3^-] = 0.13$  and  $[\text{NH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}] = 0.20$

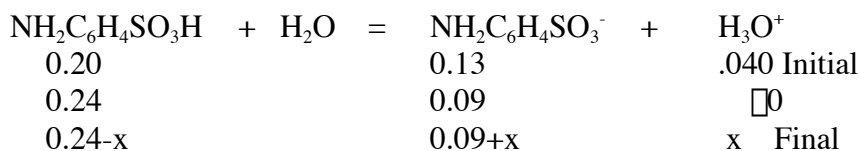


- a) The pH is computed by substituting  $0.20 \text{ M} - x$  for the concentration of sulfanilic acid and  $0.13 \text{ M} + x$  for the concentration of sulfanilate ion, solving for  $x = [\text{H}_3\text{O}^+]$  and taking the negative logarithm. However, remember from our discussion of buffers,  $x \ll 0.2, 0.13$ . 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  $0.040 \text{ mol}$  of sulfanilate ion to its conjugate acid, sulfanilic acid.



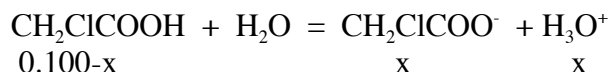
The concentrations of the two are  $0.24 \text{ M} - x$  and  $0.09 \text{ M} + x$ , respectively. Again remember from our discussion of buffers that  $x \ll .24, .09$ , so,

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

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

### Problem 10.54

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



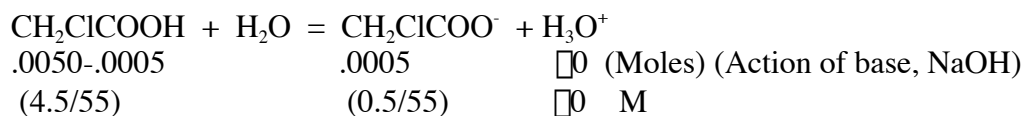
$$\frac{x^2}{0.1000 - x} = 1.4 \times 10^{-3}$$

but  $x \ll 0.100$ :

$$x = 1.18 \times 10^{-2} \text{ M} = [\text{H}_3\text{O}^+] \quad \text{pH} = 1.93$$

(More exact if solve quadratic:  $x = 1.12 \times 10^{-2} \text{ M} = [\text{H}_3\text{O}^+]$ , 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.



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

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

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

$$x = 6.67 \times 10^{-3} = [\text{H}_3\text{O}^+] \quad \text{pH} = 2.18$$

(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:

$$\frac{\frac{2.50\text{mmol}}{75.00\text{mL}} + x}{\frac{2.50\text{mmol}}{75.00\text{mL}} + x} = 1.4 \times 10^{-3}$$

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

$$x = [\text{H}_3\text{O}^+] = 1.3 \times 10^{-3}, \quad \text{pH} = 2.89$$

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

$$\frac{\frac{4.90\text{mmol}}{99.00\text{mL}} + x}{\frac{0.10\text{mmol}}{99.00\text{mL}} + x} = 1.4 \times 10^{-3}$$

$$x = 2.8 \times 10^{-5} = [\text{H}_3\text{O}^+] \quad \text{pH} = 4.56$$

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

$$\frac{\frac{4.99\text{mmol}}{99.90\text{mL}} + x}{\frac{0.010\text{mmol}}{99.90\text{mL}} + x} = 1.4 \times 10^{-3}$$

$$x = 2.7 \times 10^{-6} = [\text{H}_3\text{O}^+] \quad \text{pH} = 5.56$$

f) At the equivalence point, we have a 0.0500 M  $\text{CH}_2\text{ClCOO}^-$  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.



$$[\text{CH}_2\text{ClCOOH}] = [\text{OH}^-] = x$$

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

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

$$\text{pOH} = 6.22 \quad \text{pH} = 7.78$$

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

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

$$\text{pOH} = 4.00 \quad \text{pH} = 10.00$$

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

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

