Chapter 15 - Acid - Base Equilibria

15.17

a. 0.100 M propanoic acid ($HC_3H_5O_2$, $K_a = 1.3 \times 10^{-5}$)

$$HC_3H_5O_2 + H_2O \rightleftharpoons C_3H_5O_2^- + H_3O^+$$

$0.1 \qquad 0 \qquad \simeq 0$

$0.1 - x \qquad x \qquad x$

$$K_a = \frac{[C_3H_5O_2^-][H_3O^+]}{[HC_3H_5O_2]} = \frac{x^2}{0.1-x} \simeq \frac{x^2}{0.1} \Rightarrow x = \sqrt{K_a \times 0.1}$$

$$\Rightarrow x = \sqrt{1.3 \times 10^{-5} \times 0.1} = 1.14 \times 10^{-3}$$ app. accepted

$$\Rightarrow [H_3O^+] = 1.14 \times 10^{-3} M \Rightarrow pH = 2.94$$

b. 0.100 M sodium propanoate ($NaC_3H_5O_2$)

$$NaC_3H_5O_2 \longrightarrow Na^+ + C_3H_5O_2^-$$

$$C_3H_5O_2^- + H_2O \rightleftharpoons HC_3H_5O_2 + OH^-$$

$0.1 \qquad 0 \qquad \simeq 0$

$0.1 - x \qquad x \qquad x$

$$\Rightarrow K_b = \frac{[HC_3H_5O_2][OH^-]}{[C_3H_5O_2^-]} = \frac{x^2}{0.1-x} \simeq \frac{x^2}{0.1} \Rightarrow x = \sqrt{K_b \times 0.1}$$

$$\Rightarrow x = \sqrt{\frac{K_w}{K_a} \times 0.1} = \sqrt{\frac{10^{-14}}{1.3 \times 10^{-5}} \times 0.1} = 8.77 \times 10^{-6}$$ app. accepted

$$\Rightarrow [OH^-] = 8.77 \times 10^{-6} M \Rightarrow [H_3O^+] = 1.14 \times 10^{-9} M \Rightarrow pH = 8.94$$

c. pure H_2O ⟶ $pH = 7$

d. 0.100 M $HC_3H_5O_2$ + 0.100 M $NaC_3H_5O_2$.

$$\begin{array}{lcccc} HC_3H_5O_2 + H_2O & \rightleftharpoons & C_3H_5O_2^- & + & H_3O^+ \\ 0.1 & & 0.1 & & \simeq 0 \\ 0.1-x & & 0.1+x & & x \end{array}$$

$$K_a = \frac{[C_3H_5O_2^-][H_3O^+]}{[HC_3H_5O_2]} = \frac{(0.1+x)\,x}{0.1-x} \approx \frac{0.1\,x}{0.1} = x = 1.3\times10^{-5}$$

app. accepted

$$\Rightarrow [H_3O^+] = 1.3\times10^{-5}\ M \Rightarrow pH = 4.89$$

15.35

a. $\underbrace{0.05\ M\ NH_3 \,/\, 0.15\ M\ NH_4Cl}_{250\ mL}$ + 0.01 mol HCl

$$n_{NH_3} = 0.05\times0.25 = 1.25\times10^{-2}\ mol$$

$$n_{NH_4^+} = 0.15\times0.25 = 3.75\times10^{-2}\ mol$$

$$\begin{array}{lcccc} & NH_3 & + HCl & \longrightarrow & NH_4Cl \\ \text{Initial}: & 1.25\times10^{-2} & 0.01 & & 3.75\times10^{-2} \\ \text{Final}: & 2.5\times10^{-3} & 0 & & 3.75\times10^{-2}+10^{-2} \end{array} \left.\right\}\ \text{no. of moles}$$

$$\begin{array}{lcccc} & NH_3 + H_2O & \rightleftharpoons & NH_4^+ & + OH^- \\ \text{Initial} & \frac{2.5\times10^{-3}}{0.25} & & \frac{4.75\times10^{-2}}{0.25} & \\ \text{Equilibrium} & \frac{2.5\times10^{-3}}{0.25}-x & & \frac{4.75\times10^{-2}}{0.25}+x & x \end{array}$$

$$K_b = \frac{[NH_4^+]\,[OH^-]}{[NH_3]} = \frac{(0.19+x)\,x}{(0.01-x)} \simeq \frac{0.19\,x}{0.01}$$

$$\Rightarrow \quad x = \frac{K_b \times 0.1}{0.19} = \frac{1.8\times10^{-5}\times0.01}{0.19} = 9.47\times10^{-7}$$ app. accepted

$$\Rightarrow [OH^-] = 9.47\times10^{-7}\ M \Rightarrow [H_3O^+] = 1.06\times10^{-8}\ M \Rightarrow pH = 7.97$$

b. $\underbrace{0.5\,M\ NH_3 / 1.50\,M\ NH_4Cl}_{250\ mL} + 0.01\ mol\ HCl$

$n_{NH_3} = 0.125$ mol $\qquad n_{NH_4^+} = 0.375$ mol

$$\left.\begin{array}{ccccc}
NH_3 & + & HCl & \longrightarrow & NH_4Cl \\
 & & & & 0.375 \\
0.125 & & 0.01 & & \\
0.115 & & 0 & & 0.375+0.01
\end{array}\right\}\ \text{no. of moles.}$$

$$\begin{array}{ccccc}
NH_3 & + & H_2O & \rightleftharpoons & NH_4^+ & + & OH^- \\
\frac{0.115}{0.25} & & & & \frac{0.385}{0.25} & & \\
\frac{0.115}{0.25} - x & & & & \frac{0.385}{0.25} + x & & x
\end{array}$$

$$K_b = \cdots\cdots = \frac{(1.54+x)\,x}{0.46-x} \simeq \frac{1.54\,x}{0.46} \Rightarrow x = 5.38\times10^{-6}$$ app. accepted

$$\Rightarrow [OH^-] = 5.38\times10^{-6}\ M \Rightarrow pOH = 5.27 \Rightarrow pH = 8.73$$

c. $pH = pK_a + \log\frac{Base}{acid} = 9.26 + \log\frac{[NH_3]}{[NH_4^+]}$

In both case $\frac{[NH_3]}{[NH_4^+]} = 0.333$ ⇒ pH is the same $= 8.78$

$\Rightarrow$ A buffer with high buffer capacity will have a better resistance to pH changes. The second solution has a higher buffer capacity.

15.51

40 mL 0.2M $HClO_4$ + 0.1 M KOH

$n_{HClO_4} = 0.2 \times 0.04 = 8 \times 10^{-3}$ mol

a. 0 mL KOH added :

$$HClO_4 + H_2O \longrightarrow H_3O^+ + ClO_4^-$$

$\Rightarrow n_{H_3O^+}$ produced $= 8 \times 10^{-3}$ mol $\Rightarrow [H_3O^+] = \frac{8 \times 10^{-3}}{0.04} = 0.2M$

you can easily obtain this concentration from the original solution.

$\Rightarrow pH = -\log[H_3O^+] = 0.70$

b. 10 mL KOH added : $\Rightarrow n_{KOH} = 0.1 \times 0.01 = 10^{-3}$ mol

$$HClO_4 + KOH \longrightarrow KClO_4 + H_2O$$

8×10^{-3}	10^{-3}
7×10^{-3}	0

$\Rightarrow [HClO_4] = \frac{7 \times 10^{-3}}{(0.04 + 0.01)} = 0.14\ M = [H_3O^+] \Rightarrow pH = 0.85$

c. 40 mL KOH added $\Rightarrow n_{KOH} = 0.1 \times 0.04 = 4\times10^{-3}$ mol

$$\begin{array}{lllll} HClO_4 & + & KOH & \longrightarrow & KClO_4 + H_2O \\ 8\times10^{-3} & & 4\times10^{-3} & & \\ 4\times10^{-3} & & 0 & & \end{array}$$

$$\Rightarrow [HClO_4] = \frac{4\times10^{-3}}{(0.04+0.04)} = 0.05\,M = [H_3O^+] \Rightarrow pH = 1.30$$

d. 80 mL KOH added $\Rightarrow n_{KOH} = 0.1\times0.08 = 8\times10^{-3}$ mol

$$\begin{array}{lllll} HClO_4 & + & KOH & \longrightarrow & KClO_4 + H_2O \\ 8\times10^{-3} & & 8\times10^{-3} & & \\ 0 & & 0 & & \end{array}$$

$\Rightarrow$ the only source of H_3O^+ in the solution is the autodissociation of water molecules $\Rightarrow pH = 7$

equivalence point

e. 100 mL KOH added $\Rightarrow n_{KOH} = 0.1\times0.1 = 10^{-2}$ mol

$$\begin{array}{lllll} HClO_4 & + & KOH & \longrightarrow & KClO_4 + H_2O \\ 8\times10^{-3} & & 10^{-2} & & \\ 0 & & 2\times10^{-3} & & \end{array}$$

$\Rightarrow$ KOH is in excess.

$$[OH^-] = \frac{2\times10^{-3}}{0.04+0.1} = 1.43\times10^{-2}\,M \Rightarrow [H_3O^+] = 6.99\times10^{-13}\,M$$

$$\Rightarrow pH = 12.16$$

15.54

100 mL $\quad 0.1\ M\ H_2NNH_2\ (K_b = 3.0\times10^{-6}) + 0.2M\ HNO_3$

$n_{H_2NNH_2} = 0.1\times0.1 = 10^{-2}$ mol

a. 0 mL HNO_3 added.

$$\begin{array}{lcccc} H_2NNH_2 & + H_2O & \rightleftharpoons & H_2NNH_3^+ & + OH^- \\ 10^{-2} & & & & \\ 10^{-2}-x & & & x & x \end{array}$$

$$K_b = \frac{[H_2NNH_3^+][OH^-]}{[H_2NNH_2]} = \frac{x^2}{10^{-2}-x} \simeq \frac{x^2}{10^{-2}} \Rightarrow x = \sqrt{K_b\times10^{-2}}$$

$$\Rightarrow x = \sqrt{3.0\times10^{-6}\times10^{-2}} = 1.73\times10^{-4}$$ app. accepted

$$\Rightarrow [OH^-] = 1.73\times10^{-4}\ M \Rightarrow [H_3O^+] = 5.78\times10^{-11}\ M \Rightarrow pH = 10.24$$

b. 20 mL HNO_3 added $\Rightarrow n_{HNO_3} = 0.2\times0.02 = 4\times10^{-3}$ mol

$$\begin{array}{lcccc} H_2NNH_2 & + HNO_3 & \longrightarrow & H_2NNH_3^+ & + NO_3^- \\ 10^{-2} & 4\times10^{-3} & & & \\ 6\times10^{-3} & 0 & & 4\times10^{-3} & \end{array}$$

$$\begin{array}{lcccc} H_2NNH_2 & + H_2O & \rightleftharpoons & H_2NNH_3^+ & + OH^- \\ 6\times10^{-3}/0.12 & & & 4\times10^{-3}/0.12 & \\ \frac{6\times10^{-3}}{0.12}-x & & & \frac{4\times10^{-3}}{0.12}+x & x \end{array}$$

$$K_b = \frac{\left(\frac{4\times10^{-3}}{0.12}+x\right)x}{\left(\frac{6\times10^{-3}}{0.12}-x\right)} \simeq \frac{(4\times10^{-3}/0.12)x}{(6\times10^{-3}/0.12)} \Rightarrow x = 4.5\times10^{-6}$$ app. accepted

$$\Rightarrow [OH^-] = 4.5\times10^{-6}\ M \Rightarrow pOH = 5.35 \Rightarrow pH = 8.65$$

c. 25 mL HNO_3 added $\Rightarrow n_{HNO_3} = 5\times10^{-3}$ mol   half - equiv.

$$\begin{array}{cccc} H_2NNH_2 & + \; HNO_3 & \longrightarrow & H_2NNH_3^+ + NO_3^- \\ 10^{-2} & 5\times10^{-3} & & \\ 5\times10^{-3} & 0 & & 5\times10^{-3} \end{array}$$

$$\begin{array}{cccc} H_2NNH_2 & + \; H_2O & \rightleftharpoons & H_2NNH_3^+ \;\; + \; OH^- \\ (5\times10^{-3}/0.125) & & & (5\times10^{-3}/0.125) \\ \frac{5\times10^{-3}}{0.125} - x & & & \frac{5\times10^{-3}}{0.125} + x \qquad x \end{array}$$

$$pH = pK_a + \log\frac{base}{acid} = 8.48 + \log\frac{4\times10^{-2}}{4\times10^{-2}} = 8.48$$

d. 40 mL HNO_3 added $\Rightarrow n_{HNO_3} = 8\times10^{-3}$ mol

Similar to part c

$$pH = pK_a + \log\frac{base}{acid} = 8.48 + \log\frac{2\times10^{-3}/0.14}{8\times10^{-3}/0.14} = 7.88$$

e. 50 mL HNO_3 added $\Rightarrow n_{HNO_3} = 10^{-2}$ mol   equiv. point

$\Rightarrow H_2NNH_2$ reacts completely with HNO_3 to form $H_2NNH_3^+$ (10^{-2} mol)

$$\begin{array}{cccc} H_2NNH_3^+ & + \; H_2O & \rightleftharpoons & H_2NNH_2 \; + \; H_3O^+ \\ 6.67\times10^{-2} & & & \\ 6.67\times10^{-2} - x & & & x \qquad\quad x \end{array}$$

$$K_a = \frac{K_w}{K_b} = \frac{x^2}{6.67\times10^{-2} - x} \simeq \frac{x^2}{6.67\times10^{-2}} \Rightarrow x = 1.49\times10^{-5}$$ app. accepted

$$\Rightarrow [H_3O^+] = 1.49\times10^{-5}\ M \Rightarrow pH = 4.83$$

f. 100 mL HNO_3 added $\Rightarrow n_{HNO_3} = 2\times10^{-2}$ mol

$\Rightarrow$ HNO_3 in excess. (10^{-2} mol in excess).

At this stage, two sources of H_3O^+ exist in the solution which are the strong acid HNO_3 and the weak acid $H_2NNH_3^+$. We consider (approximation) that the H_3O^+ comes only from the strong acid

$$\Rightarrow [H_3O^+] = \frac{10^{-2}}{0.2} = 5\times10^{-2}\ M \Rightarrow pH = 1.30$$

15.59

a. 100 mL of 0.1 M $HC_7H_5O_2$ ($K_a = 6.4\times10^{-5}$) $\rightarrow n_{HC_7H_5O_2} = 10^{-2}$ mol

+ 0.1 M NaOH

$$\begin{array}{llll} HC_7H_5O_2 & + \ NaOH & \longrightarrow C_7H_5O_2Na & + H_2O \\ 10^{-2} & 5\times10^{-3} \ (V_{NaOH} = 50mL) & 0 & \\ 5\times10^{-3} & 0 & 5\times10^{-3} & \end{array}$$

$$\begin{array}{llll} HC_7H_5O_2 & + \ H_2O & \rightleftharpoons C_7H_5O_2^- & + H_3O^+ \\ 3.33\times10^{-2} & & 3.33\times10^{-2} & \\ 3.33\times10^{-2} - X & & 3.33\times10^{-2} + X & X \end{array}$$

$$pH = pK_a + \log\frac{[C_7H_5O_2^-]}{[HC_7H_5O_2]} = pK_a = 4.19$$ halfway point

when the totality of $HC_7H_5O_2$ is titrated $\Rightarrow V_{NaOH} = 100mL$

$\Rightarrow n_{C_7H_5O_2^-} = 10^{-2}$ mol

$$C_7H_5O_2^- \quad + \quad H_2O \rightleftharpoons HC_7H_5O_2 \quad + \quad OH^-$$

5×10^{-2}

$5\times10^{-2} - x \qquad\qquad x \qquad\qquad x$

$$K_b = \frac{K_w}{K_a} = \frac{x^2}{5\times10^{-2} - x} \simeq \frac{x^2}{5\times10^{-2}} \Rightarrow x = 2.80\times10^{-6}$$

$$\Rightarrow [OH^-] = 2.80\times10^{-6}\ M \Rightarrow pOH = 5.55 \Rightarrow pH = 8.45$$

b. 100 mL of 0.1 M $C_2H_5NH_2$ ($K_b = 5.6\times10^{-4}$) $\rightarrow n = 10^{-2}$ mol

+ 0.2 M HNO_3

Halfway point $\rightarrow$ $pH = pK_a = 10.75$

Eq. point $\rightarrow$ $pH = 5.96$

c. 100 mL of 0.5 M HCl + 0.25 M NaOH

Half way point $\rightarrow$ $pH = 0.90$

Eq. point $\rightarrow$ $pH = 7.00$

15.63

a. $HIn + H_2O \rightleftharpoons In^- + H_3O^+$

0.1 M HCl $\rightarrow$ pH = 1

$$pH = pK_a + \log\frac{[In^-]}{[HIn]}$$

$$\Rightarrow 1 = 9 + \log\frac{[In^-]}{[HIn]} \Rightarrow \frac{[In^-]}{[HIn]} = 10^{-8} \Rightarrow HIn \text{ is dominant}$$

$\Rightarrow$ yellow

b. The solution will start changing its color when the quantity of one form of the molecule is approximately 10x that of the other form.

$$\Rightarrow \frac{[In^-]}{[HIn]} = \frac{1}{10}$$

$$\Rightarrow pH = pKa + \log\frac{1}{10} = pK_a - 1 = 8.$$

c. $n_{HCl} = 0.1 \times 0.1 = 10^{-2}$ mol
$n_{NaOH} = 0.1 \times 0.2 = 2\times10^{-2}$ mol

$\Rightarrow n_{NaOH}$ in excess after titration $= 10^{-2}$ mol

$$\Rightarrow [NaOH] = \frac{10^{-2}}{0.3} = 3.33\times10^{-2}\ M \Rightarrow pH = 12.52$$

$$pH = pK_a + \log\frac{[In^-]}{[HIn]} \Rightarrow \log\frac{[In^-]}{[HIn]} = 12.52 - 9 = 3.52$$

$$\Rightarrow \frac{[In^-]}{[HIn]} = 10^{3.52} = 3311 \Rightarrow In^- \text{ is dominant}$$

$\Rightarrow$ the solution is blue