INTRODUCTION TO NATURAL SCIENCE

CHEMISTRY HOMEWORK – WEEK 6 – SPRING 2007

Chapter 18

① (a) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

If you add solid NH_4Cl, you are adding NH_4^+ to the above system, driving the equilibrium back. ∴ less OH^- ions in solution.

⇒ less basic.

⇒ pH goes down.

(b) $CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$

add ~~Na~~ CH_3COONa

⇒ increase CH_3COO^- concentration

⇒ equilibrium drives back

⇒ less ~~e~~ H_3O^+

⇒ pH increases.

(c) $NaOH(aq) \longrightarrow Na^+(aq) + OH^-$

add NaCl

⇒ add Na^+

⇒ ~~do~~ no equilibrium in solution

⇒ pH does not change

(3)

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

	$NH_3(aq)$	$NH_4^+(aq)$	$OH^-(aq)$
initial	0.20 M	0.20 M	
change	$-x$	$+x$	$+x$
equilibrium	$0.20-x$	$(0.20+x)$	x

$$K_b = \frac{[NH_4^+]_{eq}[OH^-]_{eq}}{[NH_3]_{eq}} = \frac{(0.20+x)(x)}{(0.20-x)} = 1.8\times10^{-5}$$

$$0.20x + x^2 = 3.6\times10^{-6} - 1.8\times10^{-5}x$$

$$x^2 + 2.00018\times10^{-1}x - 3.6\times10^{-6} = 0$$

$$x = \frac{-2.00018\times10^{-1} \pm \sqrt{(2.00018\times10^{-1})^2 + 4(3.6\times10^{-6})}}{2}$$

$$x = 1.799\times10^{-5} = [OH^-]$$

$$pOH = -\log[OH^-] = 4.74$$

$$pH = 14 - pOH = \underline{\underline{9.26}}$$

(5) C_6H_5COOH 0.015 M, 50.0 mL

# of moles of $C_6H_5COOH = 0.015\,\frac{mol}{L} \times \frac{50.0\,mL}{10^3\,mL} \times L$

$= 7.5\times10^{-4}$ mol

KOH 0.015 M, 30 mL

# of moles of KOH $= 0.015\,\frac{mol}{L} \times 30\times10^{-3}\,L$

$= 4.5\times10^{-4}$ mol

KOH is the limiting reactant

$$C_6H_5COOH(aq) + KOH(aq) \longrightarrow C_6H_5COOK(aq) + H_2O(l)$$

	C_6H_5COOH	KOH	C_6H_5COOK
	7.5×10^{-4} mol	4.5×10^{-4} mol	
reacted/produced	-4.5×10^{-4} mol	-4.5×10^{-4} mol	$+4.5\times10^{-4}$ mol
left	3.0×10^{-4} mol	$\underline{\underline{0}}$ mol	4.5×10^{-4} mol

$$C_6H_5COOK(aq)$$
$$\downarrow$$
$$C_6H_5COO^-(aq) + K^+(aq)$$
$$4.5\times10^{-4}\text{ mol}$$

When all the KOH is used up

$$C_6H_5COOH(aq) + H_2O(l) \rightleftharpoons C_6H_5COO^-(aq) + H_3O^+(l)$$

initial $\dfrac{3.0\times10^{-4}\text{ mol}}{80\times10^{-3}\text{ L}} = 3.75\times10^{-3}$ M $\qquad \dfrac{4.5\times10^{-4}\text{ mol}}{80\times10^{-3}\text{ L}} = 5.625\times10^{-3}$ M

Change $\quad -x \qquad +x \qquad +x$

equilibrium $\quad (3.75\times10^{-3}-x) \qquad (5.625\times10^{-3}+x) \qquad x$

$$K_a = \frac{[C_6H_5COO^-]_{eq}[H_3O^+]_{eq}}{[C_6H_5COOH]_{eq}} = \frac{(5.625\times10^{-3}+x)\,x}{(3.75\times10^{-3}-x)}$$

$$6.3\times10^{-5} = \frac{5.625\times10^{-3}x + x^2}{3.75\times10^{-3}-x}$$

$$x^2 + 5.688\times10^{-3}x - 2.3625\times10^{-7} = 0$$

$$x = \frac{-5.688\times10^{-3} \pm \sqrt{(5.688\times10^{-3})^2 + 4(2.3625\times10^{-7})}}{2}$$

$x = 4.123 \times 10^{-5} = [H_3O^+]$

$pH = 4.38$

(7)

$$NH_3(aq) + H_2O(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

	NH_3		NH_4^+	OH^-
initial	0.12 M			
change	$-x$		$+x$	$+x$
equilibrium	$0.12-x$		x	x

$$K_b = \frac{[NH_4^+]_{eq}[OH^-]_{eq}}{[NH_3]_{eq}} = \frac{x^2}{0.12-x} = 1.8 \times 10^{-5}$$

$$x^2 + 1.8\times10^{-5}x - 2.16\times10^{-6} = 0$$

$$x = \frac{-1.8\times10^{-5} \pm \sqrt{(1.8\times10^{-5})^2 + 4(2.16\times10^{-6})}}{2}$$

$x = [OH^-] = 1.46 \times 10^{-3}$

$pOH = 2.84 \Rightarrow pH = 11.16$

To this add 2.2 g NH_4Cl

$$2.2\text{ g } NH_4Cl \times \frac{1\text{ mol}}{53.54\text{ g}} = 4.109\times10^{-2}\text{ mol } NH_4Cl$$

$$\text{molarity of } NH_4Cl = \frac{4.109\times10^{-2}\text{ mol}}{0.250\text{ L}} = 1.644\times10^{-1}\text{ M}$$

$$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$$

1.644×10^{-1} M $\quad$ 1.644×10^{-1} M

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

	NH_3		NH_4^+	OH^-
initial	0.12M		0.164 M	
change	$-x$		$+x$	$+x$
equilibrium	$(0.12-x)$		$(0.164+x)$	x

$$K_b = \frac{[NH_4^+]_{eq}[OH^-]_{eq}}{[NH_3]_{eq}} = \frac{(0.164+x)x}{0.12-x} = 1.8\times10^{-5}$$

$$0.164x + x^2 = 2.16\times10^{-6} - x(1.8\times10^{-5})$$

$$x^2 + 0.164x - 2.16\times10^{-6} = 0$$

$$x = \frac{-0.164 \pm \sqrt{(0.164)^2 + 4(2.16\times10^{-6})}}{2}$$

$$x = 1.317\times10^{-5} = [OH^-]$$

$$pOH = 4.88 \quad \underline{pH = 9.12}$$

The final pH is less than the original ammonia solution, because NH_4^+ was added to ammonia solution.

(8) (a) moles of sodium lactate $= 2.75g \times \frac{1\ mol}{112\ g} = 2.46\times10^{-2}$ mol

molarity of sodium lactate $= \frac{2.46\times10^{-2}\ mol}{0.500L} = 4.91\times10^{-2}M$

molarity of lactate ion $= 4.91\times10^{-2}M$

$$CH_3CHOHCOOH(aq) + H_2O(l) \rightleftharpoons CH_3CHOHCOO^-(aq) + H_3O^+(aq)$$

	$CH_3CHOHCOOH$	$CH_3CHOHCOO^-$	H_3O^+
initial	0.100M	4.91×10^{-2} M	
change	$-x$	$+x$	$+x$
equilibrium	$(0.100-x)$	$(4.91 \times 10^{-2} + x)$	x

$$K_a = \frac{(4.91 \times 10^{-2} + x)x}{0.100 - x} = 1.4 \times 10^{-4}$$

$$x^2 + 4.924 \times 10^{-2} x - 1.4 \times 10^{-5} = 0$$

$$x = \frac{-4.924 \times 10^{-2} \pm \sqrt{(4.924 \times 10^{-2})^2 + 4(1.4 \times 10^{-5})}}{2}$$

$$x = 2.83 \times 10^{-4} M = [H_3O^+]$$

pH = 3.55

(b) The final pH has to be ~~lower~~ higher than the lactic acid solution because by adding sodium lactate we disturbed the equilibrium by adding more product. Therefore the reaction will reach a new equilibrium by moving in the reverse direction, decreasing $[H_3O^+]$. This increases the pH.

(10) Let the molarity of $NH_4Cl = \alpha$

$\Rightarrow$ molarity of $NH_4^+ = \alpha$

	$NH_3(aq) + H_2O(l)$	$\rightleftharpoons$	$NH_4^+(aq)$	$+ OH^-(aq)$
initial	0.10M		α	
change	$-x$		$+x$	$+x$
eq^n	$(0.10-x)$		$(\alpha+x)$	x

$$K_b = \frac{(\alpha+x)x}{0.10-x} = 1.8\times10^{-5}$$

but $x = [OH^-]$ $\qquad pH = 9.00$

$\Rightarrow p(OH) = 5.00$

$\therefore [OH^-] = 1.00\times10^{-5}\,M = x$

$$\frac{(\alpha+x)x}{0.10-x} = 1.8\times10^{-5}$$

$$\frac{(\alpha+1.00\times10^{-5})\,1.00\times10^{-5}}{9.999\times10^{-2}} = 1.8\times10^{-5}$$

$$(\alpha+1.00\times10^{-5}) = 0.1799$$

$$\alpha = 1.7997\times10^{-1}$$

molarity of $NH_4Cl = 1.799\times10^{-1}\,M$

$\therefore$ moles of $NH_4Cl = 1.799\times10^{-1}\,\frac{mol}{L}\times 0.500L$

$= 8.999 \times 10^{-2}$ mol

mass of NH_4Cl $= 8.999 \times 10^{-2}$ mol $\times \left(53.5 \frac{g}{mol}\right)$

$= \underline{\underline{4.81 g}}$

(13) (a) Using Henderson - Hasselbalch equation

$$pH = pK_a + \log \frac{[\text{conj. base}]}{[\text{acid}]}$$

$$= -\log(1.8 \times 10^{-4}) + \log\left(\frac{0.035}{0.050}\right)$$

$$= \underline{\underline{3.59}}$$

(b) If pH is increased by 0.5 units, new pH

new pH $= 3.59 + 0.50 = 4.09$

$$4.09 = -\log(1.8 \times 10^{-4}) + \log \frac{[\text{conj. base}]}{[\text{acid}]}$$

$$4.09 = 3.74 + \log \frac{[\text{conj. base}]}{[\text{acid}]}$$

$$\log \frac{[\text{conj. base}]}{[\text{acid}]} = 0.35$$

$$\Rightarrow \frac{[\text{conj. base}]}{[\text{acid}]} = ~~0.445~~ \; 2.23$$

(15) (b) NH_3 and NH_4Cl
(since pH = 9, need a buffer based on a base + conj. acid)

(17) $NaH_2PO_4(aq) \longrightarrow Na^+(aq) + H_2PO_4^-(aq)$

$Na_2HPO_4(aq) \longrightarrow 2Na^+(aq) + HPO_4^{2-}(aq)$

$$\underset{\text{acid}}{H_2PO_4^-(aq)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\text{conj. acid}}{H_3O^+(aq)} + \underset{\text{conj. base}}{HPO_4^{2-}}$$

$$pH = pKa + \log \frac{[\text{conj. base}]}{[\text{acid}]}$$

$$7.5 = -\log(6.2 \times 10^{-8}) + \log \frac{[\text{conj. base}]}{[\text{acid}]}$$

$$7.5 = 7.21 + \log \frac{[\text{conj. base}]}{[\text{acid}]}$$

$$\log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 0.29$$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 1.96 \approx 2$$

∴ We need to be sure that when preparing the buffer system we maintain the concentration ratio of Na_2HPO_4 to NaH_2PO_4 to be 2.

(19) (a) moles of CH_3COONa = $4.95 g \times \frac{1 mol}{82 g} = 6.04 \times 10^{-2} mol$

molarity of CH_3COONa = $\frac{6.04 \times 10^{-2} mol}{0.250 L} = 0.241 M$

$[CH_3COO^-] = 0.241 M$

$[CH_3COOH] = 0.150 M$

$pH = pK_a + \log \frac{[conj.\ base]}{acid}$

$= -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.241}{0.150}\right) = \underline{\underline{4.95}}$

(b) When we add the base (NaOH), it will react with the acid (CH_3COOH), ~~this~~ and produce CH_3COO^-

$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$

This will decrease the amount of acid and increase the amount of CH_3COO^-.

NaOH $\quad 82 mg \times \frac{g}{10^3 mg} \times \frac{1 mol}{40 g} = 2.05 \times 10^{-3} mol$

In 100.00 mL of buffer solution

# of moles of CH_3COOH = $0.150 M \times (100 \times 10^{-3} L) = 1.50 \times 10^{-2} mol$

~~$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$~~

~~initial 1.50×10^{-2} mol~~

# of moles of CH_3COO^- = $0.241 M \times (100 \times 10^{-3} L) = 2.41 \times 10^{-2} mol$

B 11

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$$

	$CH_3COOH(aq)$	$OH^-(aq)$	$CH_3COO^-(aq)$
initial	1.50×10^{-2} mol	2.05×10^{-3} mol	2.41×10^{-2} mol
reacted/produced	-2.05×10^{-3} mol	-2.05×10^{-3} mol	$+2.05 \times 10^{-3}$ mol
left	1.295×10^{-2} mol	ϕ	2.615×10^{-2} mol

since we have a buffer system left;

$$pH = pK_a + \log \frac{[\text{conj. base}]}{[\text{acid}]}$$

$$= -\log(1.8 \times 10^{-5}) + \log\left(\frac{2.615 \times 10^{-2}}{1.295 \times 10^{-2}}\right)$$

$$= \underline{\underline{5.05}}$$

(23) (a) moles of phenol $= 0.515\,g \times \left(\frac{mol}{94\ g}\right) = 5.48 \times 10^{-3}\ mol$

molarity of phenol $= \frac{5.48 \times 10^{-3}\ mol}{0.125\ L} = 4.38 \times 10^{-2}\ M$

	$C_6H_5\text{-}OH(aq) + H_2O(l)$	$\rightleftharpoons$	$C_6H_5O^-(aq)$	$+\ H_3O^+(aq)$
initial	$4.38 \times 10^{-2}\ M$		ϕ	ϕ
change	$-x$		$+x$	$+x$
equilibrium	$(4.38 \times 10^{-2} - x)$		x	x

$$K_a = \frac{x^2}{4.38 \times 10^{-2} - x} = 1.3 \times 10^{-10}$$

$$x^2 + 1.3 \times 10^{-10}\,x - 5.69 \times 10^{-12} = 0$$

$$x = \frac{-1.3 \times 10^{-10} \pm \sqrt{(1.3 \times 10^{-10})^2 + 4(5.69 \times 10^{-12})}}{2}$$

$$x = 2.39 \times 10^{-6}\,M = [H_3O^+]$$

$$pH = 5.62$$

(b) at the equivalence point,

moles of NaOH = moles of phenol

$= 5.48 \times 10^{-3}\ mol$

$\therefore$ Volume of NaOH $= \frac{5.48 \times 10^{-3}\ mol}{0.123\ mol/L} = 4.46 \times 10^{-2}\ L$

~~ao~~: $NaOH \longrightarrow Na^+(aq) + OH^-(aq)$

NaOH	$Na^+(aq)$	$OH^-(aq)$
5.48×10^{-3} mol	5.48×10^{-3} mol	~~[illegible]~~

$$\text{total volume} = 0.125\,L + 4.46 \times 10^{-2}\,L$$
$$= 0.1696\,L$$

$$[Na^+] = \frac{5.48 \times 10^{-3}\,mol}{0.1696\,L} = \underline{\underline{3.23 \times 10^{-2}\,M}}$$

As the base is added, it neutralizes the acid.

$$C_6H_5OH(aq) + OH^-(aq) \longrightarrow C_6H_5O^-(aq) + H_2O(l)$$

	$C_6H_5OH(aq)$	$OH^-(aq)$	$C_6H_5O^-(aq)$	$H_2O(l)$
	acid	base	conj. base	conj. acid.
initial	5.48×10^{-3} mol	5.48×10^{-3} mol	ϕ	
at end of titration	ϕ	ϕ	$\underline{\underline{5.48 \times 10^{-3}\,mol}}$	

Then the following equilibrium is established.

$$C_6H_5O^-(aq) + H_2O(l) \rightleftharpoons C_6H_5OH(aq) + OH^-(aq)$$

	$C_6H_5O^-(aq)$	$H_2O(l)$	$C_6H_5OH(aq)$	$OH^-(aq)$
initial	$\frac{5.48 \times 10^{-3}\,mol}{0.1696\,L} = 3.23 \times 10^{-2}\,M$		ϕ	ϕ
change	$-x$		$+x$	$+x$
eq^m	$(3.23 \times 10^{-2} - x)$		x	x

$$K_b(\text{of } C_6H_5O^-) = \frac{x^2}{(3.23\times10^{-2} - x)}$$

$$K_a \cdot K_b = K_w$$

$$K_b(\text{of } C_6H_5O^-) = \frac{K_w}{K_a(\text{of } C_6H_5OH)}$$

$$K_b = \frac{10^{-14}}{1.3\times10^{-10}} = 7.69\times10^{-5}$$

$$\frac{x^2}{3.23\times10^{-2} - x} = 7.69\times10^{-5}$$

$$x^2 + 7.69\times10^{-5}x - 2.48\times10^{-6} = 0$$

$$x = \frac{-7.69\times10^{-5} \pm \sqrt{(7.69\times10^{-5})^2 + 4(2.48\times10^{-6})}}{2}$$

$$x = 1.54\times10^{-3}\,M = [OH^-] = [C_6H_5O^-]$$

$$\underline{\underline{[OH^-] = 1.54\times10^{-3}\,M = [C_6H_5O^-]}}$$

$$[H^+] = \frac{10^{-14}}{[OH^-]} = \underline{\underline{6.50\times10^{-12}\,M}}$$

(e) at equivalence point $[OH^-] = 1.54\times10^{-3}\,M$

$$pOH = 2.81$$

$$\underline{\underline{pH = 11.19}}$$

(26) (a) moles of HCl = $\frac{0.175 \text{ mol}}{L} \times 0.02567 L = 4.49 \times 10^{-3}$ mol

∴ moles of aniline = 4.49×10^{-3} mol

conc. of aniline = $\frac{4.49 \times 10^{-3} \text{ mol}}{0.025 L}$ = **1.79×10^{-1} M**

(b) ~~aniline~~

$$C_6H_5NH_2(aq) + HCl(aq) \longrightarrow C_6H_5NH_3^+(aq) + Cl^-(aq)$$

	$C_6H_5NH_2$	HCl	$C_6H_5NH_3^+$	Cl^-
initial	4.49×10^{-3} mol	4.49×10^{-3} mol	~~4.49×10^{-3} mol~~ ϕ	ϕ
end of titration	ϕ	ϕ	4.49×10^{-3} mol	4.49×10^{-3} mol

Then an equilibrium is established.

$$C_6H_5NH_3^+(aq) + H_2O(aq) \rightleftharpoons C_6H_5NH_2(aq) + H_3O^+(aq)$$

initial = $\frac{4.49 \times 10^{-3} \text{ mol}}{0.05067 L} = 8.86 \times 10^{-2}$ M

	$C_6H_5NH_3^+$	$C_6H_5NH_2$	H_3O^+
change	$-x$	$+x$	$+x$
equilibrium	$(8.86 \times 10^{-2} - x)$	x	x

$$K_a(C_6H_5NH_3^+) = \frac{x^2}{(8.86 \times 10^{-2} - x)}$$

K_b of aniline = 4.0×10^{-10}

∴ K_a of $C_6H_5NH_3^+ = \frac{10^{-14}}{4.0 \times 10^{-10}} = 2.5 \times 10^{-5}$

$$\frac{x^2}{8.86\times10^{-2} - x} = 2.5\times10^{-5}$$

$$x^2 + 2.5\times10^{-5}x - 2.215\times10^{-6} = 0$$

$$x = \frac{-2.5\times10^{-5} \pm \sqrt{(2.5\times10^{-5})^2 + 4(2.215\times10^{-6})}}{2}$$

$x = 1.48\times10^{-3}\,M = [H_3O^+]$

$\therefore$ pH = 2.83 $\qquad$ pOH = 11.17 $\Rightarrow$ $[OH^-] = 6.78\times10^{-12}\,M$

$[C_6H_5NH_3^+] = 8.86\times10^{-2} - x = 8.71\times10^{-2}\,M$

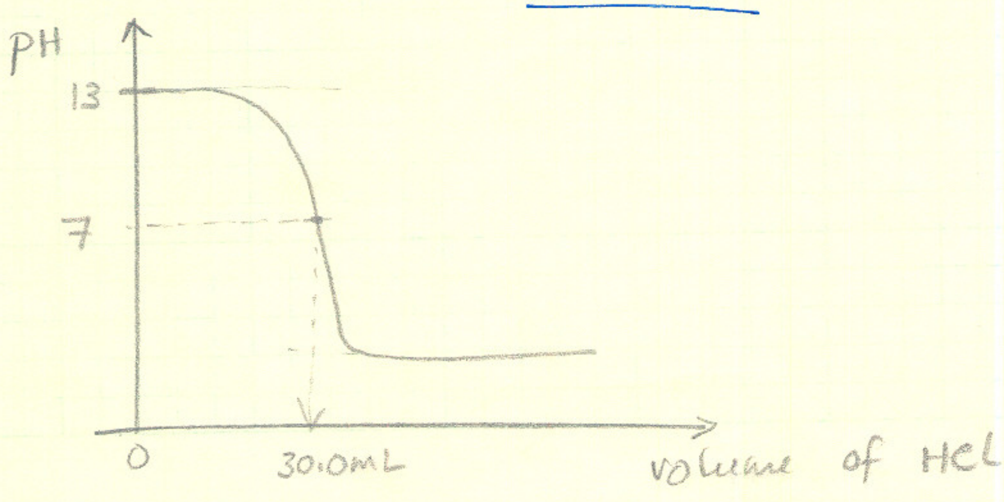
(27) $[OH^-]_{initial} = 0.10M$ $\qquad$ pOH = 1 $\qquad$ pH = 13

at equivalence point, pH = 7

since the two solutions (NaOH & HCl) have the same concentration, at the end point:

volume of HCl = volume of NaOH = 30.0mL

total volume = 60.0mL



(29) (a) $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

	NH_3		NH_4^+	OH^-
initial	0.10M			
change	$-x$		$+x$	$+x$
eq^m	$(0.10-x)$		x	x

$$K_b = \frac{x^2}{0.10-x} = 1.8\times10^{-5}$$

$$x^2 + 1.8\times10^{-5}x - 1.8\times10^{-6} = 0$$

$$x = \frac{-1.8\times10^{-5} \pm \sqrt{(1.8\times10^{-5})^2 + 4(1.8\times10^{-6})}}{2}$$

$x = 1.33\times10^{-3}$ M $= [OH^-] \Rightarrow pOH = 2.88$

$pH = 11.12$

(b) at equivalence point

moles of HCl = moles of NH_3

$$= \frac{0.10\text{ mol}}{L} \times 0.025L$$

$$= 2.5\times10^{-3}\text{ mol}$$

$NH_3(aq) + HCl(aq) \longrightarrow NH_4^+(aq) + Cl^-$

~~2.5×10^{-3} mol~~

	NH_3	HCl	NH_4^+	Cl^-
end of titration	ϕ	ϕ	2.5×10^{-3} mol	2.5×10^{-3} mol

~~2.5×10^{-3} mol~~

volume of HCl at end point $\Big\} = \dfrac{2.5\times10^{-3}\text{ mol}}{0.10\text{ mol/L}} = 2.5\times10^{-2}$ L total volume ~~at~~ end point $= (0.025 + 2.5 \times 10^{-2})\ L$

$= 5.0 \times 10^{-2}\ L$

$$[NH_4^+] \text{ at end point} = \frac{2.5 \times 10^{-3}\ mol}{5.0 \times 10^{-2}\ L}$$

$= 5.0 \times 10^{-2}\ M$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

	NH_4^+	NH_3	H_3O^+
initial	$5.0 \times 10^{-2}\ M$	ϕ	ϕ
change	$-x$	$+x$	$+x$
eq^m	$(5.0 \times 10^{-2} - x)$	x	x

$$K_a = \frac{x^2}{5.0 \times 10^{-2} - x}$$

$$K_a \text{ of } NH_4^+ = \frac{K_w}{K_b \text{ of } NH_3}$$

$$= \frac{10^{-14}}{1.8 \times 10^{-5}}$$

$K_a = 5.56 \times 10^{-10}$

$$\frac{x^2}{5.0 \times 10^{-2} - x} = 5.56 \times 10^{-10}$$

$$x^2 + 5.56 \times 10^{-10} x - 2.78 \times 10^{-11} = 0$$

$$x = \frac{-5.56 \times 10^{-10} \pm \sqrt{(5.56 \times 10^{-10})^2 + 4(2.78 \times 10^{-11})}}{2}$$

[illegible]

(c) At the half way point, there is a buffer system.

$$pH = pK_a + \log \frac{[\text{conj. base}]}{[\text{acid}]}$$ ~~where~~

[conj. base] = [acid] at half way point

$$\therefore pH = pK_a = -\log(5.56 \times 10^{-10})$$

$$= \underline{\underline{9.25}}$$

~~phenolphth~~

(d) Methyl red

(e) <u>5.00 mL of HCl</u>

moles of HCl = $0.10 \frac{mol}{L} \times 5.00 \times 10^{-3} L = 5.00 \times 10^{-4} mol$

$$NH_3(aq) + H^+(aq) \longrightarrow NH_4^+(aq)$$

	$NH_3(aq)$	$H^+(aq)$	$NH_4^+(aq)$
	2.5×10^{-3} mol	5.00×10^{-4} mol	
	-5.00×10^{-4} mol	-5.00×10^{-4} mol	$+5.00 \times 10^{-4}$ mol
end of titration	2.00×10^{-3} mol	0	5.00×10^{-4} mol

total volume: 25.00 mL + 5.00 mL = 30.00 mL

$$[NH_3] = \frac{2.00 \times 10^{-3} mol}{30.00 \times 10^{-3} L} = 6.67 \times 10^{-2} M$$

$$[NH_4^+] = \frac{5.00 \times 10^{-4} mol}{30.00 \times 10^{-3} L} = 1.67 \times 10^{-2} M$$

$$pOH = pK_b + \log \frac{[NH_4^+]}{[NH_3]}$$

$$= -\log(1.8 \times 10^{-5}) + \log\left(\frac{1.67 \times 10^{-2}}{6.67 \times 10^{-2}}\right)$$

$$= 4.14$$

$$pH = \underline{\underline{9.86}}$$

<u>add 15.00 mL HCl</u>

$$\text{moles HCl} = \frac{0.10\,\text{mol}}{L} \times 15.00 \times 10^{-3}\,L = 1.50 \times 10^{-3}\,\text{mol}$$

∴ mol of NH_4^+ at end of titration $= 1.50 \times 10^{-3}$ mol

" " NH_3 " " $= \left(2.50 \times 10^{-3} - 1.50 \times 10^{-3}\right)$ mol

$$= 1.0 \times 10^{-3}\,\text{mol}$$

total volume $= (25.00 + 15.00)$ mL $= 40.00$ mL

$$[NH_3] = \frac{1.0 \times 10^{-3}\,\text{mol}}{40.00 \times 10^{-3}\,L} = 2.50 \times 10^{-2}\,M$$

$$[NH_4^+] = \frac{1.50 \times 10^{-3}\,\text{mol}}{40.00 \times 10^{-3}\,L} = 3.75 \times 10^{-2}\,M$$

$$pOH = pK_b + \log \frac{[NH_4^+]}{[NH_3]}$$

$$pOH = 4.74 \;(\text{~~5.26~~}) + \log\left(\frac{3.75 \times 10^{-2}}{2.50 \times 10^{-2}}\right) = 4.92$$

$$pH = \underline{\underline{9.08}}$$

add 20.0 mL acid

mol of HCl = 2.00×10^{-3} mol

mol of NH_4^+ at end of titration = 2.00×10^{-3} mol

" " NH_3 " " = 0.50×10^{-3} mol

total volume = $(25.00 + 20.00) = 45.00$ mL

$$[NH_3] = \frac{0.50 \times 10^{-3}\ \text{mol}}{45.00 \times 10^{-3}\ \text{L}} = 1.11 \times 10^{-2}\ \text{M}$$

$$[NH_4^+] = \frac{2.00 \times 10^{-3}\ \text{mol}}{45.00 \times 10^{-3}\ \text{L}} = 4.44 \times 10^{-2}\ \text{M}$$

$$pOH = 4.74 + \log\left(\frac{4.44 \times 10^{-2}}{1.11 \times 10^{-2}}\right) = 5.35$$

$pH = 8.65$

add 22.0 mL HCl

mol of HCl = 2.20×10^{-3} mol

mol of NH_4^+ at end of titration = 2.20×10^{-3} mol

" " NH_3 " " = 3.0×10^{-4} mol

$$pOH = pK_b + \log \frac{[NH_4^+]}{[NH_3]}$$

$$pOH = 4.74 + \log\left(\frac{4.68 \times 10^{-2}}{6.3 \times 10^{-3}}\right) = 5.60$$

$\Rightarrow$ pH = 8.39

add 30.0 mL HCl

mol of HCl = $0.10 \frac{mol}{L} \times 30.0 \times 10^{-3} L = 3.00 \times 10^{-3}$ mol

	$NH_3(aq)$ +	$H^+(aq)$ $\longrightarrow$	$NH_4^+(aq)$
	2.50×10^{-3} mol	3.00×10^{-3} mol	
reacted	-2.50×10^{-3} mol	-2.50×10^{-3} mol	$+2.50 \times 10^{-3}$ mol
left after titration	ϕ	5.0×10^{-4} mol	2.50×10^{-3} mol

The titration is now over, because all the NH_3 has been ~~reacted~~ used up (titrated) by HCl. Total volume = 55.0 mL

The system then reaches equilibrium.

	$NH_4^+(aq)$ + $H_2O(l)$ $\rightleftharpoons$	$NH_3(aq)$ +	$H_3O^+(aq)$
initial	2.50×10^{-3} mol	ϕ	5.0×10^{-4} mol
	$\frac{2.50 \times 10^{-3} mol}{55.0 \times 10^{-3} L} = 4.545 \times 10^{-2}$ M		$\frac{5.0 \times 10^{-4} mol}{55.0 \times 10^{-3} L} = 9.091 \times 10^{-3}$ M
change	$-x$	$+x$	$+x$
equilibrium	$(4.545 \times 10^{-2} - x)$	x	$(9.091 \times 10^{-3} + x)$

$$K_a \text{ (of } NH_4^+) = \frac{[NH_3]_{eq}[H_3O^+]_{eq}}{[NH_4^+]_{eq}} = \frac{x(9.091\times10^{-3}+x)}{(4.545\times10^{-2}-x)}$$

$$5.56\times10^{-10} = \frac{x^2 + 9.091\times10^{-3}x}{4.545\times10^{-2}-x}$$

$$x^2 + 9.091\times10^{-3}x + 5.56\times10^{-10}x - 2.527\times10^{-11} = 0$$

$$x^2 + 9.091\times10^{-3}x - 2.527\times10^{-11} = 0$$

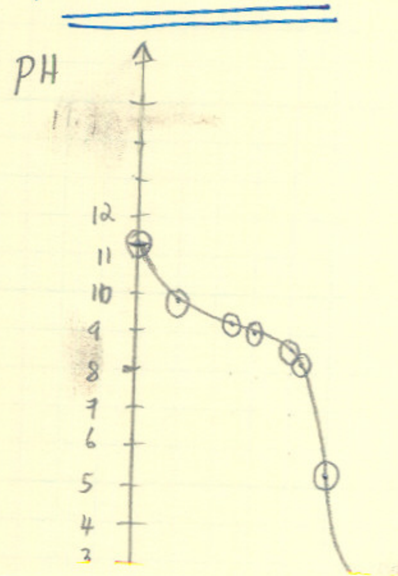
$$x = \frac{-9.091\times10^{-3} \pm \sqrt{(9.091\times10^{-3})^2 + 4(2.527\times10^{-11})}}{2}$$

$$x = 3.058\times10^{-9}\ M$$

$$[H_3O^+] = 9.091\times10^{-3} + x = 9.091\times10^{-3}\ M$$

(x is very small comparatively)

pH = 2.04



Chapter 23

(43) (a) $^{23}_{11}Na + ^{1}_{0}n \longrightarrow ^{24}_{11}Na$

$$^{24}_{11}Na \longrightarrow ^{0}_{-1}\beta + ^{24}_{12}Mg$$

$$\ln\left(\frac{A_t}{A_0}\right) = -kt$$

$$\ln\left(\frac{1.01 \times 10^{+4}}{2.54 \times 10^{+4}}\right) = -k(20\,hrs)$$

$$k = 0.046\,hrs^{-1}$$

$$t_{1/2} = \frac{0.693}{k}$$

$$= \frac{0.693}{0.046\,hrs^{-1}}$$

$$= 15.03\,hrs$$

(44) $\ln\left(\frac{A_t}{A_0}\right) = -kt \Rightarrow \ln\left(\frac{5470}{7840}\right) = -k(72\,days)$

$$k = 4.99 \times 10^{-3}\,d^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = 138.6\,days$$

(45)

$$^{239}_{94}Pu + 2\,^{1}_{0}n \longrightarrow \,^{241}_{94}Pu$$

$$^{241}_{94}Pu \longrightarrow \,^{0}_{-1}\beta + \,^{241}_{95}Am$$

(50)

(a) $^{114}_{48}Cd + \,^{2}_{1}H \longrightarrow \,^{115}_{48}Cd + \,^{1}_{1}H$

(b) $^{6}_{3}Li + \,^{2}_{1}H \longrightarrow \,^{7}_{4}Be + \,^{1}_{0}n$

(c) $^{40}_{20}Ca + \,^{2}_{1}H \longrightarrow \,^{38}_{19}K + \,^{4}_{2}He$ or $^{4}_{2}\alpha$

(d) $^{63}_{29}Cu + \,^{2}_{1}H \longrightarrow \,^{65}_{30}Zn + \,^{0}_{0}\gamma$