AP Chemistry – Other Aspects of Aqueous Equilibria (Kotz – 18))
Homework Answers 2, 7, 14, 21, 24, 30, 32, 35, 37, 41, 49, 55, 58, 65, 67

18.2 (a) pH increases ($C_2O_4^{2-}$ is a weak base)

(b) pH decreases slightly (NH_4^+, a weak acid, is being added to a solution containing a strong acid)

(c) no change (NaCl is a neutral salt)

18.7 $NH_4^+(aq) + H_2O(\ell) \leftrightarrow H_3O^+(aq) + NH_3(aq)$

$$[NH_4^+] = \frac{2.2\text{ g }NH_4Cl}{0.25\text{ L}} \cdot \frac{1\text{ mol }NH_4Cl}{53.5\text{ g}} \cdot \frac{1\text{ mol }NH_4^+}{1\text{ mol }NH_4Cl} = 0.16\text{ M}$$

$$K_a = 5.6 \times 10^{-10} = \frac{[H_3O^+][NH_3]}{[NH_4^+]} = \frac{(x)(0.12+x)}{(0.16-x)} \approx \frac{(x)(0.12)}{0.16}$$

$x = [H_3O^+] = 7.7 \times 10^{-10}$ M

pH = $-\log[H_3O^+]$ = 9.11

The buffer solution has a lower pH than the original NH_3 solution (pH = 11.17) because a weak acid (NH_4^+) was added to the ammonia solution.

18.14 (a) $pK_a = -\log(6.2 \times 10^{-8}) = 7.21$

$$5.677\text{ g} \cdot \frac{1\text{ mol }Na_2HPO_4}{141.96\text{ g}} = 0.03999\text{ mol }Na_2HPO_4$$

$$1.360\text{ g} \cdot \frac{1\text{ mol }KH_2PO_4}{136.08\text{ g}} = 0.009994\text{ mol }KH_2PO_4$$

$$pH = pK_a + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 7.21 + \log\left(\frac{0.03999}{0.009994}\right) = 7.81$$

(b) $$pH = 7.31 = 7.21 + \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$0.10 = \log\frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$\frac{[HPO_4^{2-}]}{[H_2PO_4^-]} = 1.3 = \frac{0.03999\text{ mol}}{x}$$

$x = 0.032$ mol $H_2PO_4^-$

$$0.032\text{ mol} \cdot \frac{1\text{ mol }KH_2PO_4}{1\text{ mol }H_2PO_4^-} \cdot \frac{136.1\text{ g}}{1\text{ mol }KH_2PO_4} = 4.3\text{ g}$$

mass of KH_2PO_4 to add = 4.3 g total – 1.360 g in buffer = 2.9 g

18.21 (a) $$[NH_4^+] = \frac{0.125\text{ mol}}{0.500\text{ L}} = 0.250\text{ M}$$

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4^+]} = -\log(5.6 \times 10^{-10}) + \log\left(\frac{0.500}{0.250}\right) = 9.55$$

(b) $[HCl] = \dfrac{0.0100 \text{ mol}}{0.500 \text{ L}} = 0.0200 \text{ M}$

$H_3O^+(aq) + NH_3(aq) \rightarrow H_2O(\ell) + NH_4^+(aq)$

	NH_4^+	NH_3
Initial (M)	0.250	0.500
Change (M)	+0.0200	–0.0200
Equilibrium (M)	0.270	0.480

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4^+]} = -\log(5.6 \times 10^{-10}) + \log\left(\frac{0.480}{0.270}\right) = 9.50$$

18.24 (a) $[C_6H_5CO_2H] = \dfrac{0.235 \text{ g}}{0.100 \text{ L}} \cdot \dfrac{1 \text{ mol } C_6H_5CO_2H}{122.1 \text{ g}} = 0.0192 \text{ M}$

$$K_a = 6.3 \times 10^{-5} = \frac{[C_6H_5CO_2^-][H_3O^+]}{[C_6H_5CO_2H]} = \frac{x^2}{0.0192 - x} \approx \frac{x^2}{0.0192}$$

$x = [H_3O^+] = 0.0011 \text{ M}$

$pH = -\log[H_3O^+] = 2.96$

(b)

	$C_6H_5CO_2H$ +	OH^- →	$C_6H_5CO_2^-$ + H_2O
Initial (mol)	0.00192	0.00192	0
Change (mol)	–0.00192	–0.00192	+0.00192
After reaction (mol)	0	0	0.00192

Total volume = 0.100 L + (0.00192 mol NaOH)(1 L/0.108 mol) = 0.118 L

$C_6H_5CO_2^-(aq) + H_2O(\ell) \leftrightarrow C_6H_5CO_2H(aq) + OH^-(aq)$

$[C_6H_5CO_2^-] = \dfrac{0.00192 \text{ mol}}{0.118 \text{ L}} = 0.0163 \text{ M}$

$$K_b = \frac{K_w}{K_a} = 1.6 \times 10^{-10} = \frac{[C_6H_5CO_2H][OH^-]}{[C_6H_5CO_2^-]} = \frac{x^2}{0.0163 - x} \approx \frac{x^2}{0.0163}$$

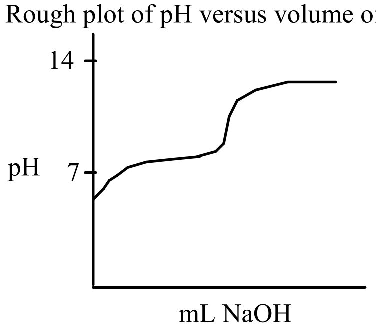
$x = 1.6 \times 10^{-6} \text{ M} = [OH^-]$

$[H_3O^+] = \dfrac{K_w}{[OH^-]} = 6.2 \times 10^{-9} \text{ M}$

$[Na^+] = [C_6H_5CO_2^-] = 0.0163 \text{ M}$

(c) $pH = -\log[H_3O^+] = 8.21$

18.30 Rough plot of pH versus volume of base:



(a) $K_a = 4.0 \times 10^{-10} = \frac{[CN^-][H_3O^+]}{[HCN]} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050}$

$x = [H_3O^+] = 4.5 \times 10^{-6}$ M

pH = –log[H_3O^+] = 5.35

(b) At the half-neutralization point, [HCN] = [CN^-], and pH = pK_a = 9.40

(c) When 95% of NaOH has been added

mol CN^- = 0.95(mol HCN)$_{initial}$ = 0.95(0.0250 L)(0.050 mol/L) = 0.0012 mol CN^-

mol HCN = 0.05(mol HCN)$_{initial}$ = 0.05(0.0250 L)(0.050 mol/L) = 6×10^{-5} mol HCN

$$\text{pH} = \text{p}K_a + \log\frac{[CN^-]}{[HCN]} = -\log(4.0 \times 10^{-10}) + \log\left(\frac{0.0012}{6 \times 10^{-5}}\right) = 10.7$$

(d) $\frac{0.050 \text{ mol HCN}}{1.0 \text{ L}} \cdot 0.0250 \text{ L} \cdot \frac{1 \text{ mol NaOH}}{1 \text{ mol HCN}} \cdot \frac{1 \text{ L}}{0.075 \text{ mol NaOH}} = 0.017 \text{ L} = 17 \text{ mL}$

(e) $CN^-(aq) + H_2O(\ell) \leftrightarrow HCN(aq) + OH^-(aq)$

$$[CN^-] = \frac{0.050 \text{ mol HCN}}{1.0 \text{ L}} \cdot 0.025 \text{ L} \cdot \frac{1 \text{ mol } CN^-}{1 \text{ mol HCN}} \cdot \frac{1}{0.042 \text{ L}} = 0.030 \text{ M}$$

$$K_b = \frac{K_w}{K_a} = 2.5 \times 10^{-5} = \frac{[HCN][OH^-]}{[CN^-]} = \frac{x^2}{0.030 - x} \approx \frac{x^2}{0.030}$$

$x = [OH^-] = 8.7 \times 10^{-4}$ M

pOH = –log[OH^-] = 3.06

pH = 14.00 – pOH = 10.94

(f) Alizarin yellow GG would be a reasonable choice for an indicator.

(g) When 105% of NaOH has been added, pH depends only on the excess OH^-

excess OH^- = = 0.05(0.017 L NaOH)(0.075 mol/L) = 6×10^{-5} mol OH^-

$$[OH^-] = \frac{6 \times 10^{-5} \text{ mol}}{0.042 \text{ L}} = 0.0015 \text{ M}$$

pOH = –log[OH^-] = 2.83

pH = 14.00 – pOH = 11.17

18.32

Titration	pH at Equiv. Point	Possible Indicator
(a) HCO_3^- titrated with NaOH	>7 (about 12-13)	alizarin yellow
(b) HClO with NaOH	>7 (about 10-11)	thymolphthalein
(c) $(CH_3)_3N$ with HCl	<7 (about 5-6)	methyl red

18.35 (a) soluble (most ammonium salts are soluble)

(b) soluble (most sulfate salts are soluble)

(c) insoluble (most sulfide salts are insoluble)

(d) insoluble (most sulfate salts are soluble, barium sulfate is an exception)

18.37 (a) $AgCN(s) \leftrightarrow Ag^+(aq) + CN^-(aq)$ $K_{sp} = [Ag^+][CN^-]$

(b) $NiCO_3(s) \leftrightarrow Ni^{2+}(aq) + CO_3^{2-}(aq)$ $K_{sp} = [Ni^{2+}][CO_3^{2-}]$

(c) $AuBr_3(s) \leftrightarrow Au^{3+}(aq) + 3\ Br^-(aq)$ $\qquad K_{sp} = [Au^{3+}][Br^-]^3$

18.41 $[F^-] = 2 \times [Sr^{2+}] = 2.06 \times 10^{-3}$ M

$K_{sp} = [Sr^{2+}][F^-]^2 = (1.03 \times 10^{-3})(2.06 \times 10^{-3})^2 = 4.37 \times 10^{-9}$

18.49

	$RaSO_4(s) \leftrightarrow$	$Ra^{2+}(aq)$ +	$SO_4^{2-}(aq)$
Initial (M)		0	0
Change (M)		$+x$	$+x$
Equilibrium (M)		x	x

$K_{sp} = [Ra^{2+}][SO_4^{2-}] = (x)(x) = x^2$

$x = \sqrt{K_{sp}} = \sqrt{3.7 \times 10^{-11}} = 6.1 \times 10^{-6}$ mol/L

$$\frac{6.1 \times 10^{-6}\ \text{mol Ra}^{2+}}{1\ \text{L}} \cdot 0.100\ \text{L} \cdot \frac{1\ \text{mol RaSO}_4}{1\ \text{mol Ra}^{2+}} \cdot \frac{322\ \text{g}}{1\ \text{mol RaSO}_4} \cdot \frac{10^3\ \text{mg}}{1\ \text{g}} = 0.20\ \text{mg RaSO}_4\ \text{dissolves}$$

18.55 (a) $K_{sp} = 8.5 \times 10^{-17} = [Ag^+][I^-] = (x)(x) = x^2$

$x = \sqrt{K_{sp}} = \sqrt{8.5 \times 10^{-17}} = 9.2 \times 10^{-9}$ mol/L

$$\frac{9.2 \times 10^{-9}\ \text{mol Ag}^+}{1\ \text{L}} \cdot \frac{1\ \text{mol AgI}}{1\ \text{mol Ag}^+} \cdot \frac{235\ \text{g}}{1\ \text{mol AgI}} \cdot \frac{10^3\ \text{mg}}{1\ \text{g}} \cdot \frac{1\ \text{L}}{10^3\ \text{mL}}$$

$= 2.2 \times 10^{-6}$ mg/mL in pure water

(b) $K_{sp} = 8.5 \times 10^{-17} = [Ag^+][I^-] = (x)(0.020 + x) \approx x(0.020)$

$x = 4.3 \times 10^{-15}$ mol/L

$$\frac{4.3 \times 10^{-15}\ \text{mol Ag}^+}{1\ \text{L}} \cdot \frac{1\ \text{mol AgI}}{1\ \text{mol Ag}^+} \cdot \frac{235\ \text{g}}{1\ \text{mol AgI}} \cdot \frac{10^3\ \text{mg}}{1\ \text{g}} \cdot \frac{1\ \text{L}}{10^3\ \text{mL}}$$

$= 1.0 \times 10^{-13}$ mg/mL in 0.020 M $AgNO_3$

18.58 (a) Ag_2CO_3

(b) $PbCO_3$

(c) AgCN

18.65 $AuCl(s) \leftrightarrow Au^+(aq) + Cl^-(aq)$ $\qquad K_{sp} = 2.0 \times 10^{-13}$

$Au^+(aq) + 2\ CN^-(aq) \leftrightarrow Au(CN)_2^-(aq)$ $\qquad K_{form} = 2.0 \times 10^{38}$

$AuCl(s) + 2\ CN^-(aq) \leftrightarrow Au(CN)_2^-(aq) + Cl^-(aq)$ $\qquad K_{net} = K_{sp} \cdot K_{form} = 4.0 \times 10^{25}$

18.67 (a) Add H_2SO_4, precipitating $BaSO_4$ and leaving $Na^+(aq)$ in solution.

(b) Add HCl or another source of chloride ion. $PbCl_2$ will precipitate, but $NiCl_2$ is water-soluble.