Chapter 1: Solutions to Review Problems

Section 1.1

1) a) $$K_p = \frac{\left(P_{NO}\right)^4 \left(P_{H_2}\right)^4}{\left(P_{N_2}\right)^2 \left(P_{H_2O}\right)^4}$$

b) $$K_p = \frac{\left(P_{O_2}\right)^{0.5}}{\left(P_{CO_2}\right)}$$

c) $$K_p = \left(P_{Xe}\right)^3$$

2) a) $4\,HCl(g) + O_2(g) \rightleftharpoons 2\,H_2O(g) + 2\,Cl_2(g)$

b) $2\,H_2O(g) + O_2(g) \rightleftharpoons 2\,H_2O_2(g)$

3) a) Homogeneous $$K_p = \frac{\left(P_{NOF_3}\right)^2}{\left(P_{NO}\right)^2 \left(P_{F_2}\right)^3}$$

b) Heterogeneous $$K_p = \frac{1}{\left(P_{O_2}\right)^{0.5}}$$

c) Heterogeneous $$K_p = \frac{\left(P_{SO_2}\right)^2}{\left(P_{O_2}\right)^3}$$

d) Heterogeneous $$K_c = \left[\mathrm{Ca^{2+}}\right]\left[\mathrm{F^-}\right]^2$$

e) Homogeneous $$K_c = \frac{\left[\mathrm{H_3O^+}\right]^2\left[\mathrm{SO_3{}^{2-}}\right]}{\left[\mathrm{H_2SO_3}\right]}$$

4) Equilibrium obtained from reactions 1) and 2):
$Cl_2(g) + 3\ F_2(g) \rightleftharpoons 2\ ClF_3(g)$
c) is the correct expression for the equilibrium constant.

5) a) i) is okay, ii) is reversed $\therefore K_3 = \frac{K_1}{K_2}$

b) Both i) and ii) are reversed and multiplied by 2 $\therefore K_3 = \frac{1}{(K_2 \times K_1)^2}$

c) i) is okay, ii) is multiplied by 2 $\therefore K_3 = K_1 \times K_2^2$

6) Reaction has been reversed. $\therefore K_p = \frac{1}{49} = 0.0204$

7) Reaction has been reversed and multiplied by 3.

$$\therefore K_c = \frac{1}{(0.77)^3} = 2.19$$

8) a) $2\ H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$

b) $K_{eq} = \frac{P_{CH_3OH}}{\left(P_{H_2}\right)^2 \left(P_{CO}\right)}$

c) $K_{eq} = \frac{P_{CH_3OH}}{\left(P_{H_2}\right)^2 \left(P_{CO}\right)}$ $\therefore K_P = \frac{1.36kPa}{(177.3kPa)^2 (71.11kPa)} = 6.08 \times 10^{-7} kPa^{-2}$

d) Reaction is: $2\ CH_3OH(g) \rightleftharpoons 4\ H_2(g) + 2\ CO(g)$

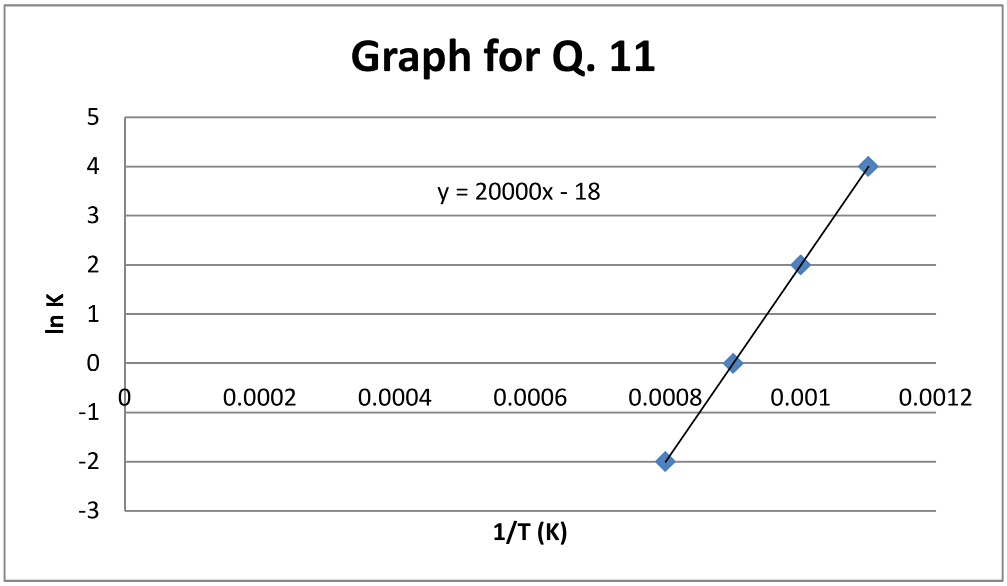
$$\therefore K_P = \left(\frac{1}{6.08 \times 10^{-7} kPa^{-2}}\right)^2 = 2.705 \times 10^{12} kPa^4$$

9)
$$\ln\frac{K_2}{K_1}=\frac{\Delta H^o_{rxn}}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$
$$\therefore \ln\frac{4.0\times10^{-1}}{1.8\times10^{2}}=\frac{\Delta H^o_{rxn}}{8.314}\left(\frac{1}{850}-\frac{1}{1100}\right)$$
$$\therefore \Delta H^o_{rxn}=-190kJmol^{-1}$$

10) $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ $K_c = 0.77$ at 1020K = K_2, $T_1 = 850$ K, so $K_1 = $?

$\Delta H^o = [(-241.8) + (-110.5)] - [(-393.5) + 0] = 41.2$ kJ
$$\ln\frac{K_2}{K_1}=\frac{\Delta H^o}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$
$$\therefore \ln\frac{0.77}{K_1}=\frac{41200}{8.314}\left(\frac{1}{850}-\frac{1}{1020}\right)$$
$$\therefore K_1=0.291$$

11)



Equation of a straight line: y = mx + b; so m = 20000; b = -18

Slope could also be determined from data points:

$$m=\frac{\Delta y}{\Delta x}=\frac{y_3-y_2}{x_3-x_2}=\frac{2.0-0}{10.0\times10^{-4}-9.0\times10^{-4}}=20,000$$

11) cont.

$$\text{b(y-intercept)} = \frac{\Delta S^o}{R} \quad \Rightarrow \quad \text{Substituting:} -18 = \frac{\Delta S^o}{8.314 Jmol^{-1}K^{-1}}$$

$$\therefore \Delta S^o = -149.7 Jmol^{-1}K^{-1}$$

$$\text{m(slope of line)} = -\frac{\Delta H^o_{rxn}}{R} \quad \Rightarrow \text{Substituting: } 20000 = -\frac{\Delta H_{rxn}{}^o}{8.314 Jmol^{-1}K^{-1}}$$

$$\therefore \Delta H^o_{rxn} = -166.3 kJmol^{-1}$$

12)

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^o_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\therefore \ln\frac{6.5}{2.5\times10^2} = \frac{\Delta H^o_{rxn}}{8.314}\left(\frac{1}{298} - \frac{1}{368}\right)$$

$$\therefore \Delta H^o_{rxn} = -47.5 kJmol^{-1}$$

13)

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^o_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\therefore \ln\frac{K_2}{6.5\times10^{-2}} = \frac{-46500}{8.314}\left(\frac{1}{358} - \frac{1}{508}\right)$$

$$\therefore K_2 = 6.45\times10^{-4}$$

14)

$$\ln\frac{K_2}{K_1} = \frac{\Delta H^o_{rxn}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\therefore \ln\frac{6.5}{4.5\times10^{-2}} = \frac{-65200}{8.314}\left(\frac{1}{383} - \frac{1}{T_2}\right)$$

$$\therefore T_2 = 308\text{K}$$

Section 1.2

1) a)

Equilibrium is:	$AgBr(s)$	$\rightleftharpoons$	$Ag^+(aq)$	$+ Br^-(aq)$
Initial:	solid		0	0
Equilibrium:	solid – x		x	x

Solubility = $1.3 \times 10^{-4}\ gL^{-1}$ = Amount of AgBr that dissolves.

$$\text{Solubility} = \frac{1.3\times10^{-4}\,gL^{-1}}{187.8\,gmol^{-1}} = 6.92\times10^{-7}\,molL^{-1} = "x"$$

$K_{sp} = [Ag^+][Br^-] = (x)(x) = x^2 = (6.92 \times 10^{-7})^2 = 4.79 \times 10^{-13}$

b)

Equilibrium is:	$SrF_2(s)$	$\rightleftharpoons$	$Sr^{2+}(aq)$	$+ 2\ F^-(aq)$
Initial:	solid		0	0
Equilibrium:	solid – x		x	2 x

Solubility = $0.13\ gL^{-1}$ = Amount of SrF_2 that dissolves.

$$\text{Solubility} = \frac{0.13\,gL^{-1}}{125.6\,gmol^{-1}} = 1.03\times10^{-3}\,molL^{-1} = "x"$$

$K_{sp} = [Sr^{2+}][F^-]^2 = (x)(2x)^2 = 4x^3 = 4(1.03 \times 10^{-3})^3 = 4.43 \times 10^{-9}$

2) a)

Equilibrium is:	$MgCO_3(s)$	$\rightleftharpoons$	$Mg^{2+}(aq)$	$+ CO_3^{2-}(aq)$	$K_{sp} = 1.0 \times 10^{-15}$
Initial:	solid		0	0	
Equilibrium:	solid – x		x	x	

$K_{sp} = [Mg^{2+}][CO_3^{2-}] = 1.0 \times 10^{-15} = x^2$ Solubility = x

$$\therefore x = \sqrt{1.0\times10^{-15}} = 3.16\times10^{-8}\,molL^{-1}$$

b)

Equilibrium is:	$Mn(OH)_2(s)$	$\rightleftharpoons$	$Mn^{2+}(aq)$	$+ 2\ OH^-(aq)$	$K_{sp} = 2.0 \times 10^{-13}$
Initial:	solid		0	0	
Equilibrium:	solid – x		x	2 x	

$K_{sp} = [Mn^{2+}][OH^-]^2 = 2.0 \times 10^{-13} = 4x^3$ Solubility = x

$$\therefore x = \sqrt[3]{\frac{2.0\times10^{-13}}{4}} = 3.68\times10^{-5}\,molL^{-1}$$

$[OH^-] = 2x = 7.36 \times 10^{-5}$
pOH = 4.13, $\therefore$ pH = 9.87

3) Equilibrium is: $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ F^{-}(aq)$ $K_{sp} = [Ca^{2+}][F^{-}]^2$

$[Ca^{2+}] = 0.070\ M$

Substitute into K_{sp} to determine maximum possible $[F^{-}]$ possible when $[Ca^{2+}] = 0.070\ M$

$K_{sp} = [Ca^{2+}][F^{-}]^2 = 3.4 \times 10^{-11} = (0.070)[F^{-}]^2$

$[F^{-}] = 2.2 \times 10^{-5}\ M$

4) Equilibrium is: $SrF_2(s) \rightleftharpoons Sr^{2+}(aq) + 2\ F^{-}(aq)$

	$SrF_2(s)$	$Sr^{2+}(aq)$	$2\ F^{-}(aq)$
Initial:	solid	0	0
Equilibrium:	solid – x	x	2 x

Solubility = 0.109 gL^{-1} = Amount of SrF_2 that dissolves.

$$\text{Solubility} = \frac{0.109\,gL^{-1}}{125.6\,gmol^{-1}} = 8.68 \times 10^{-4}\,molL^{-1} = "x"$$

$K_{sp} = [Sr^{2+}][F^{-}]^2 = (x)(2x)^2 = 4x^3 = 4(8.68 \times 10^{-4})^3 = 2.62 \times 10^{-9}$

Note: If your calculator gives you 0.000000002, you must convert to scientific notation, not just count decimal places!

5) *Ion Product* refers to the product of the ion concentrations in the solution.
Solubility Product refers to the product of the ion concentrations in a saturated solution at equilibrium.
Q will be equal to the *solubility product* at the point where precipitation of solid just begins.

6) a) Incorrect; at equilibrium, the Ion Product is equal to K_{sp}. The two ion concentrations are not necessarily equal.

b) Incorrect; while the presence of the common ion (in this case Cl^{-}) causes the equilibrium to shift to the left, thereby reducing the amount of $PbCl_2$ that dissolves, K_{sp} does not change.

c) Incorrect; if the pH of the solution is increased, the amount of OH^{-} in solution increases. This will act as a common ion, reducing the solubility of the metal hydroxide.

7) Equilibrium is: $MnS(s) \rightleftharpoons Mn^{2+}(aq) + S^{2-}(aq)$

$K_{sp} = [Mn^{2+}][S^{2-}] = 5.0 \times 10^{-14}$

$Na_2S(aq) \rightarrow Na^{+}(aq) + S^{2-}(aq)$ $\therefore [S^{2-}] = 0.025\ M$

Set Ion Product = K_{sp} : $K_{sp} = 5.0 \times 10^{-14} = [Mn^{2+}][S^{2-}] = [Mn^{2+}](0.025)$

$\therefore [Mn^{2+}] = 2.0 \times 10^{-12}\ M$

moles Mn^{2+} = $2.0 \times 10^{-12}\ M \times 0.100\ L = 2.0 \times 10^{-13}$ moles = moles $MnCl_2$ required

Mass $MnCl_2$ = 2.0×10^{-13} moles x $125.8\ gmol^{-1} = 2.5 \times 10^{-11}\ g$

8) Reaction for precipitation reaction is: $Ba^{2+}(aq) + 2\ F^{-}(aq) \rightarrow BaF_2(s)$

Equilibrium is: $BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2\ F^{-}(aq)$ $K_{sp} = [Ba^{2+}][F^{-}]^2$

$$\left[\mathrm{Ba}^{2+}\right]_{\text{after mixing}} = \frac{0.0010M \times 0.035L}{0.235L} = 1.49\times10^{-4}M$$

$$\left[\mathrm{F}^{-}\right]_{\text{after mixing}} = \frac{0.040M \times 0.200L}{0.235L} = 0.0340M$$

$K_{sp} = [Ba^{2+}][F^{-}]^2 = (1.49 \times 10^{-4})(0.0340)^2 = 1.72 \times 10^{-7}$

9) Possible precipitation reaction is: $Ag^{+}(aq) + Cl^{-}(aq) \rightarrow AgCl(s)$

Equilibrium is: $AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$ $K_{sp} = [Ag^{+}][Cl^{-}] = 1.7 \times 10^{-10}$

$$\left[\mathrm{Ag}^{+}\right]_{\text{after mixing}} = \frac{0.010M \times 0.001L}{1.00L} = 1.00\times10^{-5}M$$

$$\left[\mathrm{Cl}^{-}\right]_{\text{after mixing}} = \frac{2.0\times10^{-4}M \times 0.999L}{1.00L} = 1.998\times10^{-4}M$$

Ion Product = $[Ag^{+}][Cl^{-}] = (1.00 \times 10^{-5})(1.998 \times 10^{-4}) = 1.998 \times 10^{-9}$

Ion Product > K_{sp}, so a precipitate will form.

10) a) pH = 9.56; basic solution, so pOH = 4.44 $\therefore [OH^{-}] = 3.63 \times 10^{-5}\ M$

Equilibrium is: $Cd(OH)_2(s) \rightleftharpoons Cd^{2+}(aq) + 2\ OH^{-}(aq)$

Initial:	solid	0	0
Equilibrium:	solid – x	x	2 x

$\therefore [OH^{-}] = 2x$, so $x = 1.815 \times 10^{-5}\ M$

x is the solubility of $Cd(OH)_2$, so moles of $Cd(OH)_2 = 1.815 \times 10^{-5}$

Mass $Cd(OH)_2 = 1.815 \times 10^{-5}$ moles x 146.4 $g mol^{-1}$ = $2.66 \times 10^{-3}\ g$

b) $2.66 \times 10^{-3}\ g$ of $Cd(OH)_2$ dissolve in 1.0 L of water

$\therefore$ 1.0 g " " " x L "

x = 375.9 L

c) $K_{sp} = [Cd^{2+}][OH^{-}]^2 = (x)(2x)^2 = 4x^3 = 4(1.815 \times 10^{-5})^3 = 2.39 \times 10^{-14}$

11) a) Precipitation reaction is: $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

moles Ag^+ = 0.050 *M* x 0.050 *L* = 0.0025 moles (Limiting Reagent)

moles Cl^- = 0.10 *M* x 0.050 *L* = 0.0050 moles

$\therefore$ moles AgCl formed = 0.0025 moles

Mass AgCl = 0.0025 moles x 143.35 $gmol^{-1}$= 0.358 *g* = 358 *mg*

b) $$\left[\mathrm{Cl}^-\right]_{xs} = \frac{0.0025 moles}{0.100L} = 0.025M$$

Equilibrium is:	$AgCl(s) \rightleftharpoons$	$Ag^+(aq)$	$+ Cl^-(aq)$
Initial:	solid	0	0.0250
Equilibrium:	solid – x	x	0.0250 + x

$K_{sp} = [Ag^+][Cl^-] = 1.7 \times 10^{-10} = (x)(0.0250 + x)$

$\therefore x = 6.8 \times 10^{-9}$ *M* = $[Ag^+]$

12) pH = 5.30, pOH = 8.70, $\therefore [OH^-] = 2.0 \times 10^{-9}$ *M*

Equilibrium is: $Pb(OH)_2(s) \rightleftharpoons Pb^{2+}(aq) + 2\,OH^-(aq)$ $K_{sp} = [Pb^{2+}][OH^-]^2 = 4.2 \times 10^{-15}$

Substitute $[OH^-] = 2.0 \times 10^{-9}$ *M* into K_{sp} expression and solve for $[Pb^{2+}]$

$\therefore [Pb^{2+}] = 1.05 \times 10^{3}$ *M*

13) Equilibrium is: $Ag_2CrO_4(s) \rightleftharpoons 2\,Ag^+(aq) + CrO_4{}^{2-}(aq)$ $K_{sp} = [Ag^+]^2[CrO_4{}^{2-}]$

$$\left[\mathrm{Ag}^+\right]_{\text{after mixing}} = \frac{0.0020M \times 0.200L}{0.2005L} = 1.995 \times 10^{-3} M$$

$$\left[\mathrm{CrO_4}^{2-}\right]_{\text{after mixing}} = \frac{1.0 \times 10^{-4} M \times 0.0005L}{0.2005L} = 2.49 \times 10^{-7} M$$

$\therefore K_{sp} = [Ag^+]^2[CrO_4{}^{2-}] = (1.995 \times 10^{-3})^2(2.49 \times 10^{-7}) = 9.91 \times 10^{-13}$

14)

Equilibrium is:	$BaF_2(s) \rightleftharpoons$	$Ba^{2+}(aq)$	$+ 2\,F^-(aq)$
Initial:	solid	0	0
Equilibrium:	solid – x	x	2 x

$[F^-] = 0.015$ *M* = 2x, $\therefore$ x = 0.0075 = solubility of BaF_2

$K_{sp} = [Ba^{2+}][F^-]^2 = (x)(2x)^2 = 4x^3 = 4(0.0075)^3 = 1.69 \times 10^{-6}$

14) cont. Solubility of BaF_2 = 0.0075 $molL^{-1}$
Convert to solubility in gL^{-1}: 0.0075 $molL^{-1}$ x 175.3 $gmol^{-1}$ = 1.31 g

1.31 g of BaF_2 dissolve in 1.0 L of water
∴ 1.0 g “ “ x L “
x = 0.763 L

15) a)

Equilibrium is:	$AgOH(s)$	$\rightleftharpoons$	$Ag^+(aq)$	+	$OH^-(aq)$
Initial:	solid		0		0
Equilibrium:	solid – x		x		x

$K_{sp} = [Ag^+][OH^-] = x^2 = 2.0 \times 10^{-8}$
∴ $x = 1.414 \times 10^{-4} = [Ag^+] = [OH^-]$
pOH = 3.85, pH = 10.15

b) If $[Ag^+]$ = 0.50 M; $K_{sp} = [0.50][OH^-] = x^2 = 2.0 \times 10^{-8}$
∴ $[OH^-] = 4.0 \times 10^{-8}$
pOH = 7.40, pH = 6.60

16) Equilibrium is: $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3\,OH^-(aq)$ $K_{sp} = [Fe^{3+}][OH^-]^3 = 1.0 \times 10^{-38}$
If $[Fe^{3+}]$ = 0.10 M; $K_{sp} = [0.10][OH^-]^3 = 1.0 \times 10^{-38}$
∴ $[OH^-] = 4.64 \times 10^{-13}$
pOH = 12.33, pH = 1.67

Section 1.3

1) i) a)

Equilibrium is:	$HCOOH(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$HCOO^-(aq)$
Initial:	0.120 M		0		0
Equil:	0.120 – x		x		x

$$K_a = \frac{\left[\mathrm{H^+}\right]\left[\mathrm{HCOO^-}\right]}{\left[\mathrm{HCOOH}\right]} \rightarrow 1.9 \text{ x } 10^{-4} = \frac{(x)(x)}{0.120 - x} = \frac{x^2}{0.120 - x}$$

$$\therefore x = \sqrt{1.9 \text{ x } 10^{-4} \times 0.120} = 0.004775 = \left[\mathrm{H^+}\right]$$

$$\therefore pH = 2.32$$

b) Equilibrium is: $HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$

Initial: 1.00 M 0 0

Equil: 1.00 – x x x

$$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]} \rightarrow 4.5 \text{ x } 10^{-4} = \frac{(x)(x)}{1.00 - x} = \frac{x^2}{1.00 - x}$$

$$\therefore x = \sqrt{4.5 \text{ x } 10^{-4} \times 1.00} = 0.02121 = [H^+]$$

$$\therefore pH = 1.67$$

c) Equilibrium is: $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Initial: 0.500 M 0 0

Equil: 0.500– x x x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} \rightarrow 1.8 \text{ x } 10^{-5} = \frac{(x)(x)}{0.500 - x} = \frac{x^2}{0.500 - x}$$

$$\therefore x = \sqrt{1.8 \text{ x } 10^{-5} \times 0.500} = 0.00300 = [OH^-]$$

$$\therefore pOH = 2.52 \text{ and } \therefore pH = 11.48$$

d) Equilibrium is: $CH_3NH_2(aq) + H_2O(l) \rightleftharpoons CH_3NH_3^+(aq) + OH^-(aq)$

Initial: 1.20 M 0 0

Equil: 1.20 – x x x

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} \rightarrow 6.4 \text{ x } 10^{-4} = \frac{(x)(x)}{1.20 - x} = \frac{x^2}{1.20 - x}$$

$$\therefore x = \sqrt{6.4 \text{ x } 10^{-4} \times 1.20} = 0.02771 = [OH^-]$$

$$\therefore pOH = 1.56 \text{ and } \therefore pH = 12.44$$

ii) a) Conjugate base is formate ion; $HCOO^-$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.9 \text{ x } 10^{-4}} = 5.26 \text{ x } 10^{-11}$$

b) Conjugate base is nitrite ion; NO_2^-

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.5 \text{ x } 10^{-4}} = 2.22 \text{ x } 10^{-11}$$

c) Conjugate acid is ammonium ion; NH_4^+

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \text{ x } 10^{-5}} = 5.56 \text{ x } 10^{-10}$$

d) Conjugate acid is methylammonium ion; $CH_3NH_3^+$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{6.4 \text{ x } 10^{-4}} = 1.56 \text{ x } 10^{-11}$$

2) Equilibrium is: $CH_3CH_2COOH(aq) \rightleftharpoons H^+(aq) + CH_3CH_2COO^-(aq)$

Initial:	c	0	0
Equil:	c – x	x	x

If pH = 2.50, $[H^+]$ = 0.00316 M = x and if pK_a = 4.87, then $K_a = 1.35 \text{ x } 10^{-5}$

$$K_a = \frac{[H^+][CH_3CH_2COO^-]}{[CH_3CH_2COOH]} \rightarrow 1.35 \text{ x } 10^{-5} = \frac{(x)(x)}{c-x} = \frac{(0.00316)^2}{c-0.00316}$$

c = 0.743 M = $[CH_3CH_2COOH]$

moles CH_3CH_2COOH = 0.7428 M x 2.00 L = 1.486 moles

Mass CH_3CH_2COOH = 1.486 moles x 74.078 $g mol^{-1}$ = 110.1 g

3) Equilibrium is: $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

Initial:	0.200 M	0	0
Equil:	0.200 – x	x	x

$$\text{pH} = 1.40 \therefore [H^+] = 0.0398M = x$$

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(x)(x)}{0.200-x} = \frac{(0.0398)^2}{0.200-0.0398}$$

$$\therefore K_a = 9.89 \times 10^{-3}$$

4) i) Equilibrium is: $HOCl(aq) \rightleftharpoons H^+(aq) + OCl^-(aq)$

Initial:	1.00 M	0	0
Equil:	1.00 – x	x	x

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]} \rightarrow 3.5 \text{ x } 10^{-8} = \frac{(x)(x)}{1.00-x} = \frac{(x)^2}{1.00-x}$$

$$\therefore x = \sqrt{3.5 \text{ x } 10^{-8} \times 1.00} = 1.87 \times 10^{-4} = [H^+]$$

$$\therefore pH = 3.73$$

$$\% \text{ Ionization } = \frac{1.87 \times 10^{-4}}{1.00} \times 100\% = 0.0187\%$$

ii) Equilibrium is: $HOCl(aq) \rightleftharpoons H^+(aq) + OCl^-(aq)$

Initial:	0.0100 M	0	0
Equil:	0.0100 – x	x	x

$$K_a = \frac{[H^+][OCl^-]}{[HOCl]} \rightarrow 3.5 \text{ x } 10^{-8} = \frac{(x)(x)}{0.0100-x} = \frac{(x)^2}{0.0100-x}$$

$$\therefore x = \sqrt{3.5 \text{ x } 10^{-8} \times 0.0100} = 1.87\times10^{-5} = [H^+]$$

$$\therefore pH = 4.73$$

$$\% \text{ Ionization } = \frac{1.87\times10^{-5}}{0.0100}\times100\% = 0.187\%$$

When a weak acid is diluted, the pH increases.
The % ionization increases.

5) Equilibrium is: $(CH_3)_3N(aq) + H_2O(l) \rightleftharpoons (CH_3)_3NH^+(aq) + OH^-(aq)$

Initial:	0.35 M	0	0
Equil:	0.35 – x	x	x

$$K_b = \frac{[(CH_3)_3NH^+][OH^-]}{[(CH_3)_3N]} \rightarrow 7.4 \text{ x } 10^{-5} = \frac{(x)(x)}{0.35-x} = \frac{x^2}{0.35-x}$$

$$\therefore x = \sqrt{7.4 \text{ x } 10^{-5} \times 0.35} = 5.09\times10^{-3} = [OH^-]$$

$$\therefore pOH = 2.29 \text{ and } \therefore pH = 11.71$$

$$\% \text{ Ionization } = \frac{5.09\times10^{-3}}{0.35}\times100\% = 1.45\%$$

6) a) HCOOH; $K_a = 1.9 \text{ x } 10^{-4}$, $pK_a = 3.72$
HF; $K_a = 6.7 \text{ x } 10^{-4}$, $pK_a = 3.17$
$HC_2O_4^-$; $K_a = 5.2 \text{ x } 10^{-5}$, $pK_a = 4.28$

b) HF > HCOOH > $HC_2O_4^-$ (strongest acid to weakest acid)

c) Conjugate base of HCOOH is formate ion, $HCOO^-$
Conjugate base of HF is fluoride ion, F^-
Conjugate base of hydrogen oxalate ion is oxalate ion, $C_2O_4^{2-}$

d) $HCOO^-$: $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.9 \text{ x } 10^{-4}} = 5.26 \text{ x } 10^{-11}$

F^-: $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{6.7 \text{ x } 10^{-4}} = 1.49 \text{ x } 10^{-11}$

$C_2O_4^{2-}$: $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{5.2 \text{ x } 10^{-5}} = 1.92 \text{ x } 10^{-10}$

$C_2O_4^{2-} > HCOO^- > F^-$ (strongest base to weakest base)

7) Equilibrium is: $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

	$HA(aq)$	$H^+(aq)$	$A^-(aq)$
Initial:	0.15 M	0	0
Equil:	0.15 – x	x	x

$$\% \text{ Ionization } = \frac{x}{0.15} \times 100\% = 25\%, \quad \therefore\ x = 3.75 \times 10^{-2}$$

$$K_\text{a} = \frac{\left[\text{H}^+\right]\left[\text{A}^-\right]}{\left[\text{HA}\right]} = \frac{(x)(x)}{0.15 - x} = \frac{(0.0375x)^2}{0.15 - 0.0375} = 1.25 \times 10^{-2}$$

8) Equilibrium is: $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

	$NH_3(aq)$	$NH_4^+(aq)$	$OH^-(aq)$
Initial:	c	0	0
Equil:	c– x	x	x

If pH = 11.18, then pOH = 2.82; $[OH^-] = 1.51 \text{ x } 10^{-3}$ M = x

$$K_\text{b} = \frac{\left[\text{NH}_4^+\right]\left[\text{OH}^-\right]}{\left[\text{NH}_3\right]} = 1.8 \times 10^{-5} = \frac{(x)(x)}{c - x} = \frac{\left(1.51 \times 10^{-3}\right)^2}{c - 1.51 \times 10^{-3}}$$

c = 0.128 M = $[NH_3]$

moles NH_3 = 0.128 M x 10 L = 1.28
Mass NH_3 = 1.28 moles x 17.034 $gmol^{-1}$ = 21.80 g

9) a) $HCOOK(aq) \rightarrow HCOO^-(aq) + K^+(aq)$

$HCOO^-$ is the conjugate base of the weak acid HCOOH. It will behave like a weak base.

Equilibrium is:	$HCOO^-(aq)$ + $H_2O(l)$ $\rightleftharpoons$	$HCOOH(aq)$ +	$OH^-(aq)$
Initial:	0.500M	0	0
Equil:	0.500– x	x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.9 \text{ x } 10^{-4}} = 5.26 \text{ x } 10^{-11} = \frac{x^2}{0.500 - x}$$

$$\therefore x = \sqrt{5.26\text{x } 10^{-11} \times 0.500} = 5.13 \times 10^{-6} = \left[\text{OH}^-\right]$$

$$\text{pOH} = 5.29, \quad \therefore \text{ pH} = 8.71$$

$$\% \text{ Hydrolysis } = \frac{x}{0.500} \times 100\% = \frac{5.13 \times 10^{-6}}{0.500} \times 100\% = 1.03 \times 10^{-3}\%$$

b) $NH_4Br(aq) \rightarrow NH_4^+(aq) + Br^-(aq)$

NH_4^+ is the conjugate acid of the weak base NH_3. It will behave like a weak acid.

Equilibrium is:	$NH_4^+(aq)$ $\rightleftharpoons$	$H^+(aq)$ +	$NH_3(aq)$
Initial:	0.250M	0	0
Equil:	0.250 – x	x	x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \text{ x } 10^{-5}} = 5.56 \text{ x } 10^{-10} = \frac{x^2}{0.250 - x}$$

$$\therefore x = \sqrt{5.56\text{x } 10^{-10} \times 0.250} = 1.18 \times 10^{-5} = \left[\text{H}^+\right]$$

$$\therefore \text{pH} = 4.93$$

$$\% \text{ Hydrolysis } = \frac{x}{0.250} \times 100\% = \frac{1.18 \times 10^{-5}}{0.250} \times 100\% = 4.72 \times 10^{-3}\%$$

10) moles NH_3(a weak base)= 0.100M x 0.0500L = 0.00500 moles

moles HCl (a strong acid) = 0.250M x 0.0200L = 0.00500 moles = moles H^+

Reaction is:	$NH_3(aq)$ +	$H^+(aq)$ $\rightarrow$	$NH_4^+(aq)$
Initial: (using moles)	0.005	0.005	0
Final:	0	0	0.005

NH_4^+ is the conjugate acid of the weak base NH_3.

$$[\text{NH}_4^+] = \frac{0.00500 moles}{0.0700 L} = 0.0714 M$$

Equilibrium is:	$NH_4^+(aq)$ $\rightleftharpoons$	$H^+(aq)$ +	$NH_3(aq)$
Initial: (using M)	0.0714M	0	0
Equil:	0.0714 – x	x	x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \text{ x } 10^{-5}} = 5.56 \text{ x } 10^{-10} = \frac{x^2}{0.0714 - x}$$

$$\therefore x = \sqrt{5.56\text{x } 10^{-10} \times 0.0714} = 6.30 \times 10^{-6} = \left[\text{H}^+\right]$$

$$\therefore \text{pH} = 5.20$$

11) [HA] = 0.200 M

Equilibrium is: $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

Initial: 0.200 M 0 0

Equil: 0.200 – x x x

$$\frac{\left[A^-\right]}{\left[HA\right]} = 0.30 = \frac{x}{0.200 - x} \qquad \therefore x = 4.615\times10^{-2}$$

$$K_a = \frac{\left[H^+\right]\left[A^-\right]}{\left[HA\right]} = \frac{x^2}{0.200 - x} = \frac{\left(4.615\times10^{-2}\right)^2}{0.200 - 4.615\times10^{-2}} = 1.38\times10^{-2}$$

12) $(NH_4)_2SO_4\ (aq) \rightarrow 2\ NH_4^+(aq) + SO_4^{2-}(aq)$

$[NH_4^+] = 2[(NH_4)_2SO_4]$

$$\text{moles } \left(NH_4\right)_2 SO_4 = \frac{33.0g}{132.154 gmol^{-1}} = 0.2497 \text{ moles}$$

$$\therefore [\left(NH_4\right)_2 SO_4] = 0.2497M \Rightarrow [NH_4^+] = 0.4994M$$

NH_4^+ is the conjugate acid of the weak base NH_3.

Equilibrium is: $NH_4^+(aq) \rightleftharpoons H^+(aq) + NH_3(aq)$

Initial: (using M) 0.4994M 0 0

Equil: 0.4994 – x x x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \text{ x } 10^{-5}} = 5.56 \text{ x } 10^{-10} = \frac{x^2}{0.4994 - x}$$

$$\therefore x = \sqrt{5.56\text{x } 10^{-10} \times 0.4994} = 1.666\times10^{-5} = \left[H^+\right]$$

$$\therefore \text{pH} = 4.78$$

13) Equilibrium is: $HCOOH(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$

Initial: c M 0 0

Equil: c – x x x

pH = 4.50, $\therefore$ [H⁺] = 3.16 x 10⁻⁵ M = x

$$K_a = \frac{\left[H^+\right]\left[HCOO^-\right]}{\left[HCOOH\right]} \rightarrow 1.9 \text{ x } 10^{-4} = \frac{(x)(x)}{c - x} = \frac{\left(3.16\times10^{-5}\right)^2}{c - 3.16\times10^{-5}}$$

c = $3.69 \text{ x } 10^{-5}$ M

$$\% \text{ Ionization } = \frac{x}{c}\times100\% = \frac{3.16\times10^{-5}}{3.69\times10^{-5}}\times100\% = 85.7\%$$

14) The stronger base has the larger K_b value.

Therefore, the stronger base is ethylamine.

Equilibrium is:	$CH_3CH_2NH_2(aq) + H_2O(l)$	$\rightleftharpoons$	$CH_3CH_2NH_3^+(aq)$	+	$OH^-(aq)$
Initial:	0.50 M		0		0
Equil:	0.50 – x		x		x

$$K_b = \frac{\left[CH_3CH_2NH_3^+\right]\left[OH^-\right]}{\left[CH_3CH_2NH_2\right]} = 4.3\times10^{-4} = \frac{x^2}{0.50-x}$$

$$\therefore x = \sqrt{4.3 \text{ x } 10^{-4}\times0.50} = 1.47\times10^{-2} = \left[OH^-\right]$$

$$\therefore pOH = 1.83 \text{ and } \therefore pH = 12.17$$

$$\% \text{ Ionization } = \frac{x}{0.50}\times100\% = \frac{1.47\times10^{-2}}{0.50}\times100\% = 2.94\%$$

15) The structure of citric acid is shown in the problem; for simplicity in this solution it will be denoted as "HCit".

Equilibrium is:	HCit(aq)	$\rightleftharpoons$	$H^+(aq)$	+	$Cit^-(aq)$
Initial:	c M		0		0
Equil:	c – x		x		x

a)

$$\text{pH} = 2.3, \;\therefore [H^+] = 5.01\times10^{-3}M = [Cit^-] = x$$

$$\text{p}K_1 = 3.1, \;\therefore K_1 = 7.94\times10^{-4}$$

$$K_1 = \frac{[H^+][Cit^-]}{[HCit]} = 7.94\times10^{-4} = \frac{x^2}{c-x} = \frac{\left(5.01\times10^{-3}\right)^2}{c-x}$$

The quantity "$c-x$" is the amount of undissociated citric acid.

$c-x = 0.0316M = [HCit]$ at equilibrium.

b) Total molar concentration of citric acid, dissociated and undissociated = c.

c = c – x + x = 0.0316 + 0.00501 = 0.0366 M

c)

$$\% \text{ Ionization} = \frac{x}{c}\times100\% = \frac{5.01\times10^{-3}}{0.0366}\times100\% = 13.7\%$$

d) Assuming 1 L of lemon juice:

Mass citric acid = 0.0366 M x 192 $gmol^{-1}$ = 7.03 g

1 L of lemon juice has a mass of 1000 mL x 1.13 gmL^{-1} = 1130 g

$$\% \text{ by mass of lemon juice } = \frac{7.03g}{1130g}\times100\% = 0.622\%$$

16) When comparing acidity, the strongest acid is the one which has the most stable conjugate base. A conjugate base that is stabilized by resonance is more stable than one which is not resonance stabilized.

a) In the example of citric acid, all three COOH groups have the potential to become COO^- groups which would all be stabilized by resonance. The boxed COOH group is bonded to a C atom which is also bonded to an O atom. The other two COOH groups are bonded to a C atom which are bonded to two more H atoms. The O atom is more electronegative than the H atoms and because of this will stabilize the O^- of the COO^- group by pulling electrons away from it.

b) The *OH group is much less acidic than the three COOH groups because there is no possibility of resonance stabilization of the O^- which would result from the deprotonation of the OH group.

17) a) Trifluoroacetic acid is a stronger acid than trichloroacetic acid. This is due to the higher electronegativity of fluorine.
b) Incorrect; tricholoracetate is a stronger base than is trifluoroacetate.
c) Correct; the weaker the acid, the more positive the ΔG^o of ionization.
d) Incorrect; the stronger the acid, the more stable its conjugate base, not the acid itself.

18) a) BCl_3 is a Lewis acid.
b) PF_3 is a Lewis base.
c) H_2O is a Lewis base.
d) SO_2 will act as a Lewis acid when combined with OH^-.
e) Cu^{2+} is a Lewis acid.
f) Br^- is a Lewis base.

19) a) Fe^{3+} is a Lewis acid; H_2O is a Lewis base.
b) CO_2 is a Lewis acid; H_2O is a Lewis base.
c) Cu^{2+} is a Lewis acid; NH_3 is a Lewis base.
d) $AlCl_3$ is a Lewis acid; Cl^- is a Lewis base.
e) N_2H_4 is a Lewis base; H_3O^+ is a Lewis acid.

20) a)1st Equilibrium is:	$H_2CO_3(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$HCO_3^-(aq)$	$K_{a1} = 4.2 \times 10^{-7}$
Initial:	0.100 M		0		0	
Equil:	0.100 − x		x		x	

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.2\times10^{-7} = \frac{x^2}{0.100 - x}$$

$$\therefore x = \sqrt{4.2x\ 10^{-7} \times 0.100} = 2.05\times10^{-4} = [H^+]$$

$$\therefore \text{pH} = 3.69$$

$$\%\ \text{Dissociation} = \frac{x}{c}\times100\% = \frac{2.04\times10^{-4}}{0.100}\times100\% = 0.204\%$$

2nd Equilibrium is:	$HCO_3^-(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$CO_3^{2-}(aq)$	$K_{a2} = 4.8 \times 10^{-11}$
Initial:	2.04×10^{-4} M		2.04×10^{-4}		0	
Equil:	$2.04 \times 10^{-4} - y$		$2.04 \times 10^{-4} + y$		y	

$$K_a = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = 4.8\times10^{-11} = \frac{(2.05\times10^{-4} + y)(y)}{2.05\times10^{-4} - y}$$

$$\therefore y = 4.8\times10^{-11} = [CO_3^{2-}]$$

$$\therefore \text{pH} = 3.69$$

$$\%\ \text{Dissociation} = \frac{y}{x}\times100\% = \frac{4.8\times10^{-11}}{2.04\times10^{-4}}\times100\% = 2.35\times10^{-5}\%$$

b) pH = 5.60, $\therefore [H^+] = 2.51 \times 10^{-6}$ M = x

Using 1st equilibrium:	$H_2CO_3(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$HCO_3^-(aq)$	$K_{a1} = 4.2 \times 10^{-7}$
Initial:	c M		0		0	
Equil:	c − x		x		x	

$$K_a = \frac{[H^+][HCO_3^-]}{[H_2CO_3\ ]} = 4.2\times10^{-7} = \frac{(2.51\times10^{-6})^2}{c - 2.51\times10^{-6}}$$

$$c = 1.75\times10^{-5} = [H_2CO_3]$$

$[HCO_3^-] = 2.51 \times 10^{-6}$ M = $[H^+]$

$[CO_3^{2-}] = 4.8 \times 10^{-11}$ M

Total concentration of carbon containing species = 1.75×10^{-5} = $[H_2CO_3]$ (undissociated)

c) Reaction is: $CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$

$\therefore$ moles H_2CO_3 = moles CO_2 required = 1.75×10^{-5} for each L

Volume of CO_2 required = 1.75×10^{-5} mol x 22.4 $Lmol^{-1}$ = 3.92×10^{-4} L = 0.392 mL

d) $Na_2CO_3(aq) \rightarrow 2\ Na^+(aq) + CO_3^{2-}(aq)$

CO_3^{2-} is the conjugate base of the weak acid HCO_3^-.

Equilibrium is:	$CO_3^{2-}(aq) + H_2O(l)$ ⇌	$HCO_3^-(aq)$ +	$OH^-(aq)$
Initial:	0.100M	0	0
Equil:	0.100 – x	x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{4.8\times10^{-11}} = 2.08\times10^{-4} = \frac{\left[HCO_3^-\right]\left[OH^-\right]}{\left[CO_3^{2-}\right]} = \frac{x^2}{0.100-x}$$

$$x = \sqrt{\left(2.08\times10^{-4}\right)(0.100)}$$

$$\therefore x = 4.56\times10^{-3} = \left[OH^-\right]$$

$$\text{pOH} = 2.34 \quad \therefore \text{pH} = 11.66$$

21) a) Ascorbic acid is $C_7H_{10}O_5$; MM = 174.15 gmol^{-1}

$$\text{moles } C_7H_{10}O_5 = \frac{10.0g}{174.15gmol^{-1}} = 0.05742 \text{ moles}, \therefore [C_7H_{10}O_5] = 0.05742M$$

Equilibrium is:	$C_7H_{10}O_5\ (aq)$ ⇌	$H^+(aq)$ +	$C_7H_9O_5^-(aq)$
Initial:(using M)	0.05742M	0	0
Equil:	0.05742 – x	x	x

$$K_1 = \frac{[H^+][C_7H_9O_5^-]}{[C_7H_{10}O_5]} = 7.9\times10^{-5} = \frac{x^2}{c-x} = \frac{x^2}{0.5742-x}$$

$$\therefore x = \sqrt{7.9 \text{ x } 10^{-5}\times0.05742} = 0.002130 = [H^+]$$

pH = 2.67

b) $[C_7H_8O_5^{2-}] = K_2 = 1.6 \text{ x } 10^{-12}$

b) $[C_7H_8O_5^{2-}] = K_2 = 1.6 \text{ x } 10^{-12}$

22) $[H_2SO_3]$ = 0.100M

a) 1st Equilibrium is:	$H_2SO_3(aq)$ ⇌	$H^+(aq)$ +	$HSO_3^-(aq)$
Initial:	0.100 M	0	0
Equil:	0.100 – x	x	x

b) pH = 1.47, ∴ $[H^+]$ = 0.03388 M = x

$$\% \text{ Ionization} = \frac{x}{c}\times100\% = \frac{0.03388}{0.100}\times100\% = 33.9\%$$

c) $$K_1 = \frac{\left[H^+\right]\left[HSO_3^-\right]}{\left[H_2SO_3\right]} = \frac{x^2}{c-x} = \frac{(0.03388)^2}{0.100-0.03388} = 1.74\times10^{-2}$$

d) $[SO_3^{2-}] = K_2 = 6.2 \text{ x } 10^{-8}$

23)

1st Equilibrium is:	$H_2SO_3(aq) \rightleftharpoons$	$H^+(aq)$ +	$HSO_3^-(aq)$
Initial:	0.150 M	0	0
Equil:	0.150 – x	x	x

$$K_1 = \frac{\left[H^+\right]\left[HSO_3^-\right]}{\left[H_2SO_3\right]} = \frac{x^2}{c-x} = \frac{(x)^2}{0.150-x} = 1.2\times10^{-2}$$

Must use quadratic to solve for x. $x = 3.68 \times 10^{-2} = [H^+] = [HSO_3^-]$

pH = 1.43

At equilibrium:

$[H_2SO_3] = 0.1132$ M

$[H^+] = [HSO_3^-] = 0.0368$ M

$[SO_3^{2-}] = K_2 = 6.2 \times 10^{-8}$ M

Section 1.4

1) a) Reaction of weak acid (in excess) with strong base will produce the conjugate base of the weak acid, resulting in a buffer solution.

b) Moles of C_6H_5COONa (conjugate base of C_6H_5COOH) = moles $HClO_4$ (strong acid) This reaction will produce C_6H_5COOH, but as there is no excess $C_6H_5COO^-$, the resultant solution will not be a buffer solution.

c) moles $(CH_3)_2NH$ (weak base) = 0.125
moles $(CH_3)_2NH_2Cl$ = 0.0525 = moles $(CH_3)_2NH_2^+$ (conjugate acid of $(CH_3)_2NH$)
The mixing of these two species will produce a buffer solution.

d) moles CH_3NH_3Cl = 0.0375 = $CH_3NH_3^+$ (conjugate acid of CH_3NH_2)
moles KOH (strong base) = 0.0125
Reaction of these two species will produce CH_3NH_2 with $CH_3NH_3^+$ in excess; a buffer solution.

e) moles NH_4NO_3 = 0.046 = moles NH_4^+ (conjugate acid of NH_3)
moles HNO_3 (strong acid) = 0.022
No reaction between these two species (both acids) will occur; this is not a buffer solution.

2) a) A buffer solution contains two components, either a *weak* acid and its *conjugate base*, or a *weak* base and its *conjugate acid.*

b) The pH of a buffer depends only on the *ratio* of the concentrations of the two components, so it is *unaffected* by dilution.

c) If strong acid is added to a buffer mixture, it is removed by reaction with the *basic* component, while added strong base is removed by reaction with the *acidic* component.

3) a) HCOOH is a weak acid; HCOOK contains the $HCOO^-$ ion which is the conjugate base of HCOOH. This will be a buffer solution.

Equilibrium is: $HCOOH\,(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$

$$[\text{HCOOH}] = \frac{0.200mol}{0.750L} = 0.267M;\ \ [\text{HCOO}^-] = \frac{0.500mol}{0.750L} = 0.667M$$

$$K_a = \frac{\left[\text{H}^+\right]\left[\text{HCOO}^-\right]}{\left[\text{HCOOH}\right]} = 1.9\times10^{-4}$$

$$\text{Substituting: } 1.9\times10^{-4} = \frac{[\text{H}^+](0.667)}{0.267}$$

$$\therefore [\text{H}^+] = 7.61\times10^{-5}M;\ \ \text{pH} = 4.12$$

b) The pH of a buffer is unaffected by dilution with water.

c) $$\text{moles NaOH} = \frac{4.0g}{40.0gmol^{-1}} = 0.100 = \text{ moles OH}^-$$

Reaction is:	HCOOH	+	OH^-	→	$HCOO^-$	+	H_2O
Before: (mol)	0.200		0.100		0.500		0
After:	0.100		0		0.600		

This solution still contains a weak acid and its conjugate base; it is still a buffer solution.

Equilibrium is: $HCOOH\,(aq) \rightleftharpoons H^+(aq) + HCOO^-(aq)$

$$K_a = \frac{\left[\text{H}^+\right]\left[\text{HCOO}^-\right]}{\left[\text{HCOOH}\right]} = 1.9\times10^{-4}$$

$$\text{Substituting: } 1.9\times10^{-4} = \frac{[\text{H}^+](0.600mol)}{0.100mol}$$

$$\therefore [\text{H}^+] = 3.17\times10^{-5}M;\ \ \text{pH} = 4.50$$

Note that moles of the weak acid and its conjugate base were used in the buffer calculation rather than molarity. As both species exist in the same solution, the volume would cancel.

4) $NaNO_2 \rightarrow Na^+ + NO_2^-$

NO_2^- is the conjugate base of the weak acid HNO_2; therefore a solution which contains both species will be a buffer solution.

Equilibrium is: $HNO_2(aq) \rightleftharpoons H^+(aq) + NO_2^-(aq)$

$$K_a = 4.5\times10^{-4} = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{NO}_2^-\right]}{\left[\mathrm{HNO}_2\right]}$$

$$\mathrm{pH} = 3.50, \quad \therefore \left[\mathrm{H}^+\right] = 3.16\times10^{-4}M$$

$$\text{Substituting: } K_a = 4.5\times10^{-4} = \frac{\left(3.16\times10^{-4}\right)\left[\mathrm{NO}_2^-\right]}{(0.165)}$$

$$\left[\mathrm{NO}_2^-\right] = 0.235M, \text{ moles } \mathrm{NO}_2^- = 0.235M \times 0.700L = 0.1645\text{moles} = \text{moles NaNO}_2$$

$$\therefore \text{Mass NaNO}_2 = 0.1645 moles \times 69.00 gmol^{-1} = 11.35g$$

5) a)

Equilibrium is:	$NH_3(aq)$ + $H_2O(l)$ $\rightleftharpoons$	$NH_4^+(aq)$ +	$OH^-(aq)$
Initial:	0.12 M	0	0
Equil:	0.12– x	x	x

$$K_\mathrm{b} = \frac{\left[\mathrm{NH}_4^{\ +}\right]\left[\mathrm{OH}^-\right]}{\left[\mathrm{NH}_3\right]} \rightarrow 1.8 \text{ x } 10^{-5} = \frac{(x)(x)}{0.12-x} = \frac{x^2}{0.12-x}$$

$$\therefore x = \sqrt{1.8 \text{ x } 10^{-5} \times 0.12} = 0.00147 = \left[\mathrm{OH}^-\right]$$

$$\therefore \mathrm{pOH} = 2.83 \text{ and } \therefore \mathrm{pH} = 11.17$$

b)

$$\text{moles NH}_4\text{Cl} = \frac{4.40g}{53.49gmol^{-1}} = 0.0823 = \text{moles NH}_4^+$$

NH_4^+ is the conjugate acid of NH_3, so adding it to the NH_3 solution in a) will result in a buffer solution.

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

$$K_\mathrm{b} = \frac{\left[\mathrm{NH}_4^{\ +}\right]\left[\mathrm{OH}^-\right]}{\left[\mathrm{NH}_3\right]} = 1.8 \text{ x } 10^{-5}$$

$$\text{Substituting: } 1.8 \text{ x } 10^{-5} = \frac{\left[\mathrm{OH}^-\right](0.0823mol)}{0.0600mol}$$

$$\left[\mathrm{OH}^-\right] = 1.31\text{x } 10^{-5}, \ \mathrm{pOH} = 4.88 \quad \therefore \mathrm{pH} = 9.12$$

Change in pH from adding NH_4Cl = 11.17 – 9.12 = 2.05 pH units.

c) The pH of the buffer solution is unaffected by dilution with water.

d) HCl is a strong acid; moles of H^+ = 1.0 M x 0.050 L = 0.050 moles

Reaction in buffer solution is:	NH_3	+	H^+	→	NH_4^+
Before (using moles):	0.0600		0.050		0.0823
After:	0.0100		0		0.1323

Both NH_3 and NH_4^+ are present after the reaction is complete; this is a buffer solution.

$$K_\mathrm{b} = \frac{\left[\mathrm{NH_4}^+\right]\left[\mathrm{OH}^-\right]}{\left[\mathrm{NH_3}\right]} = 1.8 \text{ x } 10^{-5}$$

$$\text{Substituting: } 1.8 \text{ x } 10^{-5} = \frac{\left[\mathrm{OH}^-\right](0.1323 mol)}{0.0100 mol}$$

$$\left[\mathrm{OH}^-\right] = 1.36 \text{x } 10^{-6},\ \mathrm{pOH} = 5.87 \quad \therefore \mathrm{pH} = 8.13$$

6) a) Sodium acetate is CH_3COONa, which contains the acetate ion, CH_3COO^-. The acetate ion is the conjugate base of the weak acid CH_3COOH. When mixed, these two species form a buffer solution.

moles CH_3COOH = 0.150

pH = 4.5, $[H^+] = 3.16 \times 10^{-5}$ M

Equilibrium is: $CH_3COOH\,(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

$$K_a = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{CH_3COO}^-\right]}{\left[\mathrm{CH_3COOH}\right]} = 1.8\times10^{-5}$$

$$\text{Substituting: } 1.8\times10^{-5} = \frac{(3.16\times10^{-5)}[\mathrm{CH_3COO}^-]}{0.150M}$$

$$\therefore [\mathrm{CH_3COO}^-] = 0.0854M = \left[\mathrm{CH_3COONa}\right]$$

$$\text{Volume of solution is 1.0L, } \therefore \text{ mass } \mathrm{CH_3COONa} \text{ required } = 0.0854 mol\times82.03 g mol^{-1} = 7.01 g$$

b) NH_4NO_3 contains the ammonium ion, NH_4^+, which is the conjugate acid of the weak base NH_3. When mixed, these two species form a buffer solution.

pH = 9.70, so pOH = 4.30 and $[OH^-] = 5.01 \times 10^{-5}$ M

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

$$K_\mathrm{b} = \frac{\left[\mathrm{NH_4}^+\right]\left[\mathrm{OH}^-\right]}{\left[\mathrm{NH_3}\right]} = 1.8 \text{ x } 10^{-5}$$

$$\text{Substituting: } 1.8 \text{ x } 10^{-5} = \frac{\left(5.01\times10^{-5}\right)\left[\mathrm{NH_4}^+\right]}{0.85M}$$

$$\left[\mathrm{NH_4}^+\right] = 0.3054M, \text{ moles } \mathrm{NH_4^+} = 0.3054M\times0.500L = 0.1527 moles = \text{ moles } \mathrm{NH_4NO_3}$$

$$\therefore \text{Mass } \mathrm{NH_4NO_3} = 0.1527 moles\times80.05 g mol^{-1} = 12.2 g$$

7) a) Sodium acetate is CH_3COONa, which contains the acetate ion, CH_3COO^-. The acetate ion is the conjugate base of the weak acid CH_3COOH. When mixed, these two species form a buffer solution.

pH = 5.0, $[H^+] = 1.00 \times 10^{-5}$ M

Equilibrium is: $CH_3COOH\,(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8\times10^{-5}$$

$$\text{Substituting: } 1.8\times10^{-5} = \frac{(1.00\times10^{-5})[CH_3COO^-]}{1.00M}$$

$$\therefore [CH_3COO^-] = 1.8M = [CH_3COONa]$$

Volume of solution is 0.500L; moles of $CH_3COONa = 0.90\,moles$

$$\therefore \text{ mass } CH_3COONa \text{ required } = 0.90\,mol \times 82.03\,g\,mol^{-1} = 73.8\,g$$

b) i) HCl is a strong acid; moles H^+ = 0.050

Reaction with buffer solution is: $CH_3COO^- + H^+ \rightarrow CH_3COOH$

	CH_3COO^-	H^+	CH_3COOH
Before: (using moles)	0.90	0.050	0.50
After:	0.85	0	0.55

Both CH_3COOH and CH_3COO^- are present after the reaction; this is a buffer solution.

Equilibrium is: $CH_3COOH\,(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8\times10^{-5}$$

$$\text{Substituting: } 1.8\times10^{-5} = \frac{[H^+](0.85\,mol)}{0.55\,mol}$$

$$\therefore [H^+] = 1.16\times10^{-5}M;\ \text{pH} = 4.93$$

ii) NaOH is a strong base; moles OH^- = 0.050

Reaction with buffer solution is: $CH_3COOH + OH^- \rightarrow CH_3COO^-$

	CH_3COOH	OH^-	CH_3COO^-
Before: (using moles)	0.50	0.050	0.90
After:	0.45	0	0.95

Both CH_3COOH and CH_3COO^- are present after the reaction; this is a buffer solution.

Equilibrium is: $CH_3COOH\ (aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$

$$K_a = \frac{\left[\mathrm{H^+}\right]\left[\mathrm{CH_3COO^-}\right]}{\left[\mathrm{CH_3COOH}\right]} = 1.8\times10^{-5}$$

$$\text{Substituting: } 1.8\times10^{-5} = \frac{\left[\mathrm{H^+}\right](0.95mol)}{0.45mol}$$

$$\therefore \left[\mathrm{H^+}\right] = 8.52\times10^{-6}M ; \mathrm{pH} = 5.07$$

8) a)

Reaction is:	HF	+	OH^- →	F^-
Before:	0.05		0.025	0
After:	0.025		0	0.025

Both HF and F^- present after the reaction; this is a buffer solution.

Equilibrium is: $HF\ (aq) \rightleftharpoons H^+(aq) + F^-(aq)$

$$K_a = 7.2\times10^{-4} = \frac{\left[\mathrm{H^+}\right]\left[\mathrm{F^-}\right]}{\left[\mathrm{HF}\right]}$$

$$\text{Substituting: } K_a = 7.2\times10^{-4} = \frac{\left[\mathrm{H^+}\right](0.025mol)}{0.025mol}$$

$$\left[\mathrm{H^+}\right] = 7.2\times10^{-4}M \therefore \mathrm{pH} = 3.14$$

b) The reaction at this point in the titration is exactly the same reaction (with the same numbers of moles!) as in a).

Both HF and F^- present at this point in the titration; this is a buffer solution.

Equilibrium is: $HF\ (aq) \rightleftharpoons H^+(aq) + F^-(aq)$

$$K_a = 7.2\times10^{-4} = \frac{\left[\mathrm{H^+}\right]\left[\mathrm{F^-}\right]}{\left[\mathrm{HF}\right]}$$

$$\text{Substituting: } K_a = 7.2\times10^{-4} = \frac{\left[\mathrm{H^+}\right](0.025mol)}{0.025mol}$$

$$\left[\mathrm{H^+}\right] = 7.2\times10^{-4}M \therefore \mathrm{pH} = 3.14$$

c) After mixing: [HF] = 1.00 M x 50 mL / 75 mL = 0.667 M

[HCl] =1.00 M x 25 mL / 75 mL = 0.333 M = $[H^+]$

Equilibrium is: $HF(aq) \rightleftharpoons H^+(aq) + F^-(aq)$

	HF (aq)	H^+(aq)	F^-(aq)
Initial:	0.667	0.333	0
Equilibrium:	0.667 – x	0.333 + x	x

pH = 0.48

$$K_a = 7.2\times10^{-4} = \frac{\left[H^+\right]\left[F^-\right]}{[HF]}$$

Substituting: $K_a = 7.2\times10^{-4} = \dfrac{(0.333+x)(x)}{(0.667-x)}$

$x = 1.44\times10^{-3} = \left[F^-\right]$

% Ionization $= \dfrac{1.44\times10^{-3}}{0.667}\times100\% = 0.216\%$

9) a) Incorrect; mixing of two bases will not produce a buffer solution.

b) Correct; dilution does not affect the ratio of the weak species to the conjugate species.

c) Incorrect; a buffer works best of the ratio of the weak species to the conjugate species is roughly 1:1. If the ratio gets larger (or smaller) than a power of 10 (approximately), the solution will not be an effective buffer solution.

10) Equilibrium is: $H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$ $K_2 = 6.2 \times 10^{-8}$

pH = 7.40, so $[H^+] = 3.98 \times 10^{-8}$ M

$$K_a = \frac{\left[H^+\right]\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]} = 6.2\times10^{-8}$$

Substituting: $6.2\times10^{-8} = \dfrac{(3.98\times10^{-8})\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]}$

$$\frac{\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]} = 1.56, \quad \therefore \frac{\left[H_2PO_4^-\right]}{\left[HPO_4^{2-}\right]} = 0.64$$

11) a) $Na_2CO_3 \rightarrow 2\ Na^+ + CO_3^{2-}$ moles CO_3^{2-} = 0.20

$NaHCO_3 \rightarrow Na^+ + HCO_3^-$ moles HCO_3^- = 0.40

Equilibrium is: $HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{2-}(aq)$

$$K_a = \frac{\left[H^+\right]\left[CO_3^{2-}\right]}{\left[HCO_3^-\right]} = 4.7\times10^{-11}$$

Substituting: $4.7\times10^{-11} = \dfrac{\left[H^+\right](0.20mol)}{(0.40mol)}$

$\therefore \left[H^+\right] = 9.4\times10^{-11}M; \quad pH = 10.03$

b) moles H_2CO_3 = 0.010; moles HCO_3^- = 0.050

Equilibrium is: $H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq)$

$$K_a = \frac{\left[H^+\right]\left[HCO_3^-\right]}{\left[H_2CO_3\right]} = 4.4\times10^{-7}$$

Substituting: $4.4\times10^{-7} = \dfrac{\left[H^+\right](0.050mol)}{(0.010mol)}$

$\therefore \left[H^+\right] = 8.8\times10^{-8}M; \quad pH = 7.06$

12) a) Equilibrium is: $Cu(OH)_2(s) \rightleftharpoons Cu^{2+}(aq) + 2\ OH^-(aq)$ $K_{sp} = [Cu^{2+}][OH^-]^2 = 1.6 \times 10^{-19}$

In a neutral solution, pH = pOH = 7

$\therefore [OH^-] = 1.0 \times 10^{-7}$

Substitute into K_{sp} to solve for $[Cu^{2+}]$: $K_{sp} = [Cu^{2+}][1.0 \times 10^{-7}]^2 = 1.6 \times 10^{-19}$

$\therefore [Cu^{2+}] = 1.6 \times 10^{-5}\ M$

b) If a precipitate were to form (which we don't want!), the $[Cu^{2+}] = 1.0\ M$

At that point; $[OH^-] = 4.0 \times 10^{-10}\ M$ (from substitution into K_{sp})

pOH = 9.40, so pH = 4.60

The pH must be kept below 4.60 to avoid precipitation of $Cu(OH)_2$.

$\therefore [H^+] = 2.51 \times 10^{-5}\ M$, so $[H_2SO_4] = 1.26 \times 10^{-5}\ M$ to prevent precipitation.

13) a) Equilibrium for $CaCO_3$: $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$ $K_{sp} = 4.7 \times 10^{-9}$

Equilibrium for Li_2O_3: $Li_2CO_3(s) \rightleftharpoons 2\ Li^+(aq) + CO_3^{2-}(aq)$ $K_{sp} = 2.5 \times 10^{-2}$

b) HCl is a strong acid: $HCl \rightarrow H^+ + Cl^-$
In each case, the H^+ will react with the CO_3^{2-}: $2H^+ + CO_3^{2-} \rightarrow H_2O + CO_2$
The reaction takes the CO_3^{2-} out of solution, which disturbs the equilibrium.
In order to restore equilibrium, of the solid carbonate must dissolve.

c) In a saturated solution of $CaCO_3$, $[CO_3^{2-}] = 6.86 \times 10^{-5}\,M$
In a saturated solution of Li_2CO_3, $[CO_3^{2-}] = 1.84 \times 10^{-1}\,M$
NH_4^+ is a weak acid; the reaction between it and CO_3^{2-} will come to equilibrium.
Equilibrium is: $NH_4^+(aq) + CO_3^{2-}(aq) \rightleftharpoons NH_3(aq) + HCO_3^-(aq)$
When equilibrium is reached the $[CO_3^{2-}]$ will be reduced to the point where the more soluble Li_2CO_3 will dissolve. $CaCO_3$ is much less soluble; it will not dissolve.

14) moles acetic acid (CH_3COOH) = 0.200M x 0.0350 L = 0.00700 moles
At equivalence point; moles H^+ (from acid) = moles OH^- (from base)
$\therefore$ moles OH^- = 0.00700 moles

$$\text{Volume of NaOH used } = \frac{0.00700\,moles}{0.250M} = 0.02800L$$

Reaction is:	$CH_3COOH(aq)$ +	$OH^-(aq)$ →	$CH_3COO^-(aq) + H_2O$
Initial: (using moles)	0.007	0.007	0
Final:	0	0	0.007

CH_3COO^- is the conjugate base of the weak acid CH_3COOH.

$$\left[CH_3COO^-\right] = \frac{0.007\,moles}{0.0630L} = 0.111M$$

Equilibrium is:	$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons$	$CH_3COOH(aq)$ +	$OH^-(aq)$
Initial:	0.111M	0	0
Equil:	0.111− x	x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \text{ x } 10^{-5}} = 5.56 \text{ x } 10^{-10} = \frac{x^2}{0.111 - x}$$

$$\therefore x = \sqrt{5.56\text{x } 10^{-10} \times 0.111} = 7.86 \times 10^{-6} = \left[OH^-\right]$$

pOH = 5.10, $\therefore$ pH = 8.90

15) The K_a and K_b values needed may be found on Tables 1.3.1 and 1.3.2

a) Pick a volume of one species; based on molarities, calculate the volume of the other.
Use 100.0 mL of HNO_2; moles HNO_2 = 0.100 L x 0.500 M = 0.0500 moles
At equivalence point; moles H^+ (from acid) = moles OH^- (from base)
$\therefore$ moles OH^- = 0.0500 moles

$$\text{Volume of NaOH used } = \frac{0.0500 moles}{0.100M} = 0.500L$$

Reaction is:	$HNO_2(aq)$ + $OH^-(aq)$	$\rightarrow$	$NO_2^-(aq) + H_2O$
Initial: (using moles)	0.0500 0.0500		0
Final:	0 0		0.0500

NO_2^- is the conjugate base of the weak acid HNO_2.

$$\left[\mathrm{NO_2^-}\right] = \frac{0.0500 moles}{0.600L} = 0.0833M$$

Equilibrium is:	$NO_2^-(aq) + H_2O(l)$	$\rightleftharpoons$	$HNO_2(aq)$	+ $OH^-(aq)$
Initial:	0.0833M		0	0
Equil:	0.0833– x		x	x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.5 \text{ x } 10^{-4}} = 2.22 \text{ x } 10^{-11} = \frac{x^2}{0.0833 - x}$$

$$\therefore x = \sqrt{2.22\text{x } 10^{-11} \times 0.0833} = 1.36 \times 10^{-6} = \left[\mathrm{OH^-}\right]$$

pOH = 5.87, $\therefore$ pH = 8.13

b) Use 100.0 mL of methylamine; moles CH_3NH_2 = 0.100 L x 0.800 M = 0.0800 moles
At equivalence point,; moles CH_3NH_2 = moles H^+(from acid)
$\therefore$ moles H^+ = 0.0800 moles = moles HCl

$$\text{Volume of HCl used } = \frac{0.0800 moles}{0.400M} = 0.200L$$

Reaction is:	$CH_3NH_2(aq)$ + $H^+(aq)$	$\rightarrow$	$CH_3NH_3^+(aq)$
Initial: (using moles)	0.0800 0.0800		0
Final:	0 0		0.0800

$CH_3NH_3^+$ is the conjugate acid of the weak base CH_3NH_2.

$$[\mathrm{CH_3NH_3^+}] = \frac{0.0800 moles}{0.300L} = 0.267M$$

Equilibrium is:	$CH_3NH_3^+(aq)$	$\rightleftharpoons$	$H^+(aq)$	+	$CH_3NH_2(aq)$
Initial: (using M)	0.267M		0		0
Equil:	0.267 – x		x		x

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{6.4 \text{ x } 10^{-4}} = 1.56 \text{ x } 10^{-11} = \frac{x^2}{0.267 - x}$$

$$\therefore x = \sqrt{1.56\text{x } 10^{-11} \times 0.267} = 2.04 \times 10^{-6} = \left[\mathrm{H}^+\right]$$

$$\therefore \mathrm{pH} = 5.69$$

16) As the titration proceeds, the base that has been added reacts with H^+ from the acid. As both acids have the same concentration, they will both have the same number of H^+ ions. It will take the same amount of base to titrate each acid.

17) a) Weak base with strong acid; at equivalence point, $pH < 7$; use bromophenol blue
b) Strong base with strong acid; at equivalence point, $pH = 7$; use any indicator as they will all change colour very close to the equivalence point.
c) Strong base with weak acid; at equivalence point, $pH>7$; use *o*-cresolphthalein