CHAPTER 18 ACID-BASE EQUILIBRIA

18.1 The Arrhenius definition classified substances as being acids or bases by their behavior in the solvent water.

18.2 All Arrhenius acids contain hydrogen and produce hydronium ion (H_3O^+) in aqueous solution. All Arrhenius bases contain an OH group and produce hydroxide ion (OH^-) in aqueous solution. Neutralization occurs when each H_3O^+ molecule combines with an OH^- molecule to form 2 molecules of H_2O. Chemists found that the ΔH_{rxn} was independent of the combination of strong acid with strong base. In other words, the reaction of any strong base with any strong acid always produced 56 kJ/mol ($\Delta H = -56$ kJ/mol). This was consistent with Arrhenius's hypothesis describing neutralization, because all other counter ions (those present from the dissociation of the strong acid and base) were spectators and did not participate in the overall reaction.

18.3 The Arrhenius acid-base definition is limited by the fact that it only classified substances as an acid or base when dissolved in the single solvent water. The anhydrous neutralization of $NH_3(g)$ and $HCl(g)$ would not be included in the Arrhenius acid/base concept. In addition, it limited a base to a substance that contains OH in its formula. NH_3 does not contain OH in its formula but produces OH^- ions in H_2O.

18.4 Strong acids and bases dissociate completely into their ions when dissolved in water. Weak acids only partially dissociate. The characteristic property of all weak acids is that a significant number of the acid molecules are not dissociated. For a strong acid, the concentration of hydronium ions produced by dissolving the acid is equal to the initial concentration of the undissociated acid. For a weak acid, the concentration of hydronium ions produced when the acid dissolves is less than the initial concentration of the acid.

18.5 a) Water, H_2O, is an **Arrhenius acid** because it produces H_3O^+ ion in aqueous solution. Water is also an Arrhenius base because it produces the OH^- ion as well.
b) Calcium hydroxide, $Ca(OH)_2$ is a base, not an acid.
c) Phosphorous acid, H_3PO_3, is a weak **Arrhenius acid**. It is weak because the number of O atoms equals the number of ionizable Hatoms.
d) Hydroiodic acid, HI, is a strong **Arrhenius acid**.

18.6 Only **(a) $NaHSO_4$**

18.7 Barium hydroxide, $Ba(OH)_2$, and potassium hydroxide, KOH, (**b and d**) are Arrhenius bases because they contain hydroxide ions and form OH^- when dissolved in water. H_3AsO_4 and HOC,l a) and c), are Arrhenius acids, not bases.

18.8 **(b)** H_2O and **(d)** H_2NNH_2 both are very weak Arrhenius bases.

18.9 a) $HCN(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CN^-(aq)$

$$K_a = \frac{[CN^-][H_3O^+]}{[HCN]}$$

b) $HCO_3^-(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CO_3^{2-}(aq)$

$$K_a = \frac{[CO_3^{2-}][H_3O^+]}{[HCO_3^-]}$$

c) $HCOOH(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + HCOO^-(aq)$

$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$

18.10 a) $CH_3NH_3^+(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CH_3NH_2(aq)$

$$K_a = \frac{[CH_3NH_2][H_3O^+]}{[CH_3NH_3^+]}$$

b) $HClO(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + ClO^-(aq)$

$$K_a = \frac{[ClO^-][H_3O^+]}{[HClO]}$$

c) $H_2S(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + HS^-(aq)$

$$K_a = \frac{[HS^-][H_3O^+]}{[H_2S]}$$

18.11 a) $HNO_2(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + NO_2^-(aq)$

$$K_a = \frac{[NO_2^-][H_3O^+]}{[HNO_2]}$$

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

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

c) $HBrO_2(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + BrO_2^-(aq)$

$$K_a = \frac{[BrO_2^-][H_3O^+]}{[HBrO_2]}$$

18.12 a) $H_2PO_4^-(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + HPO_4^{2-}(aq)$

$$K_a = \frac{[HPO_4^{2-}][H_3O^+]}{[H_2PO_4^-]}$$

b) $H_3PO_2(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + H_2PO_2^-(aq)$

$$K_a = \frac{[H_2PO_2^-][H_3O^+]}{[H_3PO_2]}$$

c) $HSO_4^-(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + SO_4^{2-}(aq)$

$$K_a = \frac{[SO_4^{2-}][H_3O^+]}{[HSO_4^-]}$$

18.13 K_a values are listed in the Appendix. The larger the K_a value, the stronger the acid. The K_a value for hydroiodic acid, HI, is not shown because K_a approaches infinity for strong acids and is not meaningful. Therefore, HI is the strongest acid and acetic acid, CH_3COOH, is the weakest: **$CH_3COOH < HF < HIO_3 < HI$**.

18.14 **$HCl > HNO_2 > HClO > HCN$**

18.15 a) Arsenic acid, H_3AsO_4, is a **weak acid**. The number of O atoms is 4, which exceeds the number of ionizable H atoms, 3, by one. This identifies H_3AsO_4 as a weak acid.

b) Strontium hydroxide, $Sr(OH)_2$, is a **strong base**. Soluble compounds containing OH^- ions are strong bases. Sr is a Group 2 metal.

c) HIO is a **weak acid**. The number of O atoms is 1, which is equal to the number of ionizable H atoms identifying HIO as a weak acid.

d) Perchloric acid, $HClO_4$, is a **strong acid**. $HClO_4$ is one example of the type of strong acid in which the number of O atoms exceeds the number of ionizable H atoms by more than 2.

18.16 a) **weak base** b) **strong base** c) **strong acid** d) **weak acid**

18.17 a) Rubidium hydroxide, RbOH, is a **strong base** because Rb is a Group 1A(1) metal.
b) Hydrobromic acid, HBr, is a **strong acid**, because it is one of the listed hydrohalic acids.
c) Hydrogen telluride, H_2Te, is a **weak acid**, because H is not bonded to an oxygen or halide.
d) Hypochlorous acid, HClO, is a **weak acid**. The number of O atoms is 1, which is equal to the number of ionizable H atoms identifying HIO as a weak acid.

18.18 a) **weak base** b) **strong acid** c) **weak acid** d) **weak acid**

18.19 Autoionization reactions occur when a proton (or, less frequently, another ion) is transferred from one molecule of the substance to another molecule of the same substance.

$$H_2O(l) + H_2O(l) \leftrightarrows H_3O^+(aq) + OH^-(aq)$$

$$H_2SO_4(l) + H_2SO_4(l) \leftrightarrows H_3SO_4^+ \text{ (solvated)} + HSO_4^- \text{ (solvated)}$$

18.20 $H_2O(l) + H_2O(l) \leftrightarrows H_3O^+(aq) + OH^-(aq)$

$$K_c = \frac{\left[H_3O^+\right]\left[OH^-\right]}{\left[H_2O\right]^2}$$

$[H_2O]$ is a constant and is included with the value of K_c:
$K_w = [H_2O]^2 \text{ x } Kc = [H_3O^+][OH^-]$

18.21 a) pH increases by a value of 1
b) $[H_3O^+]$ increases by a factor of 1000

18.22 The lower the concentration of hydronium (H_3O^+) ions, the higher the pH:
a) At equal concentrations, the acid with the larger K_a will ionize to produce more hydronium ions than the acid with the smaller K_a. The solution of an **acid with the smaller K_a** = $4\text{x}10^{-5}$ has a lower $[H_3O^+]$ and higher pH.
b) pK_a is equal to –log K_a. The smaller the K_a, the larger the pK_a is. So the **acid with the larger pK_a**, 3.5, has a lower $[H_3O^+]$ and higher pH.
c) **Lower concentration** of the same acid means lower concentration of hydronium ions produced. The 0.01 *M* solution has a lower $[H_3O^+]$ and higher pH.
d) At the same concentration, strong acids dissociate to produce more hydronium ions than weak acids. The 0.1 *M* solution of a **weak acid** has a lower $[H_3O^+]$ and higher pH.
e) Bases produce OH^- ions in solution, so the concentration of hydronium ion for a solution of a base solution is lower than that for a solution of an acid. The 0.01 *M* **base solution** has the higher pH.
f) pOH equals –log $[OH^-]$. At 25°C, the equilibrium constant for water ionization, K_w, equals $1\text{x}10^{-14}$ so 14 = pH + pOH. As pOH decreases, pH increases. The solution of **pOH = 6.0** has the higher pH.

18.23 a) This problem can be approached two ways. Because NaOH is a strong base, the $[OH^-]_{eq} = [NaOH]_{init}$. One method involves calculating $[H_3O^+]$ using from $K_w = [H_3O^+]\,[OH^-]$, then calculating pH from the relationship pH = –log $[H_3O^+]$. The other method involves calculating pOH and then using pH + pOH = 14.00 to calculate pH.

First method:

$$[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \text{ x } 10^{-14}}{0.0111} = 9.0090 \text{ x } 10^{-13}\ M \text{ (unrounded)}$$

pH = –log $[H_3O^+]$ = –log (9.0090 x 10^{-13}) = 12.04532 = **12.05**

Second method:

pOH = –log $[OH^-]$ = –log (0.0111) = 1.954677 (unrounded)

pH = 14.00 – pOH = 14.00 – 1.954677 = 12.04532 = **12.05**

With a pH > 7, the solution is **basic**.

b) There are again two acceptable methods analogous to those in part a; only one will be used here.
For a strong acid:
$[H_3O^+] = [HCl] = 1.35 \text{ x } 10^{-3}$ *M*
pH = –log ($1.35 \text{ x } 10^{-3}$) = 2.869666 (unrounded)
pOH = 14.00 – 2.869666 = 11.1303334 = **11.13**.
With a pH < 7, the solution is **acidic**.

18.24 a) pH = –log (0.0333) = 1.47756 = **1.478**; **acidic**
b) pOH = –log (0.0347) = 1.45967 = **1.460**; **basic**

18.25 a) HI is a strong acid, so $[H_3O^+] = [HI] = 6.14 \text{ x } 10^{-3}$ *M*.
pH = –log ($6.14 \text{ x } 10^{-3}$) = 2.211832 = **2.212.** Solution is **acidic**.
b) $Ba(OH)_2$ is a strong base, so $[OH^-] = 2 \text{ x } [Ba(OH)_2]$ = 2 (2.55 *M*) = 5.10 *M*
pOH = –log (5.10) = –0.70757 = –**0.708**. Solution is **basic**.

18.26 a) pOH = –log ($7.52 \text{ x } 10^{-4}$) = 3.12378 (unrounded)
pH = 14.00 – 3.12378 = 10.87622 = **10.88** **basic**
b) pH = –log ($1.59 \text{ x } 10^{-3}$) = 2.79860 (unrounded)
pOH = 14.00 – 2.79860 = 11.20140 = **11.20** **acidic**

18.27 a) $[H_3O^+] = 10^{-\text{pH}} = 10^{-9.85} = 1.4125375 \text{ x } 10^{-10}$ = **1.4 x 10^{-10} *M* H_3O^+**
pOH = 14.00 – pH = 14.00 – 9.85 = **4.15**
$[OH^-] = 10^{-\text{pOH}} = 10^{-4.15} = 7.0794578 \text{ x } 10^{-5}$ = **7.1 x 10^{-5} *M* OH^-**
b) pH = 14.00 – pOH = 14.00 – 9.43 = **4.57**
$[H_3O^+] = 10^{-\text{pH}} = 10^{-4.57} = 2.691535 \text{ x } 10^{-5}$ = **2.7 x 10^{-5} *M* H_3O^+**
$[OH^-] = 10^{-\text{pOH}} = 10^{-9.43} = 3.7153523 \text{ x } 10^{-10}$ = **3.7 x 10^{-10} *M* OH^-**

18.28 a) $[H_3O^+] = 10^{-\text{pH}} = 10^{-3.47} = 3.38844 \text{ x } 10^{-4}$ = **3.4 x 10^{-4} *M* H_3O^+**
pOH = 14.00 – pH = 14.00 – 3.47 = **10.53**
$[OH^-] = 10^{-\text{pOH}} = 10^{-10.53} = 2.951209 \text{ x } 10^{-11}$ = **3.0 x 10^{-11} *M* OH^-**
b) pH = 14.00 – pOH = 14.00 – 4.33 = **9.67**
$[H_3O^+] = 10^{-\text{pH}} = 10^{-9.67} = 2.13796 \text{ x } 10^{-10}$ = **2.1 x 10^{-10} *M* H_3O^+**
$[OH^-] = 10^{-\text{pOH}} = 10^{-4.33} = 4.67735 \text{ x } 10^{-5}$ = **4.7 x 10^{-5} *M* OH^-**

18.29 a) $[H_3O^+] = 10^{-\text{pH}} = 10^{-4.77} = 1.69824 \text{ x } 10^{-5}$ = **1.7 x 10^{-5} *M* H_3O^+**
pOH = 14.00 – pH = 14.00 – 4.77 = **9.23**
$[OH^-] = 10^{-\text{pOH}} = 10^{-9..23} = 5.8884 \text{ x } 10^{-10}$ = **5.9 x 10^{-10} *M* OH^-**
b) pH = 14.00 – pOH = 14.00 – 5.65 = **8.35**
$[H_3O^+] = 10^{-\text{pH}} = 10^{-8.35} = 4.46684 \text{ x } 10^{-9}$ = **4.5 x 10^{-9} *M* H_3O^+**
$[OH^-] = 10^{-\text{pOH}} = 10^{-5.65} = 2.23872 \text{ x } 10^{-6}$ = **2.2 x 10^{-6} *M* OH^-**

18.30 a) $[H_3O^+] = 10^{-\text{pH}} = 10^{-8.97} = 1.071519 \text{ x } 10^{-9}$ = **1.1 x 10^{-9} *M* H_3O^+**
pOH = 14.00 – pH = 14.00 – 8.97 = **5.03**
$[OH^-] = 10^{-\text{pOH}} = 10^{-5.03} = 9.3325 \text{ x } 10^{-6}$ = **9.3 x 10^{-6} *M* OH^-**
b) pH = 14.00 - pOH = 14.00 – 11.27 = **2.73**
$[H_3O^+] = 10^{-\text{pH}} = 10^{-2.73} = 1.862087 \text{ x } 10^{-3}$ = **1.9 x 10^{-3} *M* H_3O^+**
$[OH^-] = 10^{-\text{pOH}} = 10^{-11.27} = 5.3703 \text{ x } 10^{-12}$ = **5.4 x 10^{-12} *M* OH^-**

18.31 The pH is increasing, so the solution is becoming more basic. Therefore, OH^- ion is added to increase the pH. Since 1 mole of H_3O^+ will react with 1 mole of OH^-, the difference in $[H_3O^+]$ would be equal to the $[OH^-]$ added.
$[H_3O^+] = 10^{-\text{pH}} = 10^{-3.15} = 7.07945 \text{ x } 10^{-4}$ *M* H_3O^+ (unrounded)
$[H_3O^+] = 10^{-\text{pH}} = 10^{-3.65} = 2.23872 \text{ x } 10^{-4}$ *M* H_3O^+ (unrounded)
Add ($7.07945 \text{ x } 10^{-4}$ *M* – $2.23872 \text{ x } 10^{-4}$ *M*) = $4.840737 \text{ x } 10^{-4}$ = **4.8 x 10^{-4} mol of OH^- per liter**.

18.32 The pH is decreasing so the solution is becoming more acidic. Therefore, H_3O^+ ion is added to decrease the pH.

$[H_3O^+] = 10^{-pH} = 10^{-9.33} = 4.67735 \times 10^{-10}\ M\ H_3O^+$ (unrounded)
$[H_3O^+] = 10^{-pH} = 10^{-9.07} = 8.51138 \times 10^{-10}\ M\ H_3O^+$ (unrounded)
Add $(8.51138 \times 10^{-10}\ M - 4.67735 \times 10^{-10}\ M) = 3.83403 \times 10^{-10} =$ **3.8×10^{-10} mol of H_3O^+ per liter**.

18.33 The pH is increasing so the solution is becoming more basic. Therefore, OH^- ion is added to increase the pH. Since 1 mole of H_3O^+ reacts with 1 mole of OH^-, the difference in $[H_3O^+]$ would be equal to the $[OH^-]$ added.

$[H_3O^+] = 10^{-pH} = 10^{-4.52} = 3.01995 \times 10^{-5}\ M\ H_3O^+$ (unrounded)
$[H_3O^+] = 10^{-pH} = 10^{-5.25} = 5.623413 \times 10^{-6}\ M\ H_3O^+$ (unrounded)
$3.01995 \times 10^{-5}\ M - 5.623413 \times 10^{-6}\ M = 2.4576 \times 10^{-5}\ M\ OH^-$ must be added.

$$\frac{2.4576 \times 10^{-5}\ \text{mol}}{\text{L}}(5.6\ \text{L}) = 1.3763 \times 10^{-4} = \mathbf{1.4 \times 10^{-4}\ mol\ of\ OH^-}$$

18.34 The pH is decreasing so the solution is becoming more acidic. Therefore, H_3O^+ ion is added to decrease the pH.

$[H_3O^+] = 10^{-pH} = 10^{-8.92} = 1.20226 \times 10^{-9}\ M\ H_3O^+$ (unrounded)
$[H_3O^+] = 10^{-pH} = 10^{-6.33} = 4.67735 \times 10^{-7}\ M\ H_3O^+$ (unrounded)
Add $(4.67735 \times 10^{-7}\ M - 1.20226 \times 10^{-9}\ M)$ (87.5 mL) $(10^{-3}$ L / 1 mL$)$
$= 4.08216 \times 10^{-8} =$ **4.1×10^{-8} mol of H_3O^+**

18.35 Scene A has a pH of 4.8.
$[H_3O^+] = 10^{-pH} = 10^{-4.8} = 1.58489 \times 10^{-5}\ M\ H_3O^+$
Scene B:

$$[H_3O^+] = \left(1.58489 \times 10^{-5}\ \text{M}\ H_3O^+\right)\left(\frac{25\ \text{spheres}}{2\ \text{spheres}}\right) = 1.98 \times 10^{-4}\ \text{M}\ H_3O^+$$

$pH = -\log[H_3O^+] = -\log[1.98 \times 10^{-4}] =$ **3.7**

18.36 a) Heat is absorbed in an endothermic process: $2\ H_2O(l) + \text{heat} \rightarrow H_3O^+(aq) + OH^-(aq)$. As the temperature increases, the reaction shifts to the formation of products. Since the products are in the numerator of the K_w expression, rising temperature **increases** the value of K_w.
b) Given that the pH is 6.80, the $[H_3O^+]$ can be calculated. The problem specifies that the solution is neutral, meaning $[H_3O^+] = [OH^-]$. A new K_w can then be calculated.

$[H_3O^+] = 10^{-pH} = 10^{-6.80} = 1.58489 \times 10^{-7}\ M\ H_3O^+ =$ **$1.6 \times 10^{-7}\ M$ $[H_3O^+] = [OH^-]$**
$K_w = [H_3O^+]\ [OH^-] = (1.58489 \times 10^{-7})\ (1.58489 \times 10^{-7}) = 2.511876 \times 10^{-14} =$ **2.5×10^{-14}**
For a neutral solution: pH = **pOH = 6.80**

18.37 The Brønsted-Lowry theory defines acids as proton donors and bases as proton acceptors, while the Arrhenius definition looks at acids as containing ionizable H atoms and at bases as containing hydroxide ions. In both definitions, an acid produces hydronium ions and a base produces hydroxide ions when added to water. Ammonia, NH_3, and carbonate ion, CO_3^{2-}, are two Brønsted-Lowry bases that are not Arrhenius bases because they do not contain hydroxide ions. Brønsted-Lowry acids must contain an ionizable H atom in order to be proton donors, so a Brønsted-Lowry acid that is not an Arrhenius acid cannot be identified. (Other examples are also acceptable.)

18.38 Every acid has a conjugate base, and every base has a conjugate acid. The acid has one more H and one more positive charge than the base from which it was formed.

18.39 a) Acid-base reactions are proton transfer processes. Thus, the proton will be transferred from the stronger acid to the stronger base to form the weaker acid and weaker base.
b) $HB(aq) + A^-(aq) \rightarrow HA(aq) + B^-(aq)$
The spontaneous direction of a Bronsted-Lowry acid-base reaction is that the stronger acid will transfer a proton to the stronger base to produce the weaker acid and base. Thus at equilibrium there should be relatively more of weaker acid and base present than there will be of the stronger acid and base. Since there is more HA and B^- in sample and less HB and A^-, **HB** must be the stronger acid and **A^-** must be the stronger base.

18.40 An amphoteric substance can act as either an acid or a base. In the presence of a strong base (OH^-), the dihydrogen phosphate ion acts like an acid by donating hydrogen:
$H_2PO_4^-(aq) + OH^-(aq) \rightarrow H_2O(aq) + HPO_4^{2-}(aq)$
In the presence of a strong acid (HCl), the dihydrogen phosphate ion acts like a base by accepting hydrogen:
$H_2PO_4^-(aq) + HCl(aq) \rightarrow H_3PO_4(aq) + Cl^-(aq)$

18.41 a) When phosphoric acid is dissolved in water, a proton is donated to the water and dihydrogen phosphate ions are generated.

$$H_3PO_4(aq) + H_2O(l) \leftrightarrows H_2PO_4^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{\left[H_3O^+\right]\left[H_2PO_4^-\right]}{\left[H_3PO_4\right]}$$

b) Benzoic acid is an organic acid and has only one proton to donate from the carboxylic acid group. The H atoms bonded to the benzene ring are not acidic hydrogens.

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

$$K_a = \frac{\left[H_3O^+\right]\left[C_6H_5COO^-\right]}{\left[C_6H_5COOH\right]}$$

c) Hydrogen sulfate ion donates a proton to water and forms the sulfate ion.

$$HSO_4^-(aq) + H_2O(l) \leftrightarrows SO_4^{2-}(aq) + H_3O^+(aq)$$

$$K_a = \frac{\left[H_3O^+\right]\left[SO_4^{2-}\right]}{\left[HSO_4^-\right]}$$

18.42 a) Formic acid, an organic acid, has only one proton to donate from the carboxylic acid group. The remaining H atom, bonded to the carbon, is not an acidic hydrogen.

$$HCOOH(aq) + H_2O(l) \leftrightarrows HCOO^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{\left[H_3O^+\right]\left[HCOO^-\right]}{\left[HCOOH\right]}$$

b) When chloric acid is dissolved in water, a proton is donated to the water and chlorate ions are generated.

$$HClO_3(aq) + H_2O(l) \leftrightarrows ClO_3^-(aq) + H_3O^+(aq)$$

$$K_a = \frac{\left[H_3O^+\right]\left[ClO_3^-\right]}{\left[HClO_3\right]}$$

c) The dihydrogen arsenate ion donates a proton to water and forms the hydrogen arsenate ion.

$$H_2AsO_4^-(aq) + H_2O(l) \leftrightarrows HAsO_4^{2-}(aq) + H_3O^+(aq)$$

$$K_a = \frac{\left[H_3O^+\right]\left[HAsO_4^{2-}\right]}{\left[H_2AsO_4^-\right]}$$

18.43 To derive the conjugate base, remove one H and decrease the charge by 1. Since each formula is neutral, the conjugate base will have a charge of –1.
a) $\mathbf{Cl^-}$ b) $\mathbf{HCO_3^-}$ c) $\mathbf{OH^-}$

18.44 a) $\mathbf{PO_4^{3-}}$ b) $\mathbf{NH_3}$ c) $\mathbf{S^{2-}}$

18.45 To derive the conjugate acid, add an H and increase the charge by 1.
a) $\mathbf{NH_4^+}$ b) $\mathbf{NH_3}$ c) $\mathbf{C_{10}H_{14}N_2H^+}$

18.46 a) $\mathbf{OH^-}$ b) $\mathbf{HSO_4^-}$ c) $\mathbf{H_3O^+}$

18.47 The acid donates the proton to form its conjugate base; the base accepts a proton to form its conjugate acid:

a)

HCl	+	H_2O	$\leftrightarrows$	Cl^-	+	H_3O^+
acid		base		conjugate base		conjugate acid

Conjugate acid/base pairs: HCl/Cl^- and H_3O^+/H_2O

b)

$HClO_4$	+	H_2SO_4	$\leftrightarrows$	ClO_4^-	+	$H_3SO_4^+$
acid		base		conjugate base		conjugate acid

Conjugate acid/base pairs: $HClO_4/ClO_4^-$ and $H_3SO_4^+/H_2SO_4$

Note: Perchloric acid is able to protonate another strong acid, H_2SO_4, because perchloric acid is a stronger acid. ($HClO_4$'s oxygen atoms exceed its hydrogen atoms by one more than H_2SO_4.)

c)

HPO_4^{2-}	+	H_2SO_4	$\leftrightarrows$	$H_2PO_4^-$	+	HSO_4^-
base		acid		conjugate acid		conjugate base

Conjugate acid/base pairs: H_2SO_4/HSO_4^- and $H_2PO_4^-/HPO_4^{2-}$

18.48 a)

NH_3	+	HNO_3	$\leftrightarrows$	NH_4^+	+	NO_3^-
base		acid		conjugate acid		conjugate base

Conjugate pairs: HNO_3/NO_3^- ; NH_4^+/NH_3

b)

O^{2-}	+	H_2O	$\leftrightarrows$	OH^-	+	OH^-
base		acid		conjugate acid		conjugate base

Conjugate pairs: OH^-/O^{2-}; H_2O/OH^-

c)

NH_4^+	+	BrO_3^-	$\leftrightarrows$	NH_3	+	$HBrO_3$
acid		base		conjugate base		conjugate acid

Conjugate pairs: NH_4^+/NH_3; $HBrO_3/BrO_3^-$

18.49 The acid donates the proton to form its conjugate base; the base accepts a proton to form its conjugate acid:

a)

NH_3	+	H_3PO_4	$\leftrightarrows$	NH_4^+	+	$H_2PO_4^-$
base		acid		conjugate acid		conjugate base

Conjugate acid-base pairs: $H_3PO_4/H_2PO_4^-$; NH_4^+/NH_3

b)

CH_3O^-	+	NH_3	$\leftrightarrows$	CH_3OH	+	NH_2^-
base		acid		conjugate acid		conjugate base

Conjugate acid-base pairs: NH_3/NH_2^-; CH_3OH/CH_3O^-

c)

HPO_4^{2-}	+	HSO_4^-	$\leftrightarrows$	$H_2PO_4^-$	+	SO_4^{2-}
base		acid		conjugate acid		conjugate base

Conjugate acid-base pairs: HSO_4^-/SO_4^{2-}; $H_2PO_4^-/HPO_4^{2-}$

18.50 a)

NH_4^+	+	CN^-	$\leftrightarrows$	NH_3	+	HCN
acid		base		conjugate base		conjugate acid

Conjugate acid-base pairs: NH_4^+/NH_3; HCN/CN^-

b)

H_2O	+	HS^-	$\leftrightarrows$	OH^-	+	H_2S
acid		base		conjugate base		conjugate acid

Conjugate acid-base pairs: H_2O/OH^-; H_2S/HS^-

c)

HSO_3^-	+	CH_3NH_2	$\leftrightarrows$	SO_3^{2-}	+	$CH_3NH_3^+$
acid		base		conjugate base		conjugate acid

Conjugate acid-base pairs: HSO_3^-/SO_3^{2-}; $CH_3NH_3^+/CH_3NH_2$

18.51 Write total ionic equations and then remove the spectator ions to write the net ionic equations. The (*aq*) subscript denotes that each species is soluble and dissociates in water.

a) $\cancel{Na^+(aq)} + OH^-(aq) + \cancel{Na^+(aq)} + H_2PO_4^-(aq) \leftrightarrows H_2O(l) + \cancel{2\ Na^+(aq)} + HPO_4^{2-}(aq)$

Net: $OH^-(aq)$	+	$H_2PO_4^-(aq)$	$\leftrightarrows$	$H_2O(l)$	+	$HPO_4^{2-}(aq)$
base		acid		conjugate acid		conjugate base

Conjugate acid/base pairs: $H_2PO_4^-/HPO_4^{2-}$ and H_2O/OH^-

b) ~~$K^+(aq)$~~ + $HSO_4^-(aq)$ + ~~$2\ K^+(aq)$~~ + $CO_3^{2-}(aq) \leftrightarrows$ ~~$2\ K^+(aq)$~~ + $SO_4^{2-}(aq)$ + ~~$K^+(aq)$~~ + $HCO_3^-(aq)$

Net: $HSO_4^-(aq) + CO_3^{2-}(aq) \leftrightarrows SO_4^{2-}(aq) + HCO_3^-(aq)$
acid base conjugate base conjugate acid
Conjugate acid/base pairs: HSO_4^-/SO_4^{2-} and HCO_3^-/CO_3^{2-}

18.52 a) $H_3O^+(aq) + CO_3^{2-}(aq) \leftrightarrows HCO_3^-(aq) + H_2O(l)$
acid base conjugate acid conjugate base
Conjugate pairs: H_3O^+/H_2O; HCO_3^-/CO_3^{2-}

b) $NH_4^+(aq) + OH^-(aq) \leftrightarrows NH_3(aq) + H_2O(l)$
acid base conjugate base conjugate acid
Conjugate pairs: NH_4^+/NH_3; H_2O/OH^-

18.53 The conjugate pairs are H_2S (acid)/HS^- (base) and HCl (acid)/Cl^- (base). The reactions involve reacting one acid from one conjugate pair with the base from the other conjugate pair. Two reactions are possible:

(1) $HS^- + HCl \leftrightarrows H_2S + Cl^-$ and (2) $H_2S + Cl^- \leftrightarrows HS^- + HCl$

The first reaction is the reverse of the second. To decide which will have an equilibrium constant greater than 1, look for the stronger acid producing a weaker acid. HCl is a strong acid and H_2S a weak acid. The reaction that favors the products ($K_c > 1$) is the first one where the strong acid produces the weak acid. Reaction (2) with a weaker acid forming a stronger acid favors the reactants and $K_c < 1$.

18.54 $K_c > 1$: $HNO_3 + F^- \leftrightarrows NO_3^- + HF$
$K_c < 1$: $NO_3^- + HF \leftrightarrows HNO_3 + F^-$

18.55 a) $HCl + NH_3 \leftrightarrows NH_4^+ + Cl^-$
strong acid stronger base weak acid weaker base

HCl is ranked above NH_4^+ in the list of conjugate acid-base pair strength and is the stronger acid. NH_3 is ranked above Cl^- and is the stronger base. NH_3 is shown as a "stronger" base because it is stronger than Cl^-, but is not considered a "strong" base. The reaction proceeds towards the production of the weaker acid and base, i.e., the reaction as written proceeds to the right and $\boldsymbol{K_c > 1}$. The stronger acid is more likely to donate a proton than the weaker acid.

b) $H_2SO_3 + NH_3 \leftrightarrows HSO_3^- + NH_4^+$
stronger acid stronger base weaker base weaker acid

H_2SO_3 is ranked above NH_4^+ and is the stronger acid. NH_3 is a stronger base than HSO_3^-. The reaction proceeds towards the production of the weaker acid and base, i.e., the reaction as written proceeds to the right and $\boldsymbol{K_c > 1}$.

18.56 **Neither a or b have $\boldsymbol{K_c > 1}$.**

18.57 a) $NH_4^+ + HPO_4^{2-} \leftrightarrows NH_3 + H_2PO_4^-$
weaker acid weaker base stronger base stronger acid

$\boldsymbol{K_c < 1}$ The reaction proceeds towards the production of the weaker acid and base, i.e., the reaction as written proceeds to the left.

b) $HSO_3^- + HS^- \leftrightarrows H_2SO_3 + S^{2-}$
weaker base weaker acid stronger acid stronger base

$\boldsymbol{K_c < 1}$ The reaction proceeds towards the production of the weaker acid and base, i.e., the reaction as written proceeds to the left.

18.58 a) **Kc < 1** b) **Kc > 1**

18.59 a) The concentration of a strong acid is **<u>very different</u>** before and after dissociation since a strong acid exhibits 100% dissociation. After dissociation, the concentration of the strong acid approaches 0, or $[HA] \approx 0$.
b) A weak acid dissociates to a very small extent (<<100%), so the acid concentration after dissociation is **<u>nearly the same</u>** as before dissociation.
c) Same as (b), but the percent, or extent, of dissociation is greater than in (b).
d) Same as (a)

18.60 **No**, HCl and CH_3COOH are never of equal strength because HCl is a strong acid with $K_a > 1$ and CH_3COOH is a weak acid with $K_a < 1$. The K_a of the acid, not the concentration of H_3O^+ in a solution of the acid, determines the strength of the acid.

18.61 Water will add approximately 10^{-7} *M* to the H_3O^+ concentration. (The value will be slightly lower than for pure water.)

a) $CH_3COOH(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CH_3COO^-(aq)$

$0.10 - x \qquad x \qquad x$

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{\left[H_3O^+\right]\left[CH_3COO^-\right]}{\left[CH_3COOH\right]}$$

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{(x)(x)}{(0.1 - x)}$$ Assume x is small compared to 0.1 so 0.1 – x = 0.1.

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{(x)(x)}{(0.1)}$$

$x = 1.3416 \text{ x } 10^{-3}$ *M* (unrounded)

Since the H_3O^+ concentration from CH_3COOH is many times greater than that from H_2O, $[H_3O^+] = [CH_3COO^-]$.

b) The extremely low CH_3COOH concentration means the H_3O^+ concentration from CH_3COOH is near that from H_2O. Thus $[H_3O^+] = [CH_3COO^-]$.

c) $CH_3COOH(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CH_3COO^-(aq)$

$CH_3COONa(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq)$

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{(x)(0.1 + x)}{(0.1 - x)}$$ Assume x is small compared to 0.1.

$x = [H_3O^+] = 1.8 \text{ x } 10^{-5}$

$[CH_3COO^-] = 0.1 + x = 0.1$ *M*

Thus, $[CH_3COO^-] > [H_3O^+]$

18.62 The higher the negative charge on a species, the more difficult it is to remove a positively charged H^+ ion.

18.63 Butanoic acid dissociates according to the following equation:

$CH_3CH_2CH_2COOH(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CH_3CH_2CH_2COO^-(aq)$

Initial:	0.15 M	0	0
Change:	–x	+x	+x
Equilibrium:	0.15 – x	+x	+x

According to the information given in the problem, $[H_3O^+]eq = 1.51 \text{ x } 10^{-3}$ *M* = x

Thus, $[H_3O^+] = [CH_3CH_2CH_2COO^-] = 1.51 \text{ x } 10^{-3}$ *M*

$[CH_3CH_2CH_2COOH] = (0.15 - x) = (0.15 - 1.51 \text{ x } 10^{-3})$ *M* = 0.14849 *M*

$$K_a = \frac{\left[H_3O^+\right]\left[CH_3CH_2CH_2COO^-\right]}{\left[CH_3CH_2CH_2COOH\right]}$$

$$K_a = \frac{\left(1.51 \text{ x } 10^{-3}\right)\left(1.51 \text{ x } 10^{-3}\right)}{(0.14849)} = 1.53552 \text{ x } 10^{-5} = \mathbf{1.5 \text{ x } 10^{-5}}$$

18.64 Any weak acid dissociates according to the following equation:

$HA(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + A^-(aq)$

$[H_3O^+] = 10^{-pH} = 10^{-4.88} = 1.318 \text{ x } 10^{-5}$ *M* (unrounded)

Thus, $[H_3O^+] = [A^-] = 1.318 \text{ x } 10^{-5}$ *M*, and $[HA] = (0.035 - 1.318 \text{ x } 10^{-5}) = 0.03499$ *M*

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_a = \frac{(1.318 \text{ x } 10^{-5})(1.318 \text{ x } 10^{-5})}{(0.03499)} = 4.965 \text{ x } 10^{-9} = \mathbf{5.0 \text{ x } 10^{-9}}$$

18.65 For a solution of a weak acid, the acid dissociation equilibrium determines the concentrations of the weak acid, its conjugate base and H_3O^+. The acid dissociation reaction for HNO_2 is:

Concentration	$HNO_2(aq)$	+	$H_2O(l)$	$\leftrightarrows$	$H_3O^+(aq)$	+	$NO_2^-(aq)$
Initial	0.60		—		0		0
Change	–x				+x		+x
Equilibrium	0.60 – x				x		x

(The H_3O^+ contribution from water has been neglected.)

$$K_a = 7.1 \text{ x } 10^{-4} = \frac{[H_3O^+][NO_2^-]}{[HNO_2]}$$

$$K_a = 7.1 \text{ x } 10^{-4} = \frac{(x)(x)}{(0.60 - x)}$$ Assume x is small compared to 0.60: 0.60 – x = 0.60

$$K_a = 7.1 \text{ x } 10^{-4} = \frac{(x)(x)}{(0.60)}$$

x = 0.020639767 (unrounded)

Check assumption: (0.020639767 / 0.60) x 100% = 3.4% error, so the assumption is valid.

$[H_3O^+] = [NO_2^-] = \mathbf{2.1 \text{ x } 10^{-2}}$ ***M***

The concentration of hydroxide ion is related to concentration of hydronium ion through the equilibrium for water: $2\ H_2O(l) \leftrightarrows H_3O^+(aq) + OH^-(aq)$ with $K_w = 1.0 \text{ x } 10^{-14}$

$[OH^-] = 1.0 \text{ x } 10^{-14} / 0.020639767 = 4.84502 \text{ x } 10^{-13} = \mathbf{4.8 \text{ x } 10^{-13}}$ ***M*** **OH^-**

18.66 For a solution of a weak acid, the acid dissociation equilibrium determines the concentrations of the weak acid, its conjugate base and H_3O^+. The acid dissociation reaction for HF is:

Concentration	$HF(aq)$	+	$H_2O(l)$	$\leftrightarrows$	$H_3O^+(aq)$	+	$F^-(aq)$
Initial	0.75		—		0		0
Change	–x				+x		+x
Equilibrium	0.75 – x				x		x

(The H_3O^+ contribution from water has been neglected.)

$$K_a = 6.8 \text{ x } 10^{-4} = \frac{[H_3O^+][F^-]}{[HF]}$$

$$K_a = 6.8 \text{ x } 10^{-4} = \frac{(x)(x)}{(0.75 - x)}$$ Assume x is small compared to 0.75.

$$K_a = 6.8 \text{ x } 10^{-4} = \frac{(x)(x)}{(0.75)}$$

x = 0.02258 (unrounded)

Check assumption: (0.02258 / 0.75) x 100% = 3% error, so the assumption is valid.

$[H_3O^+] = [F^-] = \mathbf{2.3 \text{ x } 10^{-2}}$ ***M***

$[OH^-] = 1.0 \text{ x } 10^{-14} / 0.02258 = 4.42869796 \text{ x } 10^{-13} = \mathbf{4.4 \text{ x } 10^{-13}}$ ***M*** **OH^-**

18.67 Write a balanced chemical equation and equilibrium expression for the dissociation of chloroacetic acid and convert pK_a to K_a.

$K_a = 10^{-pKa} = 10^{-2.87} = 1.34896 \text{ x } 10^{-3}$ (unrounded)

Concentration	$ClCH_2COOH(aq) + H_2O(l) \leftrightarrows$	$H_3O^+(aq)$	$+ ClCH_2COO^-(aq)$
Initial	1.25	0	0
Change	–x	+x	+x
Equilibrium	1.25 – x	x	x

$$K_a = 1.34896 \text{ x } 10^{-3} = \frac{(H_3O^+)(ClCH_2COO^-)}{(ClCH_2COOH)}$$

$$K_a = 1.34896 \text{ x } 10^{-3} = \frac{(x)(x)}{(1.25 - x)}$$ Assume x is small compared to 1.25.

$$K_a = 1.34896 \text{ x } 10^{-3} = \frac{(x)(x)}{(1.25)}$$

x = 0.04106336 (unrounded)

Check assumption: (0.04106336 / 1.25) x 100% = 3.3%. The assumption is good.

$[H_3O^+] = [ClCH_2COO^-] =$ **0.041 *M***

$[ClCH_2COOH] = 1.25 - 0.04106336 = 1.20894 =$ **1.21 *M***

$pH = -\log [H_3O^+] = -\log (0.04106336) = 1.3865 =$ **1.39**

18.68 Write a balanced chemical equation and equilibrium expression for the dissociation of hypochlorous acid and convert pK_a to K_a.

$K_a = 10^{-pKa} = 10^{-7.54} = 2.88403 \text{ x } 10^{-8}$ (unrounded)

$HClO(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + ClO^-(aq)$

0.115 – x x x

$$K_a = 2.88403 \text{ x } 10^{-8} = \frac{[H_3O^+][ClO^-]}{[HClO]}$$

$$K_a = 2.88403 \text{ x } 10^{-8} = \frac{(x)(x)}{(0.115 - x)}$$ Assume x is small compared to 0.115.

$$K_a = 2.88403 \text{ x } 10^{-8} = \frac{(x)(x)}{(0.115)}$$

$x = 5.75902 \text{ x } 10^{-5}$ (unrounded)

Check assumption: $(5.75902 \text{ x } 10^{-5} / 0.115) \text{ x } 100\% = 0.05\%$. The assumption is good.

$[H_3O^+] = [ClO^-] =$ **$5.8 \text{ x } 10^{-5}$ *M***

$[HClO] = 0.115 - 5.75902 \text{ x } 10^{-5} = 0.11494 =$ **0.115 *M***

$pH = -\log [H_3O^+] = -\log (5.75902 \text{ x } 10^{-5}) = 4.2396 =$ **4.24**

18.69 Percent dissociation refers to the amount of the initial concentration of the acid that dissociates into ions. Use the percent dissociation to find the concentration of acid dissociated. HA will be used as the formula of the acid.

a) The concentration of acid dissociated is equal to the equilibrium concentrations of A^- and H_3O^+. Then pH and $[OH^-]$ are determined from $[H_3O^+]$.

$$\text{Percent HA} = \frac{\text{Dissociated Acid}}{\text{Initial Acid}} \text{ x } 100\%$$

$$3.0\ \% = \frac{x}{0.20}(100)$$

[Dissociated Acid] = x = $6.0 \text{ x } 10^{-3}$ *M*

Concentration	$HA(aq) + H_2O(l) \rightleftarrows$	$H_3O^+(aq)$	$A^-(aq)$
Initial:	0.20	0	0
Change:	–x	+x	+x
Equilibrium:	0.20 – x	x	x

[Dissociated Acid] = x = $[H_3O^+]$ = **6.0×10^{-3} *M***

pH = $-\log [H_3O^+] = -\log (6.0 \times 10^{-3}) = 2.22185 =$ **2.22**

$$[OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \times 10^{-14}}{6.0 \times 10^{-3}} = 1.6666667 \times 10^{-12} = \mathbf{1.7 \times 10^{-12}}\ \boldsymbol{M}$$

pOH = $-\log [OH^-] = -\log (1.6666667 \times 10^{-12}) = 11.7782 =$ **11.78**

b) In the equilibrium expression, substitute the concentrations above and calculate K_a.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(6.0 \times 10^{-3})(6.0 \times 10^{-3})}{(0.20 - 6.0 \times 10^{-3})} = 1.85567 \times 10^{-4} = \mathbf{1.9 \times 10^{-4}}$$

18.70 Percent dissociation refers to the amount of the initial concentration of the acid that dissociates into ions. Use the percent dissociation to find the concentration of acid dissociated. HA will be used as the formula of the acid.

a) The concentration of acid dissociated is equal to the equilibrium concentrations of A^- and H_3O^+. Then, pH and $[OH^-]$ are determined from $[H_3O^+]$.

$$\text{Percent HA Dissociated} = \frac{\text{Dissociated Acid}}{\text{Initial Acid}} \text{x} 100\%$$

$$12.5\ \% = \frac{x}{0.735}(100)$$

[Dissociated Acid] = 9.1875×10^{-2} *M* (unrounded)

$HA(aq) + H_2O(l) \rightleftarrows$	$H_3O^+(aq)$	$A^-(aq)$
0.735 – x	x	x

[Dissociated Acid] = x = $[H_3O^+]$ = **9.19×10^{-2} *M***

pH = $-\log [H_3O^+] = -\log (9.1875 \times 10^{-2}) = 1.03680 =$ **1.037**

$[OH^-] = K_w / [H_3O^+] = (1.0 \times 10^{-14}) / (9.1875 \times 10^{-2}) = 1.0884 \times 10^{-13} =$ **1.1×10^{-13} *M***

pOH = $-\log [OH^-] = -\log (1.0884 \times 10^{-13}) = 12.963197 =$ **12.963**

b) In the equilibrium expression, substitute the concentrations above and calculate K_a.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(9.1875 \times 10^{-2})(9.1875 \times 10^{-2})}{(0.735 - 9.1875 \times 10^{-2})} = 1.3125 \times 10^{-2} = \mathbf{1.31 \times 10^{-2}}$$

18.71 Calculate the molarity of HX by dividing moles by volume. Convert pH to $[H_3O^+]$ and substitute into the equilibrium expression.

$$\text{Concentration of HX} = \left(\frac{0.250\ \text{mol}}{655\ \text{mL}}\right)\left(\frac{1\ \text{mL}}{10^{-3}\ \text{L}}\right) = 0.381679\ M$$

Concentration	$HX(aq) + H_2O(l) \rightleftarrows$	$H_3O^+(aq)$	$X^-(aq)$
Initial:	0.381679	0	0
Change:	–x	+x	+x
Equilibrium:	0.381679 – x	x	x

$[H_3O^+] = 10^{-pH} = 10^{-3.54} = 2.88403 \times 10^{-4}\ M = x$

Thus, $[H_3O^+] = [X^-] = 2.88403 \times 10^{-4}\ M$, and $[HX] = (0.381679 - 2.88403 \times 10^{-4})\ M$

$$K_a = \frac{[H_3O^+][X^-]}{[HX]} = \frac{(2.88403 \times 10^{-4})(2.88403 \times 10^{-4})}{(0.381679 - 2.88403 \times 10^{-4})} = 2.18087 \times 10^{-7} = \mathbf{2.2 \times 10^{-7}}$$

18.72 Calculate the molarity of HY by dividing moles by volume. Convert pH to $[H_3O^+]$ and substitute into the equilibrium expression.

Concentration of HY = (4.85×10^{-3} mol / 0.095 L) = 0.0510526 *M* (unrounded)

$HY(aq) \quad + \quad H_2O(l) \quad \rightleftarrows \quad H_3O^+(aq) \; + \; Y^-(aq)$

$0.0510526 - x \qquad\qquad x \qquad\qquad x$

$[H_3O^+] = 10^{-pH} = 10^{-2.68} = 2.089296 \times 10^{-3}$ *M* (unrounded) = x

Thus, $[H_3O^+] = [Y^-] = 2.089296 \times 10^{-3}$ *M*, and $[HX] = (0.0510526 - 2.089296 \times 10^{-3})$ *M*

$$K_a = \frac{\left[H_3O^+\right]\left[Y^-\right]}{\left[HY\right]} = \frac{\left(2.089296 \times 10^{-3}\right)\left(2.089296 \times 10^{-3}\right)}{\left(0.0510526 - 2.089296 \times 10^{-3}\right)} = 8.91516 \times 10^{-5} = \mathbf{8.9 \times 10^{-5}}$$

18.73 a) Begin with a reaction table, then use the K_a expression as in earlier problems.

Concentration	$HZ(aq)$	+	$H_2O(l)$	$\rightleftarrows$	$H_3O^+(aq)$	+	$Z^-(aq)$
Initial	0.075		—		0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$0.075 - x$				x		x

(The H_3O^+ contribution from water has been neglected.)

$$K_a = 2.55 \times 10^{-4} = \frac{\left[H_3O^+\right]\left[Z^-\right]}{\left[HZ\right]}$$

$$K_a = 2.55 \times 10^{-4} = \frac{(x)(x)}{(0.075 - x)}$$ Assume x is small compared to 0.075.

$$K_a = 2.55 \times 10^{-4} = \frac{(x)(x)}{(0.075)}$$

$[H_3O^+] = x = 4.3732 \times 10^{-3}$ (unrounded)

Check assumption: (4.3732×10^{-3} / 0.075) x 100% = 6% error, so the assumption is not valid.

Since the error is greater than 5%, it is not acceptable to assume x is small compared to 0.045, and it is necessary to use the quadratic equation.

$$K_a = 2.55 \times 10^{-4} = \frac{(x)(x)}{(0.075 - x)}$$

$x^2 + 2.55 \times 10^{-4}\, x - 1.9125 \times 10^{-5} = 0$

$a = 1 \qquad b = 2.55 \times 10^{-4} \qquad c = -1.9125 \times 10^{-5}$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-(2.55 \times 10^{-4}) \pm \sqrt{\left(2.55 \times 10^{-4}\right)^2 - 4(1)\left(-1.9125 \times 10^{-5}\right)}}{2(1)}$$

x = 0.00425 or –0.004503 (unrounded)

(The –0.004503 value is not possible.)

$pH = -\log [H_3O^+] = -\log (0.00425) = 2.3716 =$ **2.37**

b) Begin this part like part a.

Concentration	$HZ(aq)$	+	$H_2O(l)$	$\rightleftarrows$	$H_3O^+(aq)$	+	$Z^-(aq)$
Initial	0.045		—		0		0
Change	$-x$				$+x$		$+x$
Equilibrium	$0.045 - x$				x		x

(The H_3O^+ contribution from water has been neglected.)

$$K_a = 2.55 \times 10^{-4} = \frac{\left[H_3O^+\right]\left[Z^-\right]}{\left[HZ\right]}$$

$$K_a = 2.55 \text{ x } 10^{-4} = \frac{(x)(x)}{(0.045 - x)}$$ Assume x is small compared to 0.045.

$$K_a = 2.55 \text{ x } 10^{-4} = \frac{(x)(x)}{(0.045)}$$

$[H_3O^+] = x = 3.3875 \text{ x } 10^{-3}$ (unrounded)
Check assumption: ($3.3875 \text{ x } 10^{-3}$ / 0.045) x 100% = 7.5% error, so the assumption is not valid.
Since the error is greater than 5%, it is not acceptable to assume x is small compared to 0.045, and it is necessary to use the quadratic equation.

$$K_a = 2.55 \text{ x } 10^{-4} = \frac{(x)(x)}{(0.045 - x)}$$

$x^2 = (2.55 \text{ x } 10^{-4})(0.045 - x) = 1.1475 \text{ x } 10^{-5} - 2.55 \text{ x } 10^{-4}\text{ x}$
$x^2 + 2.55 \text{ x } 10^{-4}\text{ x} - 1.1475 \text{ x } 10^{-5} = 0$
$a = 1 \quad b = 2.55 \text{ x } 10^{-4} \quad c = -1.1475 \text{ x } 10^{-5}$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-2.55 \text{ x } 10^{-4} \pm \sqrt{\left(2.55 \text{ x } 10^{-4}\right)^2 - 4(1)\left(-1.1475 \text{ x } 10^{-5}\right)}}{2(1)}$$

$x = 3.3899 \text{ x } 10^{-3}\ M\ H_3O^+$

$$[OH^-] = [OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1.0 \text{ x } 10^{-14}}{3.3899 \text{ x } 10^{-3}} = 2.94994 \text{ x } 10^{-12}\ M$$

pOH = $-\log [OH^-] = -\log (2.94994 \text{ x } 10^{-12}) = 11.5302 =$ **11.53**

18.74 Calculate K_a from pK_a.
$K_a = 10^{-pK_a} = 10^{-4.89} = 1.2882 \text{ x } 10^{-5}$ (unrounded)
a) Begin with a reaction table, and then use the K_a expression as in earlier problems.

Concentration	$HQ(aq)$	+	$H_2O(l)$ ⇆	$H_3O^+(aq)$	+	$Q^-(aq)$
Initial	$3.5 \text{ x } 10^{-2}$		—	0		0
Change	–x			+x		+x
Equilibrium	$3.5 \text{ x } 10^{-2} - x$			x		x

(The H_3O^+ contribution from water has been neglected.)

$$K_a = 1.2882 \text{ x } 10^{-5} = \frac{[H_3O^+][Q^-]}{[HQ]}$$

$$K_a = 1.2882 \text{ x } 10^{-5} = \frac{(x)(x)}{(0.035 - x)}$$ Assume x is small compared to 0.035.

$$K_a = 1.2882 \text{ x } 10^{-5} = \frac{(x)(x)}{(0.035)}$$

$[H_3O^+] = x = 6.714685 \text{ x } 10^{-4}$ (unrounded)
Check assumption: ($6.714685 \text{ x } 10^{-4}$ / 0.035) x 100% = 2% error, so the assumption is valid.
$[H_3O^+] =$ **$6.7 \text{ x } 10^{-4}\ M$**

b) Begin this problem like part a.

Concentration	$HQ(aq)$	+	$H_2O(l)$ ⇆	$H_3O^+(aq)$	+	$Q^-(aq)$
Initial	0.65		—	0		0
Change	–x			+x		+x
Equilibrium	0.65 – x			x		x

(The H_3O^+ contribution from water has been neglected.)

$$K_a = 1.2882 \text{ x } 10^{-5} = \frac{\left[H_3O^+\right]\left[Q^-\right]}{\left[HQ\right]}$$

$$K_a = 1.2882 \text{ x } 10^{-5} = \frac{(x)(x)}{(0.65 - x)}$$ Assume x is small compared to 0.035.

$$K_a = 1.2882 \text{ x } 10^{-5} = \frac{(x)(x)}{(0.65)}$$

$[H_3O^+]$ = x = 2.893665 x 10^{-3} (unrounded)

Check assumption: (2.893665 x 10^{-3} / 0.65) x 100% = 0.4% error, so the assumption is valid.

$[OH^-] = K_w / [H_3O^+]$ = (1.0 x 10^{-14}) / (2.893665 x 10^{-3}) = 3.455825 x 10^{-12} = **3.5 x 10^{-12} *M***

18.75 a) Begin with a reaction table, then use the K_a expression as in earlier problems.

Concentration	$HY(aq)$	+	$H_2O(l)$	$\leftrightarrows$	$H_3O^+(aq)$	+	$Y^-(aq)$
Initial	0.175		—		0		0
Change	–x				+x		+x
Equilibrium	0.175 – x				x		x

(The H_3O^+ contribution from water has been neglected.)

$$K_a = 1.50 \text{ x } 10^{-4} = \frac{\left(H_3O^+\right)\left(Y^-\right)}{\left(HY\right)}$$

$$K_a = 1.50 \text{ x } 10^{-4} = \frac{(x)(x)}{(0.175 - x)}$$ Assume x is small compared to 0.175.

$$K_a = 1.50 \text{ x } 10^{-4} = \frac{(x)(x)}{(0.175)}$$

$[H_3O^+]$ = x = 5.1235 x 10^{-3} (unrounded)

Check assumption: (5.1235 x 10^{-3} / 0.175) x 100% = 3% error, so the assumption is valid.

pH = –log $[H_3O^+]$ = –log (5.1235 x 10^{-3}) = 2.29043 = **2.290**

b) Begin this part like part a.

Concentration	$HX(aq)$	+	$H_2O(l)$	$\leftrightarrows$	$H_3O^+(aq)$	+	$X^-(aq)$
Initial	0.175		—		0		0
Change	–x				+x		+x
Equilibrium	0.175 – x				x		x

(The H_3O^+ contribution from water has been neglected.)

$$K_a = 2.00 \text{ x } 10^{-2} = \frac{\left(H_3O^+\right)\left(X^-\right)}{\left(HX\right)}$$

$$K_a = 2.00 \text{ x } 10^{-2} = \frac{(x)(x)}{(0.175 - x)}$$ Assume x is small compared to 0.175.

$$K_a = 2.00 \text{ x } 10^{-2} = \frac{(x)(x)}{(0.175)}$$

$[H_3O^+]$ = x = 5.9161 x 10^{-2} (unrounded)

Check assumption: (5.9161 x 10^{-2} / 0.175) x 100% = 34% error, so the assumption is not valid.

Since the error is greater than 5%, it is not acceptable to assume x is small compared to 0.175, and it is necessary to use the quadratic equation.

$$K_a = 2.00 \text{ x } 10^{-2} = \frac{(x)(x)}{(0.175 - x)}$$

x^2 = = (2.00 x 10^{-2}) (0.175 – x) = 0.0035 – 2.00 x 10^{-2} x

x^2 + 2.00 x 10^{-2} x – 0.0035 = 0

a = 1 b = 2.00 x 10^{-2} c = –0.0035

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-2.00 \text{ x } 10^{-2} \pm \sqrt{\left(2.00 \text{ x } 10^{-2}\right)^2 - 4(1)(-0.0035)}}{2(1)}$$

$x = 5.00 \text{ x } 10^{-2}\ M\ H_3O^+$

$[OH^-] = K_w / [H_3O^+] = (1.0 \text{ x } 10^{-14}) / (5.00 \text{ x } 10^{-2}) = 2.00 \text{ x } 10^{-13}\ M$

pOH = –log [OH^-] = –log ($2.00 \text{ x } 10^{-13}$) = 12.69897 = **12.699**

18.76 a) Begin with a reaction table, then use the K_a expression as in earlier problems.

Concentration	$HCN(aq)$	+	$H_2O(l)$	⇆	$H_3O^+(aq)$	+	$CN^-(aq)$
Initial	0.55		—		0		0
Change	–x				+x		+x
Equilibrium	0.55 – x				x		x

(The H_3O^+ contribution from water has been neglected.)

$$K_a = 6.2 \text{ x } 10^{-10} = \frac{\left[H_3O^+\right]\left[CN^-\right]}{[HCN]}$$

$$K_a = 6.2 \text{ x } 10^{-10} = \frac{(x)(x)}{(0.55 - x)}$$ Assume x is small compared to 0.55.

$$K_a = 6.2 \text{ x } 10^{-10} = \frac{(x)(x)}{(0.55)}$$

$[H_3O^+] = x = 1.84662 \text{ x } 10^{-5}$ (unrounded)

Check assumption: ($1.84662 \text{ x } 10^{-5} / 0.55$) x 100% = 0.0034% error, so the assumption is valid.

pH = –log [H_3O^+] = –log ($1.84662 \text{ x } 10^{-5}$) = 4.7336 = **4.73**

b) Begin this part like part a.

Concentration	$HIO_3(aq)$	+	$H_2O(l)$	⇆	$H_3O^+(aq)$	+	$IO_3^-(aq)$
Initial	0.044		—		0		0
Change	–x				+x		+x
Equilibrium	0.044 – x				x		x

(The H_3O^+ contribution from water has been neglected.)

$$K_a = 0.16 = \frac{\left[H_3O^+\right]\left[IO_3^-\right]}{\left[HIO_3\right]}$$

$$K_a = 0.16 = \frac{(x)(x)}{(0.044 - x)}$$ Assume x is small compared to 0.044.

$$K_a = 0.16 = \frac{(x)(x)}{(0.044)}$$

$[H_3O^+] = x = 8.3905 \text{ x } 10^{-2}$ (unrounded)

Check assumption: ($8.3905 \text{ x } 10^{-2} / 0.044$) x 100% = 191% error, so the assumption is not valid.

Since the error is greater than 5%, it is not acceptable to assume x is small compared to 0.044, and it is necessary to use the quadratic equation.

$$K_a = 0.16 = \frac{(x)(x)}{(0.044 - x)}$$

$x^2 = = (0.16)\ (0.044 - x) = 0.00704 - 0.16\ x$

$x^2 + 0.16\ x - 0.00704 = 0$

$a = 1 \qquad b = 0.16 \qquad c = -0.00704$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-0.16 \pm \sqrt{(0.16)^2 - 4(1)(-0.00704)}}{2(1)}$$

$x = 0.03593\ M\ H_3O^+$

$[OH^-] = K_w / [H_3O^+] = (1.0 \text{ x } 10^{-14}) / (0.03593) = 2.78 \text{ x } 10^{-13}\ M$

$pOH = -\log [OH^-] = -\log (2.78 \text{ x } 10^{-13}) = 12.55547 = \mathbf{12.56}$

18.77 First, find the concentration of benzoate ion at equilibrium. Then use the initial concentration of benzoic acid and equilibrium concentration of benzoate to find % dissociation.

Concentration	$C_6H_5COOH(aq)$ +	$H_2O(l)$ ⇆	$H_3O^+(aq)$ +	$C_6H_5COO^-(aq)$
Initial	0.55	—	0	0
Change	–x		+x	+x
Equilibrium	0.55 – x		x	x

$$K_a = 6.3 \text{ x } 10^{-5} = \frac{[H_3O^+][C_6H_5COO^-]}{[C_6H_5COOH]}$$

$$K_a = 6.3 \text{ x } 10^{-5} = \frac{[x][x]}{[0.55 - x]}$$ Assume x is small compared to 0.55.

$$K_a = 6.3 \text{ x } 10^{-5} = \frac{[x][x]}{[0.55]}$$

$x = 5.8864 \text{ x } 10^{-3}$ (unrounded)

Check assumption: $(5.8864 \text{ x } 10^{-3} / 0.55) \text{ x } 100\% = 1\%$ error, so the assumption is valid.

$$\text{Percent } C_6H_5COOH \text{ Dissociated} = \frac{\text{Dissociated Acid}}{\text{Initial Acid}} \text{ x } 100\%$$

$$\text{Percent } C_6H_5COOH \text{ Dissociated} = \frac{x}{0.55} \text{ x } 100\% = \frac{5.8864 \text{ x } 10^{-3}}{0.55} \text{ x } 100\% = 1.07025 = \mathbf{1.1\%}$$

18.78 First, find the concentration of acetate ion at equilibrium. Then use the initial concentration of acetic acid and equilibrium concentration of acetate to find % dissociation.

Concentration	$CH_3COOH(aq)$ +	$H_2O(l)$ ⇆	$H_3O^+(aq)$ +	$CH_3COO^-(aq)$
Initial	0.050	—	0	0
Change	–x		+x	+x
Equilibrium	0.050 – x		x	x

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{[x][x]}{[0.050 - x]}$$ Assume x is small compared to 0.050.

$$K_a = 1.8 \text{ x } 10^{-5} = \frac{[x][x]}{[0.050]}$$

$x = 9.48683 \text{ x } 10^{-4}$ (unrounded)

Check assumption: $(9.48683 \text{ x } 10^{-4} / 0.050) \text{ x } 100\% = 2\%$ error, so the assumption is valid.

$$\text{Percent } C_6H_5COOH \text{ Dissociated} = \frac{\text{Dissociated Acid}}{\text{Initial Acid}} \text{ x } 100\%$$

$$\text{Percent } C_6H_5COOH \text{ Dissociated} = \frac{x}{0.050} \times 100\% = \frac{9.48683 \times 10^{-3}}{0.050} \times 100\% = 1.897367 = \mathbf{1.9\%}$$

18.79 Write balanced chemical equations and corresponding equilibrium expressions for dissociation of hydrosulfuric acid (H_2S).

$H_2S(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + HS^-(aq)$ $\qquad$ $HS^-(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + S^{2-}(aq)$

$K_{a1} = 9 \times 10^{-8} = \dfrac{[H_3O^+][HS^-]}{[H_2S]}$ $\qquad$ $K_{a2} = 1 \times 10^{-17} = \dfrac{[H_3O^+][S^{2-}]}{[HS^-]}$

Assumptions:

1) Since $K_{a1} >> K_{a2}$, assume that almost all of the H_3O^+ comes from the first dissociation.

2) Since K_{a1} is so small, assume that the dissociation of H_2S is negligible and $[H_2S]_{eq} = 0.10 - x \approx \mathbf{0.10\ M}$.

Concentration	$H_2S(aq)$ +	$H_2O(l)$	$\leftrightarrows$	$H_3O^+(aq)$ +	$HS^-(aq)$
Initial	0.10	—		0	0
Change	$-x$			$+x$	$+x$
Equilibrium	$0.10 - x$			x	x

$$K_{a1} = 9 \times 10^{-8} = \frac{[H_3O^+][HS^-]}{[H_2S]}$$

$$K_{a1} = 9 \times 10^{-8} = \frac{[x][x]}{[0.10 - x]} \qquad \text{Assume x is small compared to 0.10.}$$

$$K_{a1} = 9 \times 10^{-8} = \frac{[x][x]}{[0.10]}$$

$x = 9.48683 \times 10^{-5}$ (unrounded)

$[H_3O^+] = [HS^-] = x = \mathbf{9 \times 10^{-5}}$ ***M***

$\text{pH} = -\log [H_3O^+] = -\log (9.48683 \times 10^{-5}) = 4.0228787 = \mathbf{4.0}$

$[OH^-] = K_w / [H_3O^+] = (1.0 \times 10^{-14}) / (9.48683 \times 10^{-5}) = 1.05409 \times 10^{-10} = \mathbf{1 \times 10^{-10}}$ ***M***

$\text{pOH} = -\log [OH^-] = -\log (1.05409 \times 10^{-10}) = 9.9771 = \mathbf{10.0}$

$[H_2S] = (0.10 - 9.48683 \times 10^{-5})\ M = 0.099905 = \mathbf{0.10}$ ***M***

Concentration is limited to one significant figure because K_a is given to only one significant figure. The pH is given to what appears to be 2 significant figures because the number before the decimal point (4) represents the exponent and the number after the decimal point represents the significant figures in the concentration.

Calculate $[S^{2-}]$ by using the K_{a2} expression and assuming that $[HS^-]$ and $[H_3O^+]$ come mostly from the first dissociation. This new calculation will have a new x value.

Concentration	$HS^-(aq)$ +	$H_2O(l)$	$\leftrightarrows$	$H_3O^+(aq)$	+	$S^{2-}(aq)$
Initial	9.48683×10^{-5}			9.48683×10^{-5}		0
Change	$-x$			$+x$		$+x$
Equilibrium	$9.48683 \times 10^{-5} - x$			$9.48683 \times 10^{-5} + x$		x

$$K_{a2} = 1 \times 10^{-17} = \frac{[H_3O^+][S^{2-}]}{[HS^-]}$$

$$K_{a2} = 1 \times 10^{-17} = \frac{(9.48683 \times 10^{-5} + x)(x)}{(9.48683 \times 10^{-5} - x)}$$

$$K_{a2} = 1 \times 10^{-17} = \frac{(9.48683 \times 10^{-5})(x)}{(9.48683 \times 10^{-5})} \qquad \text{Assume x is small compared to } 9.48683 \times 10^{-5}.$$

$x = [S^{2-}] = \mathbf{1 \times 10^{-17}}$ ***M***

The small value of x means that it is not necessary to recalculate the $[H_3O^+]$ and $[HS^-]$ values.

18.80 Write balanced chemical equations and corresponding equilibrium expressions for dissociation of oxalic acid ($H_2C_2O_4$).

$H_2C_2O_4(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + HC_2O_4^-(aq)$ $HC_2O_4^-(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + C_2O_4^{2-}(aq)$

$K_{a1} = 5.6 \times 10^{-2} = \frac{(H_3O^+)(HC_2O_4^-)}{(H_2C_2O_4)}$ $K_{a2} = 5.4 \times 10^{-5} = \frac{(H_3O^+)(C_2O_4^{2-})}{(HC_2O_4^-)}$

Assumptions:

1) Since $K_{a1} >> K_{a2}$, assume that almost all of the H_3O^+ comes from the first dissociation.

2) Since K_{a1} is so small, assume that the dissociation of $H_2C_2O_4$ is negligible and $[H_2C_2O_4]_{eq} = 0.200 - x \approx 0.200$.

$H_2C_2O_4(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + HC_2O_4^-(aq)$

0.200 – x x x

$$K_{a1} = 5.6 \times 10^{-2} = \frac{(H_3O^+)(HC_2O_4^-)}{(H_2C_2O_4)}$$

$$K_{a1} = 5.6 \times 10^{-2} = \frac{(x)(x)}{(0.200 - x)}$$

The relatively large K_{a1} value means a quadratic will need to be done.

$x^2 = K_a(0.200 - x) = (5.6 \times 10^{-2})(0.200 - x) = 1.12 \times 10^{-2} - 5.6 \times 10^{-2}\,x$

$x^2 + 5.6 \times 10^{-2}\,x - 1.12 \times 10^{-2} = 0$

$a = 1 \quad b = 5.6 \times 10^{-2} \quad c = -1.12 \times 10^{-2}$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-5.6 \times 10^{-2} \pm \sqrt{(5.6 \times 10^{-2})^2 - 4(1)(-1.12 \times 10^{-2})}}{2(1)}$$

$x = 8.1471 \times 10^{-2}$ (unrounded)

$[H_3O^+] = [HC_2O_4^-] = x =$ **8.1×10^{-2} *M***

$pH = -\log[H_3O^+] = -\log(8.1471 \times 10^{-2}) = 1.08899 =$ **1.09**

$[OH^-] = K_w / [H_3O^+] = (1.0 \times 10^{-14}) / (8.1471 \times 10^{-2}) = 1.22743 \times 10^{-13} =$ **1.2×10^{-13} *M***

$pOH = -\log[OH^-] = -\log(1.22743 \times 10^{-13}) = 12.9110 =$ **12.91**

$[H_2S] = (0.200 - 8.1471 \times 10^{-2})\,M = 0.118529 =$ **0.12 *M***

Concentration is limited to two significant figures because K_a is given to only two significant figures. The pH is given to what appears to be 3 significant figures because the number before the decimal point (1) represents the exponent and the number after the decimal point represents the significant figures in the concentration.

Calculate $[C_2O_4^{2-}]$ by using the K_{a2} expression and assuming that $[HC_2O_4^-]$ and $[H_3O^+]$ come mostly from the first dissociation. This new calculation will have a new x value.

$HC_2O_4^-(aq)$	+	$H_2O(l)$ $\leftrightarrows$	$H_3O^+(aq)$	+	$C_2O_4^{2-}(aq)$
$8.1471 \times 10^{-2} - x$			$8.1471 \times 10^{-2} + x$		x

$$K_{a2} = 5.4 \times 10^{-5} = \frac{(H_3O^+)(C_2O_4^{2-})}{(HC_2O_4^-)}$$

$$K_{a2} = 5.4 \times 10^{-5} = \frac{(8.1471 \times 10^{-2} + x)(x)}{(8.1471 \times 10^{-2} - x)}$$

$$K_{a2} = 5.4 \times 10^{-5} = \frac{(8.1471 \times 10^{-2})(x)}{(8.1471 \times 10^{-2})}$$

Assume x is small compared to 8.1471×10^{-2}.

$x = [C_2O_4^{2-}] = 5.4 \times 10^{-5} =$ **5.4×10^{-5} *M***

18.81 Write balanced chemical equations and corresponding equilibrium expressions for dissociation of aspirin ($HC_9H_7O_4$).

$HC_9H_7O_4(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + C_9H_7O_4^-(aq)$

$0.018 - x \qquad\qquad x \qquad\qquad x$

$$K_a = 3.6 \text{ x } 10^{-4} = \frac{[H_3O^+][C_9H_7O_4^-]}{[HC_9H_7O_4]}$$

$$K_a = 3.6 \text{ x } 10^{-4} = \frac{(x)(x)}{(0.018 - x)}$$ Assume x is small compared to 0.018.

$$K_a = 3.6 \text{ x } 10^{-4} = \frac{(x)(x)}{(0.018)}$$

$[H_3O^+] = x = 2.54558 \text{ x } 10^{-3}$ (unrounded)

Check assumption: $(2.54558 \text{ x } 10^{-3} / 0.018) \text{ x } 100\% = 14\%$ error, so the assumption is not valid.

Since the error is greater than 5%, it is not acceptable to assume x is small compared to 0.045, and it is necessary to use the quadratic equation.

$x^2 = (3.6 \text{ x } 10^{-4})(0.018 - x) = 6.48 \text{ x } 10^{-6} - 3.6 \text{ x } 10^{-4} x$

$x^2 + 3.6 \text{ x } 10^{-4} x - 6.48 \text{ x } 10^{-6} = 0$

$a = 1 \qquad b = 3.6 \text{ x } 10^{-4} \qquad c = -6.48 \text{ x } 10^{-6}$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-3.6 \text{ x } 10^{-4} \pm \sqrt{(3.6 \text{ x } 10^{-4})^2 - 4(1)(-6.48 \text{ x } 10^{-6})}}{2(1)}$$

$x = 2.37194 \text{ x } 10^{-3}\ M\ H_3O^+$

$pH = -\log [H_3O^+] = -\log (2.37194 \text{ x } 10^{-3}) = 2.624896 = \mathbf{2.62}$

18.82 First, find the concentration of formate ion at equilibrium. Then use the initial concentration of formic acid and equilibrium concentration of formate to find% dissociation.

Concentration	$HCOOH(aq)$	$+\ H_2O(l)$	$\leftrightarrows H_3O^+(aq)$	$+\ HCOO^-(aq)$
Initial	0.75		0	0
Change	$-x$		$+x$	$+x$
Equilibrium	$0.75 - x$		x	x

$$K_a = 1.8 \text{ x } 10^{-4} = \frac{[H_3O^+][HCOO^-]}{[HCOOH]}$$

$$K_a = 1.8 \text{ x } 10^{-4} = \frac{(x)(x)}{(0.75 - x)}$$ Assume x is small compared to 0.75.

$$K_a = 1.8 \text{ x } 10^{-4} = \frac{(x)(x)}{(0.75)}$$

$x = 1.161895 \text{ x } 10^{-2}$ (unrounded)

Check assumption: $(1.161895 \text{ x } 10^{-2} / 0.75) \text{ x } 100\% = 2\%$ error, so the assumption is valid.

$$\text{Percent HCOOH Dissociated} = \frac{\text{Dissociated Acid}}{\text{Initial Acid}} \text{ x } 100\%$$

$$\text{Percent HCOOH Dissociated} = \frac{x}{0.75} \text{ x } 100\% = \frac{1.161895 \text{ x } 10^{-2}}{0.75} \text{ x } 100\% = 1.54919 = \mathbf{1.5\%}$$

18.83 All Brønsted-Lowry bases contain at least one lone pair of electrons. This lone pair binds with an H^+ and allows the base to act as a proton-acceptor.

18.84 The negative charge and lone pair of the anion in many cases is able to abstract a proton from water forming OH^- ions. Non-basic anions are from strong acids and include I^-, NO_3^-, Cl^-, ClO_4^-.

18.85 a) The species present are: **$CH_3COOH(aq)$, $CH_3COO^-(aq)$, $H_3O^+(aq)$, and $OH^-(aq)$.**

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

The solution is acidic because H_3O^+ ions are formed.

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

The solution is basic because OH^- ions are formed.

18.86 a) A base accepts a proton from water in the base dissociation reaction:

$C_5H_5N(aq) + H_2O(l) \leftrightarrows OH^-(aq) + C_5H_5NH^+(aq)$

$$K_b = \frac{\left[C_5H_5NH^+\right]\left[OH^-\right]}{\left[C_5H_5N\right]}$$

b) The primary reaction is involved in base dissociation of carbonate ion is:

$CO_3^{2-}(aq) + H_2O(l) \leftrightarrows OH^-(aq) + HCO_3^-(aq)$

$$K_b = \frac{\left[HCO_3^-\right]\left[OH^-\right]}{\left[CO_3^{2-}\right]}$$

The bicarbonate can then also dissociate as a base, but this occurs to an insignificant amount in a solution of carbonate ions.

18.87 a) $C_6H_5COO^-(aq) + H_2O(l) \leftrightarrows OH^-(aq) + C_6H_5COOH(aq)$

$$K_b = \frac{\left[C_6H_5COOH\right]\left[OH^-\right]}{\left[C_6H_5COO^-\right]}$$

b) $(CH_3)_3N(aq) + H_2O(l) \leftrightarrows OH^-(aq) + (CH_3)_3NH^+(aq)$

$$K_b = \frac{\left[(CH_3)_3NH^+\right]\left[OH^-\right]}{\left[(CH_3)_3N\right]}$$

18.88 a) Hydroxylamine has a lone pair of electrons on the nitrogen atom that acts like the Lewis base:

$HONH_2(aq) + H_2O(l) \leftrightarrows OH^-(aq) + HONH_3^+(aq)$

$$K_b = \frac{\left[HONH_3^+\right]\left[OH^-\right]}{\left[HONH_2\right]}$$

b) The hydrogen phosphate ion contains oxygen atoms with lone pairs of electrons that act as proton acceptors.

$HPO_4^{2-}(aq) + H_2O(l) \leftrightarrows H_2PO_4^-aq) + OH^-(aq)$

$$K_b = \frac{\left[H_2PO_4^-\right]\left[OH^-\right]}{\left[HPO_4^{2-}\right]}$$

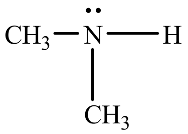
18.89 a) $(NH_2)_2C{=}NH(aq) + H_2O(l) \leftrightarrows OH^-(aq) + (NH_2)_2C{=}NH_2^+(aq)$

$$K_b = \frac{\left[(H_2N)_2C = NH_2^+\right]\left[OH^-\right]}{\left[(H_2N)_2C = NH\right]}$$

b) $HCC^-(aq) + H_2O(l) \leftrightarrows OH^-(aq) + HCCH(aq)$

$$K_b = \frac{\left[HC \equiv CH\right]\left[OH^-\right]}{\left[HC \equiv C^-\right]}$$

18.90 The formula of dimethylamine has two methyl (CH_3–) groups attached to a nitrogen:



$$\begin{array}{l} CH_3-\ddot{N}-H \\ \quad\ \ | \\ \quad CH_3 \end{array}$$

The nitrogen has a lone pair of electrons that will accept the proton from water in the base dissociation reaction:
The value for the dissociation constant is from Appendix C.

Concentration	$(CH_3)_2NH(aq)$	$+ H_2O(l) \rightleftarrows$	$OH^-(aq)$	$+ (CH_3)_2NH_2^+(aq)$
Initial	0.070		0	0
Change	–x		+x	+x
Equilibrium	0.070 – x		x	x

$$K_b = \frac{\left[(CH_3)_2NH_2^+\right]\left[OH^-\right]}{\left[(CH_3)_2NH\right]} = 5.9 \text{ x } 10^{-4}$$

$$K_b = \frac{[x][x]}{[0.070 - x]} = 5.9 \text{ x } 10^{-4}$$ Assume 0.070 – x =0.070

$$\frac{[x][x]}{[0.070]} = 5.9 \text{ x } 10^{-4}$$

$x = 6.4265 \text{ x } 10^{-3}\ M$

Check assumption: $(6.4265 \text{ x } 10^{-3} / 0.070) \text{ x } 100\% = 9\%$ error, so the assumption is invalid.
The problem will need to be solved as a quadratic.

$$\frac{[x][x]}{[0.070 - x]} = 5.9 \text{ x } 10^{-4}$$

$x^2 = (5.9 \text{ x } 10^{-4})(0.070 - x) = 4.13 \text{ x } 10^{-5} - 5.9 \text{ x } 10^{-4}\ x$

$x^2 + 5.9 \text{ x } 10^{-4}\ x - 4.13 \text{ x } 10^{-5} = 0$

$a = 1 \quad b = 5.9 \text{ x } 10^{-4} \quad c = -4.13 \text{ x } 10^{-5}$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-5.9 \text{ x } 10^{-4} \pm \sqrt{\left(5.9 \text{ x } 10^{-4}\right)^2 - 4(1)\left(-4.13 \text{ x } 10^{-5}\right)}}{2(1)} = 6.13827 \text{ x } 10^{-3}\ M\ OH^- \text{ (unrounded)}$$

$$[H_3O]^+ = \frac{K_w}{\left[OH^-\right]} = \frac{1.0 \text{ x } 10^{-14}}{6.13827 \text{ x } 10^{-3}} = 1.629124 \text{ x } 10^{-12}\ M\ H_3O^+ \text{ (unrounded)}$$

pH = $-\log [H_3O^+] = -\log (1.629124 \text{ x } 10^{-12}) = 11.7880 =$ **11.79**

18.91 $(CH_3CH_2)_2NH(aq) + H_2O(l) \rightleftarrows OH^-(aq) + (CH_3CH_2)_2NH_2^+(aq)$
0.12 – x x x

$$K_b = \frac{\left[(CH_3CH_2)_2NH_2^+\right]\left[OH^-\right]}{\left[(CH_3CH_2)_2NH\right]} = 8.6 \text{ x } 10^{-4}$$

$$K_b = \frac{[x][x]}{[0.12 - x]} = 8.6 \text{ x } 10^{-4}$$

The problem will need to be solved as a quadratic.

$x^2 = (8.6 \text{ x } 10^{-4})(0.12 - x) = 1.032 \text{ x } 10^{-4} - 8.6 \text{ x } 10^{-4}\ x$

$x^2 + 8.6 \text{ x } 10^{-4}\ x - 1.032 \text{ x } 10^{-4} = 0$

$a = 1 \quad b = 8.6 \text{ x } 10^{-4} \quad c = -1.032 \text{ x } 10^{-4}$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-8.6 \text{ x } 10^{-4} \pm \sqrt{\left(8.6 \text{ x } 10^{-4}\right)^2 - 4(1)\left(-1.032 \text{ x } 10^{-4}\right)}}{2(1)}$$

$x = 9.7378 \text{ x } 10^{-3}$ M OH^- (unrounded)
$[H_3O]^+ = K_w / [OH^-] = (1.0 \text{ x } 10^{-14}) / (9.7378 \text{ x } 10^{-3}) = 1.02692 \text{ x } 10^{-12}$ M H_3O^+ (unrounded)
pH = $-\log [H_3O^+] = -\log (1.02692 \text{ x } 10^{-12}) = 11.98846 =$ **11.99**

18.92 Write a balanced equation and equilibrium expression for the reaction. Make simplifying assumptions (if valid), solve for $[OH^-]$, convert to $[H_3O^+]$ and calculate pH.

Concentration	$HOCH_2CH_2NH_2(aq) + H_2O(l) \leftrightarrows$	$OH^-(aq)$ +	$HOCH_2CH_2NH_3^+(aq)$
Initial	0.25	0	0
Change	–x	+x	+x
Equilibrium	0.25 – x	x	x

$$K_b = \frac{\left[HOCH_2CH_2NH_3^+\right]\left[OH^-\right]}{\left[HOCH_2CH_2NH_2\right]} = 3.2 \text{ x } 10^{-5}$$

$$K_b = \frac{[x][x]}{[0.25 - x]} = 3.2 \text{ x } 10^{-5}$$ Assume x is small compared to 0.25.

$$K_b = 3.2 \text{ x } 10^{-5} = \frac{(x)(x)}{(0.25)}$$

$x = 2.8284 \text{ x } 10^{-3}$ M OH^- (unrounded)
Check assumption: $(2.8284 \text{ x } 10^{-3} / 0.25) \text{ x } 100\% = 1\%$ error, so the assumption is valid.
$[H_3O]^+ = K_w / [OH^-] = (1.0 \text{ x } 10^{-14}) / (2.8284 \text{ x } 10^{-3}) = 3.535568 \text{ x } 10^{-12}$ M H_3O^+ (unrounded)
pH = $-\log [H_3O^+] = -\log (3.535568 \text{ x } 10^{-12}) = 11.4515 =$ **11.45**

18.93 $C_6H_5NH_2(aq) + H_2O(l) \leftrightarrows OH^-(aq) + C_6H_5NH_3^+(aq)$
0.26 – x x x

$$K_b = \frac{\left[C_6H_5NH_3^+\right]\left[OH^-\right]}{\left[C_6H_5NH_2\right]} = 4.0 \text{ x } 10^{-10}$$

$$K_b = \frac{[x][x]}{[0.26 - x]} = 4.0 \text{ x } 10^{-10}$$ Assume x is small compared to 0.26.

$$K_b = 4.0 \text{ x } 10^{-10} = \frac{(x)(x)}{(0.26)}$$

$x = 1.01980 \text{ x } 10^{-5}$ M OH^- (unrounded)
Check assumption: $(1.01980 \text{ x } 10^{-5} / 0.26) \text{ x } 100\% = 0.004\%$ error, so the assumption is valid.
$[H_3O]^+ = K_w / [OH^-] = (1.0 \text{ x } 10^{-14}) / (1.01980 \text{ x } 10^{-5}) = 9.80584 \text{ x } 10^{-10}$ M H_3O^+ (unrounded)
pH = $-\log [H_3O^+] = -\log (9.80584 \text{ x } 10^{-10}) = 9.008515 =$ **9.01**

18.94 a) Acetate ion, CH_3COO^-, is the conjugate base of acetic acid, CH_3COOH. The K_b for acetate ion is related to the K_a for acetic acid through the equation $K_w = K_a \text{ x } K_b$.
K_b of $CH_3COO^- = K_w / K_a = (1.0 \text{ x } 10^{-14}) / (1.8 \text{ x } 10^{-5}) = 5.55556 \text{ x } 10^{-10} =$ **$5.6 \text{ x } 10^{-10}$**
b) Anilinium ion is the conjugate acid of aniline so the K_a for anilinium ion is related to the K_b of aniline by the relationship $K_w = K_a \text{ x } K_b$.
K_a of $C_6H_5NH_3^+ = K_w / K_b = (1.0 \text{ x } 10^{-14}) / (4.0 \text{ x } 10^{-10}) =$ **$2.5 \text{ x } 10^{-5}$**

18.95 a) Benzoate ion, $C_6H_5COO^-$, is the conjugate base of benzoic acid, C_6H_5COOH. The K_b for benzoate ion is related to the K_a for benzoic acid through the equation $K_w = K_a \text{ x } K_b$.

K_b of $C_6H_5COO^- = K_w / K_a = (1.0 \text{ x } 10^{-14}) / (6.3 \text{ x } 10^{-5}) = 1.58730 \text{ x } 10^{-10} = \mathbf{1.6 \text{ x } 10^{-10}}$

b) The 2-hydroxyethylammonium ion is the conjugate acid of 2-hydroxyethylamine so the pK_a for 2–hydroxyethylammonium ion is related to the pK_b of 2-hydroxyethylamine by the relationship 14.00 = pK_a + pK_b. The K_a may be calculated from the pK_a.

$14.00 = pK_a + pK_b$

$14.00 = pK_a + 4.49$

$pK_a = 14.00 - 4.49 = 9.51$

$K_a = 10^{-pKa} = 10^{-9.51} = 3.090295 \text{ x } 10^{-12} = \mathbf{3.1 \text{ x } 10^{-10}}$

18.96 a) The K_a of chlorous acid, $HClO_2$, is reported in the Appendix. $HClO_2$ is the conjugate acid of chlorite ion, ClO_2^-
. The K_b for chlorite ion is related to the K_a for chlorous acid through the equation $K_w = K_a \text{ x } K_b$, and pK_b = –log K_b.

$$K_b \text{ of } ClO_2^- = \frac{K_w}{K_a} = \frac{1.0 \text{ x } 10^{-14}}{1.1 \text{ x } 10^{-2}} = 9.0909 \text{ x } 10^{-13} \text{ (unrounded)}$$

$pK_b = -\log (9.0909 \text{ x } 10^{-13}) = 12.04139 = \mathbf{12.04}$

b) The K_b of dimethylamine, $(CH_3)_2NH$, is reported in the Appendix . $(CH_3)_2NH$ is the conjugate base of $(CH_3)_2NH_2^+$. The K_a for $(CH_3)_2NH_2^+$ is related to the K_b for $(CH_3)_2NH$ through the equation $K_w = K_a \text{ x } K_b$, and pK_a = –log K_a.

$$K_a \text{ of } (CH_3)_2NH_2^+ = \frac{K_w}{K_b} = \frac{1.0 \text{ x } 10^{-14}}{5.9 \text{ x } 10^{-4}} = 1.694915 \text{ x } 10^{-11} \text{ (unrounded)}$$

$pK_a = -\log (1.694915 \text{ x } 10^{-11}) = 10.77085 = \mathbf{10.77}$

18.97 a) The K_a of nitrous acid, HNO_2, is reported in Appendix C. HNO_2 is the conjugate acid of nitrite ion, NO_2^-. The K_b for nitrite ion is related to the K_a for nitrous acid through the equation $K_w = K_a \text{ x } K_b$, and pK_b = –log K_b.

$$K_b \text{ of } NO_2^- = \frac{K_w}{K_a} = \frac{1.0 \text{ x } 10^{-14}}{7.1 \text{ x } 10^{-4}} = 1.4084507 \text{ x } 10^{-11} \text{ (unrounded)}$$

$pK_b = -\log (1.4084507 \text{ x } 10^{-11}) = 10.851258 = \mathbf{10.85}$

b) The K_b of hydrazine, H_2NNH_2, is reported in the problem. Hydrazine is the conjugate base of $H_2N\text{–}NH_3^+$. The K_a for $H_2N\text{–}NH_3^+$ is related to the K_b for H_2NNH_2 through the equation $K_w = K_a \text{ x } K_b$, and pK_a = –log K_a.

$$K_a \text{ of } H_2N\text{–}NH_3^+ = \frac{K_w}{K_b} = \frac{1.0 \text{ x } 10^{-14}}{8.5 \text{ x } 10^{-7}} = 1.17647 \text{ x } 10^{-8} \text{ (unrounded)}$$

$pK_a = -\log (1.17647 \text{ x } 10^{-8}) = 7.9294 = \mathbf{7.93}$

18.98 a) Potassium cyanide, when placed in water, dissociates into potassium ions, K^+, and cyanide ions, CN^-. Potassium ion is the conjugate acid of a strong base, KOH, so K^+ does not react with water. Cyanide ion is the conjugate base of a weak acid, HCN, so it does react with the base dissociation reaction:

$$CN^-(aq) + H_2O(l) \leftrightarrows HCN(aq) + OH^-(aq)$$

To find the pH first set up a reaction table and use K_b for CN^- to calculate $[OH^-]$.

Concentration (M)	$CN^-(aq)$ +	$H_2O(l)$ ⇆	$HCN(aq)$ +	$OH^-(aq)$
Initial	0.150	—	0	0
Change	–x	—	+x	+x
Equilibrium	0.150 – x	—	x	x

$$K_b \text{ of } CN^- = \frac{K_w}{K_a} = \frac{1.0 \text{ x } 10^{-14}}{6.2 \text{ x } 10^{-10}} = 1.612903 \text{ x } 10^{-5} \text{ (unrounded)}$$

$$K_b = \frac{[HCN][OH^-]}{[CN^-]} = 1.612903 \text{ x } 10^{-5}$$

$$K_b = \frac{[x][x]}{[0.150 - x]} = 1.612903 \text{ x } 10^{-5}$$ Assume x is small compared to 0.150: 0.150 – x = 0.150.

$$K_b = 1.612903 \text{ x } 10^{-5} = \frac{(x)(x)}{(0.150)}$$

$x = 1.555 \text{ x } 10^{-3}$ *M* OH^- (unrounded)

Check assumption: $(1.555 \text{ x } 10^{-3} / 0.150) \text{ x } 100\% = 1\%$ error, so the assumption is valid.

$$[H_3O]^+ = \frac{K_w}{OH^-} = \frac{1.0 \text{ x } 10^{-14}}{1.555 \text{ x } 10^{-3}} = 6.430868 \text{ x } 10^{-12}\ M\ H_3O^+ \text{ (unrounded)}$$

pH = $-\log [H_3O^+] = -\log (6.430868 \text{ x } 10^{-12}) = 11.19173 =$ **11.19**

b) The salt triethylammonium chloride in water dissociates into two ions: $(CH_3CH_2)_3NH^+$ and Cl^-. Chloride ion is the conjugate base of a strong acid so it will not influence the pH of the solution. Triethylammonium ion is the conjugate acid of a weak base, so the acid dissociation reaction below determines the pH of the solution.

Concentration (*M*)	$(CH_3CH_2)_3NH^+(aq)$	$+ H_2O(l)$	$\rightleftarrows$	$(CH_3CH_2)_3N(aq)$	$+ H_3O^+(aq)$
Initial	0.40	—		0	0
Change	–x	—		+x	+x
Equilibrium	0.40 – x	—		x	x

$$K_a \text{ of } (CH_3CH_2)_3NH^+ = \frac{K_w}{K_b} = \frac{1.0 \text{ x } 10^{-14}}{5.2 \text{ x } 10^{-4}} = 1.9230769 \text{ x } 10^{-11} \text{ (unrounded)}$$

$$K_a = 1.9230769 \text{ x } 10^{-11} = \frac{\left[H_3O^+\right]\left[(CH_3CH_2)_3N\right]}{\left[(CH_3CH_2)_3NH^+\right]}$$

$$K_a = 1.9230769 \text{ x } 10^{-11} = \frac{(x)(x)}{(0.40 - x)}$$

Assume x is small compared to 0.40: 0.40 – x = 0.40.

$$K_a = 1.9230769 \text{ x } 10^{-11} = \frac{(x)(x)}{(0.40)}$$

$[H_3O^+] = x = 2.7735 \text{ x } 10^{-6}$ (unrounded)

Check assumption: $(2.7735 \text{ x } 10^{-6} / 0.40) \text{ x } 100\% = 0.0007\%$ error, so the assumption is valid.

pH = $-\log [H_3O^+] = -\log (2.7735 \text{ x } 10^{-6}) = 5.55697 =$ **5.56**

18.99 a) Sodium phenolate, when placed in water, dissociates into sodium ions, Na^+, and phenolate ions, $C_6H_5O^-$. Sodium ion is the conjugate acid of a strong base, NaOH, so Na^+ does not react with water. Phenolate ion is the conjugate base of a weak acid, C_6H_5OH, so it does react with the base dissociation reaction:

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

To find the pH first set up a reaction table and use K_b for $C_6H_5O^-$ to calculate $[OH^-]$.

Concentration (*M*)	$C_6H_5O^-(aq)$	+	$H_2O(l)$	$\rightleftarrows$	$C_6H_5OH(aq)$	+	$OH^-(aq)$
Initial	0.100		—		0		0
Change	–x		—		+x		+x
Equilibrium	0.100 – x		—		x		x

K_b of $C_6H_5O^- = K_w / K_a = (1.0 \text{ x } 10^{-14}) / (1.0 \text{ x } 10^{-10}) = 1.0 \text{ x } 10^{-4}$

$$K_b = \frac{\left[C_6H_5OH\right]\left[OH^-\right]}{\left[C_6H_5O^-\right]} = 1.0 \text{ x } 10^{-4}$$

$$K_b = \frac{[x][x]}{[0.100 - x]} = 1.0 \text{ x } 10^{-4}$$

Assume x is small compared to 0.100.

$$K_b = 1.0 \text{ x } 10^{-4} = \frac{(x)(x)}{(0.100)}$$

$x = 3.16227766 \text{ x } 10^{-3}$ *M* OH^- (unrounded)

Check assumption: $(3.16227766 \text{ x } 10^{-3} / 0.100) \text{ x } 100\% = 3\%$ error, so the assumption is valid.

$[H_3O]^+ = K_w / [OH^-] = (1.0 \text{ x } 10^{-14}) / (3.16227766 \text{ x } 10^{-3}) = 3.16227766 \text{ x } 10^{-12}\ M\ H_3O^+$ (unrounded)

pH = $-\log [H_3O^+] = -\log (3.16227766 \text{ x } 10^{-12}) =$ **11.50**

b) The salt methylammonium bromide in water dissociates into two ions: $CH_3NH_3^+$ and Br^-. Bromide ion is the conjugate base of a strong acid so it will not influence the pH of the solution. Methylammonium ion is the conjugate acid of a weak base, so the acid dissociation reaction below determines the pH of the solution.

Concentration (M)	$CH_3NH_3^+(aq)$	+	$H_2O(l)$	$\leftrightarrows$	$CH_3NH_2(aq)$	+	$H_3O^+(aq)$
Initial	0.15		—		0		0
Change	–x		—		+x		+x
Equilibrium	0.15 – x		—		x		x

K_a of $CH_3NH_3^+ = K_w / K_b = (1.0 \times 10^{-14}) / (4.4 \times 10^{-4}) = 2.272727 \times 10^{-11}$ (unrounded)

$$K_a = 2.272727 \times 10^{-11} = \frac{[H_3O^+][CH_3NH_2]}{[CH_3NH_3^+]}$$

$$K_a = 2.272727 \times 10^{-11} = \frac{(x)(x)}{(0.15 - x)}$$ Assume x is small compared to 0.15.

$$K_a = 2.272727 \times 10^{-11} = \frac{(x)(x)}{(0.15)}$$

$[H_3O^+] = x = 1.84637 \times 10^{-6}$ (unrounded)

Check assumption: $(1.84637 \times 10^{-6} / 0.15) \times 100\% = 0.001\%$ error, so the assumption is valid.

pH = $-\log [H_3O^+] = -\log (1.84637 \times 10^{-6}) = 5.73368 =$ **5.73**

18.100 a) The formate ion, $HCOO^-$, acts as the base shown by the following equation:

$$HCOO^-(aq) + H_2O(l) \leftrightarrows HCOOH(aq) + OH^-(aq)$$

Because HCOOK is a soluble salt, $[HCOO^-] = [HCOOK]$. The potassium ion is from a strong base; therefore, it will not affect the pH, and can be ignored.

Concentration (M)	$HCOO^-(aq)$	+	$H_2O(l)$	$\leftrightarrows$	$HCOOH(aq)$	+	$OH^-(aq)$
Initial	0.65		—		0		0
Change	–x		—		+x		+x
Equilibrium	0.65 – x		—		x		x

K_b of $HCOO^- = K_w / K_a = (1.0 \times 10^{-14}) / (1.8 \times 10^{-4}) = 5.55556 \times 10^{-11}$

$$K_b = \frac{[HCOOH][OH^-]}{[HCOO^-]} = 5.55556 \times 10^{-11}$$

$$K_b = \frac{[x][x]}{[0.65 - x]} = 5.55556 \times 10^{-11}$$ Assume x is small compared to 0.65.

$$K_b = 5.55556 \times 10^{-11} = \frac{(x)(x)}{(0.65)} = 6.00925 \times 10^{-6}\ M\ OH^-$$ (unrounded)

Check assumption: $(6.00925 \times 10^{-6} / 0.65) \times 100\% = 0.0009\%$ error, so the assumption is valid.

$[H_3O]^+ = K_w / [OH^-] = (1.0 \times 10^{-14}) / (6.00925 \times 10^{-6}) = 1.66410 \times 10^{-9}\ M\ H_3O^+$ (unrounded)

pH = $-\log [H_3O^+] = -\log (1.66410 \times 10^{-9}) = 8.7788 =$ **8.78**

b) The ammonium ion, NH_4^+, acts as an acid shown by the following equation:

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

Because NH_4Br is a soluble salt, $[NH_4^+] = [NH_4Br]$. The bromide ion is from a strong acid; therefore, it will not affect the pH, and can be ignored.

Concentration (M)	$NH_4^+(aq)$	+	$H_2O(l)$	$\leftrightarrows$	$NH_3(aq)$	+	$H_3O^+(aq)$
Initial	0.85		—		0		0
Change	–x		—		+x		+x
Equilibrium	0.85 – x		—		x		x

K_a of $NH_4^+ = K_w / K_b = (1.0 \times 10^{-14}) / (1.76 \times 10^{-5}) = 5.681818 \times 10^{-10}$ (unrounded)

$$K_a = 5.681818 \times 10^{-10} = \frac{[H_3O^+][NH_3]}{[NH_4^+]}$$

$K_a = 5.681818 \times 10^{-10} = \dfrac{[x][x]}{[0.85 - x]}$ Assume x is small compared to 0.85.

$K_a = 5.681818 \times 10^{-10} = \dfrac{[x][x]}{[0.85]}$

$[H_3O^+] = x = 2.1976 \times 10^{-5}$ (unrounded)

Check assumption: $(2.1976 \times 10^{-5} / 0.85) \times 100\% = 0.003\%$ error, so the assumption is valid.

$pH = -\log [H_3O^+] = -\log (2.1976 \times 10^{-5}) = 4.65805 =$ **4.66**

18.101 The fluoride ion, F^-, acts as the base as shown by the following equation:

$$F^-(aq) + H_2O(l) \rightleftarrows HF(aq) + OH^-(aq)$$

Because NaF is a soluble salt, $[F^-] = [NaF]$. The sodium ion is from a strong base; therefore, it will not affect the pH, and can be ignored.

Concentration (M)	$F^-(aq)$	+	$H_2O(l)$	$\rightleftarrows$	$HF(aq)$	+	$OH^-(aq)$
Initial	0.53		—		0		0
Change	–x		—		+x		+x
Equilibrium	0.53 – x		—		x		x

K_b of $F^- = K_w / K_a = (1.0 \times 10^{-14}) / (6.8 \times 10^{-4}) = 1.470588 \times 10^{-11}$

$K_b = \dfrac{[HF][OH^-]}{[F^-]} = 1.470588 \times 10^{-11}$

$K_b = \dfrac{[x][x]}{[0.75 - x]} = 1.470588 \times 10^{-11}$ Assume x is small compared to 0.75.

$K_b = 1.470588 \times 10^{-11} = \dfrac{(x)(x)}{(0.75)}$

$x = 3.3210558 \times 10^{-6}\ M\ OH^-$ (unrounded)

Check assumption: $(3.3210558 \times 10^{-6} / 0.75) \times 100\% = 0.0004\%$ error, so the assumption is valid.

$[H_3O]^+ = K_w / [OH^-] = (1.0 \times 10^{-14}) / (3.3210558 \times 10^{-6}) = 3.01109 \times 10^{-9}\ M\ H_3O^+$ (unrounded)

$pH = -\log [H_3O^+] = -\log (3.01109 \times 10^{-9}) = 8.521276 =$ **8.52**

b) The pyridinium ion, $C_5H_5NH^+$, acts as an acid shown by the following equation:

$$C_5H_5NH^+(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + C_5H_5N(aq)$$

Because C_5H_5NHCl is a soluble salt, $[C_5H_5NH^+] = [C_5H_5NHCl]$. The chloride ion is from a strong acid; therefore, it will not affect the pH, and can be ignored.

Concentration (M)	$C_5H_5NH^+(aq)$	+	$H_2O(l)$	$\rightleftarrows$	$C_5H_5NH(aq)$	+	$H_3O^+(aq)$
Initial	0.88		—		0		0
Change	–x		—		+x		+x
Equilibrium	0.88 – x		—		x		x

K_a of $NH_4^+ = K_w / K_b = (1.0 \times 10^{-14}) / (1.7 \times 10^{-9}) = 5.88235 \times 10^{-6}$ (unrounded)

$K_a = 5.88235 \times 10^{-6} = \dfrac{[H_3O^+][C_5H_5N]}{[C_5H_5NH^+]}$

$K_a = 5.88235 \times 10^{-6} = \dfrac{[x][x]}{[0.88 - x]}$ Assume x is small compared to 0.88.

$K_a = 5.88235 \times 10^{-6} = \dfrac{(x)(x)}{(0.88)}$

$[H_3O^+] = x = 2.275185 \times 10^{-3}$ (unrounded)

Check assumption: $(2.275185 \times 10^{-3} / 0.88) \times 100\% = 0.3\%$ error, so the assumption is valid.

$pH = -\log [H_3O^+] = -\log (2.275185 \times 10^{-3}) = 2.64298 =$ **2.64**

18.102 First, calculate the initial molarity of ClO^-. Then, set up reaction table with base dissociation of OCl^-:

$$[ClO^-] = \left(\frac{1\ \text{mL Solution}}{10^{-3}\ \text{L Solution}}\right)\left(\frac{1.0\ \text{g Solution}}{1\ \text{mL Solution}}\right)\left(\frac{6.5\%\ \text{NaOCl}}{100\%\ \text{Solution}}\right)\left(\frac{1\ \text{mol NaOCl}}{74.44\ \text{g NaOCl}}\right)\left(\frac{1\ \text{mol OCl}^-}{1\ \text{mol NaOCl}}\right)$$

$= 0.873186\ M\ OCl^-$ (unrounded)

The sodium ion is from a strong base; therefore, it will not affect the pH, and can be ignored.

Concentration (M)	$OCl^-(aq)$	+	$H_2O(l)$	$\leftrightarrows$	$HOCl(aq)$	+	$OH^-(aq)$
Initial	0.873186		—		0		0
Change	–x		—		+x		+x
Equilibrium	0.873186 – x		—		x		x

$$K_b \text{ of } OCl^- = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2.9 \times 10^{-8}} = 3.448275862 \times 10^{-7}$$

$$K_b = \frac{[HOCl][OH^-]}{[ClO^-]} = 3.448275862 \times 10^{-7}$$

$$K_b = \frac{[x][x]}{[0.873186 - x]} = 3.448275862 \times 10^{-7}$$ Assume x is small compared to 0.873186.

$$K_b = 3.448275862 \times 10^{-7} = \frac{(x)(x)}{(0.873186)}$$

$x = 5.4872 \times 10^{-4} =$ **$5.5 \times 10^{-4}\ M\ OH^-$**

Check assumption: $(5.4872 \times 10^{-4} / 0.873186) \times 100\% = 0.06\%$ error, so the assumption is valid.

$$[H_3O]^+ = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{5.4872 \times 10^{-4}} = 1.82242 \times 10^{-11}\ M\ H_3O^+ \text{ (unrounded)}$$

$pH = -\log [H_3O^+] = -\log (1.82242 \times 10^{-11}) = 10.73935 =$ **10.74**

18.103 The cation ion, $HC_{18}H_{21}NO_3^+$, acts as an acid shown by the following equation:

$$HC_{18}H_{21}NO_3^+(aq) + H_2O(l) \leftrightarrows C_{18}H_{21}NO_3(aq) + H_3O^+(aq)$$

Because $HC_{18}H_{21}NO_3Cl$ is a soluble salt, $[HC_{18}H_{21}NO_3^+] = [HC_{18}H_{21}NO_3Cl]$. The chloride ion is from a strong acid; therefore, it will not affect the pH, and can be ignored.

Concentration (M)	$HC_{18}H_{21}NO_3^+(aq)$	+	$H_2O(l)$	$\leftrightarrows$	$C_{18}H_{21}NO_3(aq)$	+	$H_3O^+(aq)$
Initial	0.050		—		0		0
Change	–x		—		+x		+x
Equilibrium	0.050 – x		—		x		x

$K_b = 10^{-pK_b} = 10^{-5.80} = 1.58489 \times 10^{-6}$ (unrounded)

K_a of $HC_{18}H_{21}NO_3^+ = K_w / K_b = (1.0 \times 10^{-14}) / (1.58489 \times 10^{-6}) = 6.309586 \times 10^{-9}$ (unrounded)

$$K_a = 6.309586 \times 10^{-9} = \frac{[H_3O^+][C_{18}H_{21}NO_3]}{[HC_{18}H_{21}NO_3^+]}$$

$$K_a = 6.309586 \times 10^{-9} = \frac{(x)(x)}{(0.050 - x)}$$ Assume x is small compared to 0.050.

$$K_a = 6.309586 \times 10^{-9} = \frac{(x)(x)}{(0.050)}$$

$[H_3O^+] = x = 1.7761737 \times 10^{-5}$ (unrounded)

Check assumption: $(1.7761737 \times 10^{-5} / 0.050) \times 100\% = 0.03\%$ error, so the assumption is valid.

$pH = -\log [H_3O^+] = -\log (1.7761737 \times 10^{-5}) = 4.75051 =$ **4.75**

18.104 Electronegativity increases left to right across a period. As the nonmetal becomes more electronegative, the acidity of the binary hydride increases. The electronegative nonmetal attracts the electrons more strongly in the polar bond, shifting the electron density away from H^+ and making the H^+ more easily transferred to a surrounding water molecule to make H_3O^+.

18.105 As the nonmetal increases in size, its bond to hydrogen becomes longer and weaker, so that H^+ is more easily lost, and a stronger acid results.

18.106 There is an inverse relationship between the strength of the bond to the acidic proton and the strength of the acid. A weak bond means the hydrogen ion is more easily lost, and hence the acid is stronger.

18.107 The two factors that explain the greater acid strength of $HClO_4$ are:
1) Chlorine is more electronegative than iodine, so chlorine more strongly attracts the electrons in the bond with oxygen. This makes the H in $HClO_4$ less tightly held by the oxygen than the H in HIO.
2) Perchloric acid has more oxygen atoms than HIO, which leads to a greater shift in electron density from the hydrogen atom to the oxygens making the H in $HClO_4$ more susceptible to transfer to a base.

18.108 For oxyacids, acid strength increases with increasing number of oxygen atoms and increasing electronegativity of the nonmetal in the acid. For binary acids, acid strength increases with increasing electronegativity across a row and increases with increasing size of the nonmetal in a column.
a) Selenic acid, $\mathbf{H_2SeO_4}$, is the stronger acid because it contains more oxygen atoms.
b) Phosphoric acid, $\mathbf{H_3PO_4}$, is the stronger acid because P is more electronegative than As.
c) Hydrotelluric acid, $\mathbf{H_2Te}$, is the stronger acid because Te is larger than S and so the Te-H bond is weaker.

18.109 a) $\mathbf{H_2Se}$ b) $\mathbf{H_2SO_4}$ c) $\mathbf{H_2SO_3}$

18.110 For oxyacids, acid strength increases with increasing number of oxygen atoms and increasing electronegativity of the nonmetal in the acid. For binary acids, acid strength increases with increasing electronegativity across a row and increases with increasing size of the nonmetal in a column.
a) $\mathbf{H_2Se}$, hydrogen selenide, is a stronger acid than H_3As, arsenic hydride, because Se is more electronegative than As.
b) $\mathbf{B(OH)_3}$, boric acid also written as H_3BO_3, is a stronger acid than $Al(OH)_3$, aluminum hydroxide, because boron is more electronegative than aluminum.
c) $\mathbf{HBrO_2}$, bromous acid, is a stronger acid than HBrO, hypobromous acid, because there are more oxygen atoms in $HBrO_2$ than in HBrO.

18.111 a) **HBr** b) $\mathbf{H_3AsO_4}$ c) $\mathbf{HNO_2}$

18.112 Acidity increases as the value of K_a increases. Determine the ion formed from each salt and compare the corresponding K_a values from Appendix C.
a) Copper(II) sulfate, $CuSO_4$, contains Cu^{2+} ion with $K_a = 3 \times 10^{-8}$. Aluminum sulfate, $Al_2(SO_4)_3$, contains Al^{3+} ion with $K_a = 1 \times 10^{-5}$. The concentrations of Cu^{2+} and Al^{3+} are equal, but the K_a of $Al_2(SO_4)_3$ is almost three orders of magnitude greater. Therefore, $\mathbf{0.05\ \mathit{M}\ Al_2(SO_4)_3}$ is the stronger acid and would have the lower pH.
b) Zinc chloride, $ZnCl_2$, contains the Zn^{2+} ion with $K_a = 1 \times 10^{-9}$. Lead chloride, $PbCl_2$, contains the Pb^{2+} ion with $K_a = 3 \times 10^{-8}$. Since both solutions have the same concentration, and $K_a (Pb^{2+}) > K_a (Zn^{2+})$, $\mathbf{0.1\ \mathit{M}\ PbCl_2}$ is the stronger acid and would have the lower pH.

18.113 a) $\mathbf{FeCl_3}$ b) $\mathbf{BeCl_2}$

18.114 A higher pH (more basic solution) results when an acid has a lower K_a (from the Appendix).
a) The $\mathbf{Ni(NO_3)_2}$ solution has a higher pH than the $Co(NO_3)_2$ solution because K_a of Ni^{2+} (1×10^{-10}) is smaller than the K_a of Co^{2+} (2×10^{-10}). Note that nitrate ions are the conjugate bases of a strong acid and therefore do not influence the pH of the solution.
b) The $\mathbf{Al(NO_3)_3}$ solution has a higher pH than the $Cr(NO_3)_2$ solution because K_a of Al^{3+} (1×10^{-5}) is smaller than the K_a of Cr^{3+} (1×10^{-4}).

18.115 a) **NaCl** b) $\mathbf{Co(NO_3)_2}$

18.116 Salts that contain anions of weak acids and cations of strong bases are basic. Salts that contain cations of weak bases or small, highly charged metal cations, and anions of strong acids are acidic. Salts that contain cations of strong bases and anions of strong acids are neutral.
<u>Basic salt</u>: KCN (K^+ is the cation from the strong base KOH; CN^- is the anion from the weak acid, HCN)
<u>Acid salt</u>: $FeCl_3$ or NH_4NO_3 (Fe^{3+} is a small, highly charged metal cation and Cl^- is the anion of the strong acid HCl; NH_4^+ is the cation of the weak base NH_3 while NO_3^- is the anion of the strong acid HNO_3.)
<u>Neutral salt</u>: KNO_3 (K^+ is the cation of the strong base KOH while NO_3^- is the anion of the strong acid HNO_3).

18.117 Sodium fluoride, NaF, contains the cation of a strong base, NaOH, and anion of a weak acid, HF. This combination yields a salt that is basic in aqueous solution as the F^- ion acts as a base:

$$F^-(aq) + H_2O(l) \leftrightarrows HF(aq) + OH^-(aq)$$

Sodium chloride, NaCl, is the salt of a strong base, NaOH, and strong acid, HCl. This combination yields a salt that is neutral in aqueous solution as neither Na^+ or Cl^- react in water to change the $[H^+]$.

18.118 If K_a for the conjugate acid of the anion is approximately equal to K_b for the conjugate base, the solution will be close to neutral. Otherwise, the solution will be acidic or basic. In this case, the K_a for the conjugate acid (CH_3COOH) is 1.8×10^{-5}, and the K_b for the conjugate base (NH_3) is 1.76×10^{-5}.

18.119 For each salt, first break into the ions present in solution and then determine if either ion acts as a weak acid or weak base to change the pH of the solution. Cations are neutral if they are from a strong base; other cations will be weakly acidic. Anions are neutral if they are from a strong acid; other anions are weakly basic.

a) $KBr(s) \xrightarrow{H_2O} K^+(aq) + Br^-(aq)$

K^+ is the conjugate acid of a strong base, so it does not influence pH.
Br^- is the conjugate base of a strong acid, so it does not influence pH.
Since neither ion influences the pH of the solution, it will remain at the **neutral** pH of pure water.

b) $NH_4I(s) \xrightarrow{H_2O} NH_4^+(aq) + I^-(aq)$

NH_4^+ is the conjugate acid of a weak base, so it will act as a weak acid in solution and produce H_3O^+ as represented by the acid dissociation reaction:

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

I^- is the conjugate base of a strong acid, so it will not influence the pH.
The production of H_3O^+ from the ammonium ion makes the solution of NH_4I **acidic**.

c) $KCN(s) \xrightarrow{H_2O} K^+(aq) + CN^-(aq)$

K^+ is the conjugate acid of a strong base, so it does not influence pH.
CN^- is the conjugate base of a weak acid, so it will act as a weak base in solution and impact pH by the base dissociation reaction:

$$CN^-(aq) + H_2O(l) \leftrightarrows HCN(aq) + OH^-(aq)$$

Hydroxide ions are produced in this equilibrium so solution will be **basic**.

18.120 a) $Cr(NO_3)_3(s) + nH_2O(l) \rightarrow Cr(H_2O)_n^{3+}(aq) + 3NO_3^-(aq)$

$Cr(H_2O)_n^{3+}(aq) + H_2O(l) \leftrightarrows Cr(H_2O)_{n-1}OH^{2+}(aq) + H_3O^+(aq)$ **acidic**

b) $NaHS(s) + H_2O(l) \rightarrow Na^+(aq) + HS^-(aq)$

$HS^-(aq) + H_2O(l) \leftrightarrows OH^-(aq) + H_2S(aq)$ **basic**

c) $Zn(CH_3COO)_2(s) + nH_2O(l) \rightarrow Zn(H_2O)_n^{2+}(aq) + 2CH_3COO^-(aq)$

$Zn(H_2O)_n^{2+}(aq) + H_2O(l) \leftrightarrows Zn(H_2O)_{n-1}OH^+(aq) + H_3O^+(aq)$
$CH_3COO^-(aq) + H_2O(l) \leftrightarrows OH^-(aq) + CH_3COOH(aq)$
$K_a(Zn(H_2O)_n^{2+}) = 1 \times 10^{-9}$
$K_b(CH_3COO^-) = K_w / K_a = (1.0 \times 10^{-14}) / (1.8 \times 10^{-5}) = 5.5556 \times 10^{-10}$ (unrounded)
The two K values are similar, so the solution is close to **neutral**.

18.121 For each salt, first break into the ions present in solution and then determine if either ion acts as a weak acid or weak base to change the pH of the solution. Cations are neutral if they are from a strong base; other cations will be weakly acidic. Anions are neutral if they are from a strong acid; other anions are weakly basic.

a) The two ions that comprise sodium carbonate, Na_2CO_3, are sodium ion, Na^+, and carbonate ion, CO_3^{2-}.

$Na_2CO_3(s) \xrightarrow{H_2O} 2\ Na^+(aq) + CO_3^{2-}(aq)$

Sodium ion is derived from the strong base NaOH. Carbonate ion is derived from the weak acid HCO_3^-. A salt derived from a strong base and a weak acid produces a **basic** solution.

Na^+ does not react with water.

$CO_3^{2-}(aq) + H_2O(l) \leftrightarrows HCO_3^-(aq) + OH^-(aq)$

b) The two ions that comprise calcium chloride, $CaCl_2$, are calcium ion, Ca^{2+}, and chloride ion, Cl^-.

$CaCl_2(s) \xrightarrow{H_2O} Ca^{2+}(aq) + 2\ Cl^-(aq)$

Calcium ion is derived from the strong base $Ca(OH)_2$. Chloride ion is derived from the strong acid HCl. A salt derived from a strong base and strong acid produces a **neutral** solution.

Neither Ca^{2+} nor Cl^- reacts with water.

c) The two ions that comprise cupric nitrate, $Cu(NO_3)_2$, are the cupric ion, Cu^{2+}, and the nitrate ion, NO_3^-.

$Cu(NO_3)_2(s) \xrightarrow{H_2O} Cu^{2+}(aq) + 2\ NO_3^-(aq)$

Small metal ions are acidic in water (assume the hydration of Cu^{2+} is 6):

$Cu(H_2O)_6^{2+}(aq) + H_2O(l) \leftrightarrows Cu(H_2O)_5OH^+(aq) + H_3O^+(aq)$

Nitrate ion is derived from the strong acid HNO_3. Therefore, NO_3^- does not react with water. A solution of cupric nitrate is **acidic**.

18.122 a) $CH_3NH_3Cl(s) + H_2O(l) \rightarrow CH_3NH_3^+(aq) + Cl^-(aq)$

$CH_3NH_3^+(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CH_3NH_2(aq)$ **acidic**

b) $KClO_4(s) + H_2O(l) \rightarrow K^+(aq) + ClO_4^-(aq)$ **neutral**

c) $CoF_2(s) + nH_2O(l) \rightarrow Co(H_2O)_n^{2+}(aq) + 2F^-(aq)$

$Co(H_2O)_n^{2+}(aq) + H_2O(l) \leftrightarrows Co(H_2O)_{n-1}OH^+(aq) + H_3O^+(aq)$

$F^-(aq) + H_2O(l) \leftrightarrows OH^-(aq) + HF(aq)$

$K_a\ (Co(H_2O)_n^{2+}) = 2 \times 10^{-10}$

$K_b\ (F^-) = K_w / K_a = (1.0 \times 10^{-14}) / (6.8 \times 10^{-4}) = 1.47 \times 10^{-11}$ (unrounded)

The two K values are similar so the solution is close to **neutral**.

18.123 For each salt, first break into the ions present in solution and then determine if either ion acts as a weak acid or weak base to change the pH of the solution. Cations are neutral if they are from a strong base; other cations will be weakly acidic. Anions are neutral if they are from a strong acid; other anions are weakly basic.

a) A solution of strontium bromide is **neutral** because Sr^{2+} is the conjugate acid of a strong base, $Sr(OH)_2$ and Br^- is the conjugate base of a strong acid, HBr, so neither change the pH of the solution.

b) A solution of barium acetate is **basic** because CH_3COO^- is the conjugate base of a weak acid and therefore forms OH^- in solution whereas Ba^{2+} is the conjugate acid of a strong base, $Ba(OH)_2$, and does not influence solution pH. The base dissociation reaction of acetate ion is

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

c) A solution of dimethylammonium bromide is **acidic** because $(CH_3)_2NH_2^+$ is the conjugate acid of a weak base and therefore forms H_3O^+ in solution whereas Br^- is the conjugate base of a strong acid and does not influence the pH of the solution. The acid dissociation reaction for methylammonium ion is

$$(CH_3)_2NH_2^+(aq) + H_2O(l) \leftrightarrows (CH_3)_2NH(aq) + H_3O^+(aq).$$

18.124 a) $Fe(HCOO)_3(s) + n\ H_2O(l) \rightarrow Fe(H_2O)_n^{3+}(aq) + 3\ HCOO^-(aq)$

$Fe(H_2O)_n^{3+}(aq) + H_2O(l) \leftrightarrows Fe(H_2O)_{n-1}OH^{2+}(aq) + H_3O^+(aq)$

$HCOO^-(aq) + H_2O(l) \leftrightarrows OH^-(aq) + HCOOH(aq)$

$K_a\ (Fe^{3+}) = 6 \times 10^{-3}$

$K_b\ (HCOO^-) = K_w / K_a = (1.0 \times 10^{-14}) / (1.8 \times 10^{-4}) = 5.5556 \times 10^{-11}$ (unrounded)

$K_a\ (Fe^{3+}) > K_b\ (HCOO^-)$ **acidic**

b) $KHCO_3(s) + H_2O(l) \rightarrow K^+(aq) + HCO_3^-(aq)$

$HCO_3^-(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CO_3^{2-}(aq)$

$HCO_3^-(aq) + H_2O(l) \leftrightarrows OH^-(aq) + H_2CO_3(aq)$ Since $K_b\ (HCO_3^-) > K_a\ (HCO_3^-)$ **basic**

c) $K_2S(s) + H_2O(l) \leftrightarrows 2\ K^+(aq) + S^{2-}(aq)$

$S^{2-}(aq) + H_2O(l) \leftrightarrows OH^-(aq) + HS^-(aq)$ **basic**

18.125 For each salt, first break into the ions present in solution and then determine if either ion acts as a weak acid or weak base to change the pH of the solution. Cations are neutral if they are from a strong base; other cations will be weakly acidic. Anions are neutral if they are from a strong acid; other anions are weakly basic.

a) The two ions that comprise ammonium phosphate, $(NH_4)_3PO_4$, are the ammonium ion, NH_4^+, and the phosphate ion, PO_4^{3-}.

$NH_4^+(aq) + H_2O(l) \leftrightarrows NH_3(aq) + H_3O^+(aq)$ $\quad K_a = K_w / K_b\ (NH_3) = 5.7 \times 10^{-10}$

$PO_4^{3-}(aq) + H_2O(l) \leftrightarrows HPO_4^{2-}(aq) + OH^-(aq)$ $\quad K_b = K_w / K_{a3}\ (H_3PO_4) = 2.4 \times 10^{-2}$

A comparison of K_a and K_b is necessary since both ions are derived from a weak base and weak acid. The K_a of NH_4^+ is determined by using the K_b of its conjugate base, NH_3 (Appendix). The K_b of PO_4^{3-} is determined by using the K_a of its conjugate acid, HPO_4^{2-}. The K_a of HPO_4^{2-} comes from K_{a3} of H_3PO_4 (Appendix). Since $K_b > K_a$, a solution of $(NH_4)_3PO_4$ is **basic**.

b) The two ions that comprise sodium sulfate, Na_2SO_4, are sodium ion, Na^+, and sulfate ion, SO_4^{2-}. The sodium ion is derived from the strong base NaOH. The sulfate ion is derived from the weak acid, HSO_4^-.

$SO_4^{2-}(aq) + H_2O(l) \leftrightarrows HSO_4^-(aq) + OH^-(aq)$

A solution of sodium sulfate is **basic**.

c) The two ions that comprise lithium hypochlorite, LiClO, are lithium ion, Li^+, and hypochlorite ion, ClO^-. Lithium ion is derived from the strong base LiOH. Hypochlorite ion is derived from the weak acid, HClO (hypochlorous acid).

$ClO^-(aq) + H_2O(l) \leftrightarrows HClO(aq) + OH^-(aq)$

A solution of lithium hypochlorite is **basic**.

18.126 a) $Pb(CH_3COO)_2)(s) + n\ H_2O(l) \rightarrow Pb(H_2O)_n^{2+}(aq) + 2\ CH_3COO^-(aq)$

$Pb(H_2O)_n^{2+}(aq) + H_2O(l) \leftrightarrows Pb(H_2O)_{n-1}OH^+(aq) + H_3O^+(aq)$

$K_a\ (Pb^{2+}) = 3 \times 10^{-8}$

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

$K_b\ (CH_3COO^-) = K_w / K_a = (1.0 \times 10^{-14}) / (1.8 \times 10^{-5}) = 5.5556 \times 10^{-10}$ (unrounded)

$K_a\ (Pb^{2+}) > K_b\ (CH_3COO^-)$ **acidic**

b) $Cr(NO_2)_3(s) + n\ H_2O(l) \rightarrow Cr(H_2O)_n^{3+}(aq) + 3\ NO_2^-(aq)$

$Cr(H_2O)_n^{3+}(aq) + H_2O(l) \leftrightarrows Cr(H_2O)_{n-1}OH^{2+}(aq) + H_3O^+(aq)$

$NO_2^-(aq) + H_2O(l) \leftrightarrows OH^-(aq) + HNO_2(aq)$

$K_a\ (Cr^{3+}) = 1 \times 10^{-4}$

$K_b\ (NO_2^-) = K_w / K_a = (1.0 \times 10^{-14}) / (7.1 \times 10^{-4}) = 1.40845 \times 10^{-11}$ (unrounded)

$K_a\ (Cr^{3+}) > K_b\ (NO_2^-)$ **acidic**

c) $CsI(s) + H_2O(l) \rightarrow Cs^+(aq) + I^-(aq)$ **neutral**

18.127 a) Order of increasing pH: **$Fe(NO_3)_2 < KNO_3 < K_2SO_3 < K_2S$** (assuming concentrations equivalent)

Iron(II) nitrate, $Fe(NO_3)_2$, is an acidic solution because the iron ion is a small, highly charged metal ion that acts as a weak acid and nitrate ion is the conjugate base of a strong acid, so it does not influence pH.

Potassium nitrate, KNO_3, is a neutral solution because potassium ion is the conjugate acid of a strong base and nitrate ion is the conjugate base of a strong acid, so neither influences solution pH.

Potassium sulfite, K_2SO_3, and potassium sulfide, K_2S, are similar in that the potassium ion does not influence solution pH but the anions do because they are conjugate bases of weak acids. K_a for HSO_3^- is 6.5×10^{-8}, so K_b for SO_3^- is 1.5×10^{-7}, which indicates that sulfite ion is a weak base. K_a for HS^- is 1×10^{-17} (see the Table of K_a values for polyprotic acids), so sulfide ion has a K_b equal to 1×10^3. Sulfide ion is thus a strong base. The solution of a strong base will have a greater concentration of hydroxide ions (and higher pH) than a solution of a weak base of equivalent concentrations.

b) In order of increasing pH: **$NaHSO_4 < NH_4NO_3 < NaHCO_3 < Na_2CO_3$**

In solutions of ammonium nitrate, only the ammonium will influence pH by dissociating as a weak acid:

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

with $K_a = 1.0 \times 10^{-14} / 1.8 \times 10^{-5} = 5.6 \times 10^{-10}$

Therefore, the solution of ammonium nitrate is acidic.

In solutions of sodium hydrogen sulfate, only HSO_4^- will influence pH. The hydrogen sulfate ion is amphoteric so both the acid and base dissociations must be evaluated for influence on pH. As a base, HSO_4^- is the conjugate base of a strong acid, so it will not influence pH. As an acid, HSO_4^- is the conjugate acid of a weak base, so the acid dissociation applies

$$HSO_4^-(aq) + H_2O(l) \leftrightarrows SO_4^{2-}(aq) + H_3O^+(aq) \quad K_{a2} = 1.2 \times 10^{-2}$$

In solutions of sodium hydrogen carbonate, only the HCO_3^- will influence pH and it, like HSO_4^-, is amphoteric:

As an acid: $HCO_3^-(aq) + H_2O(l) \leftrightarrows CO_3^{2-}(aq) + H_3O^+(aq)$

$K_a = 4.7 \times 10^{-11}$, the second K_a for carbonic acid

As a base: $HCO_3^-(aq) + H_2O(l) \leftrightarrows H_2CO_3(aq) + OH^-(aq)$

$K_b = 1.0 \times 10^{-14} / 4.5 \times 10^{-7} = 2.2 \times 10^{-8}$

Since $K_b > K_a$, a solution of sodium hydrogen carbonate is basic.

In a solution of sodium carbonate, only CO_3^{2-} will influence pH by acting as a weak base:

$CO_3^{2-}(aq) + H_2O(l) \leftrightarrows HCO_3^-(aq) + OH^-(aq)$

$K_b = 1.0 \times 10^{-14} / 4.7 \times 10^{-11} = 2.1 \times 10^{-4}$

Therefore, the solution of sodium carbonate is basic.

Two of the solutions are acidic. Since the K_a of HSO_4^- is greater than that of NH_4^+, the solution of sodium hydrogen sulfate has a lower pH than the solution of ammonium nitrate, assuming the concentrations are relatively close.

Two of the solutions are basic. Since the K_b of CO_3^{2-} is greater than that of HCO_3^-, the solution of sodium carbonate has a higher pH than the solution of sodium hydrogen carbonate, assuming concentrations are not extremely different.

18.128 a) **$KClO_2 > MgCl_2 > FeCl_2 > FeCl_3$**

b) **$NaBrO_2 > NaClO_2 > NaBr > NH_4Br$**

18.129 Both methoxide ion and amide ion produce OH^- in aqueous solution. In water, the strongest base possible is OH^-. Since both bases produce OH^- in water, both bases appear equally strong.

$CH_3O^-(aq) + H_2O(l) \rightarrow OH^-(aq) + CH_3OH(aq)$

$NH_2^-(aq) + H_2O(l) \rightarrow OH^-(aq) + NH_3(aq)$

18.130 H_2SO_4 is a strong acid and would be 100% dissociated in H_2O and any solvent more basic than H_2O (such as NH_3). It would be less than 100% dissociated in solvents more acidic than H_2O (such as CH_3COOH).

18.131 Ammonia, NH_3, is a more basic solvent than H_2O. In a more basic solvent, weak acids like HF act like strong acids and are 100% dissociated.

18.132 A Lewis base must have an electron pair to donate. A Lewis acid must have a vacant orbital or the ability to rearrange its bonding to make one available. The Lewis acid-base reaction involves the donation and acceptance of an electron pair to form a new covalent bond in an adduct.

18.133 A Lewis acid is defined as an electron pair acceptor, while a Brønsted-Lowry acid is a proton donor. If only the proton in a Brønsted-Lowry acid is considered, then every Brønsted-Lowry acid fits the definition of a Lewis acid since the proton is accepting an electron pair when it bonds with a base. There are Lewis acids that do not include a proton, so all Lewis acids are not Brønsted-Lowry acids.

A Lewis base is defined as an electron pair donor and a Brønsted-Lowry base is a proton acceptor. In this case, the two definitions are essentially the same.

18.134 a) **No**, a weak Brønsted-Lowry base is not necessarily a weak Lewis base. For example, water molecules solvate metal ions very well:

$Zn^{2+}(aq) + 4\ H_2O(l) \leftrightarrows Zn(H_2O)_6^{2+}(aq)$

Water is a very weak Brønsted-Lowry base, but forms the Zn complex fairly well and is a reasonably strong Lewis base.

b) The **cyanide ion** has a lone pair to donate from either the C or the N, and donates an electron pair to the $Cu(H_2O)_6^{2+}$ complex. It is the Lewis base for the forward direction of this reaction. In the reverse direction, **water** donates one of the electron pairs on the oxygen to the $Cu(CN)_4^{2-}$ and is the Lewis base.

c) Because $K_c > 1$, the reaction proceeds in the direction written (left to right) and is driven by the stronger Lewis base, the **cyanide ion**.

18.135 All three concepts can have water as the product in an acid/base neutralization reaction. It is the only product in an Arrhenius neutralization reaction.

18.136 a) NH_3 can only act as a Brønsted-Lowry or Lewis base.
b) $AlCl_3$ can only act as a Lewis acid.

18.137 a) Cu^{2+} is a **Lewis acid** because it accepts electron pairs from molecules such as water.
b) Cl^- is a **Lewis base** because it has lone pairs of electrons it can donate to a Lewis acid.
c) Tin(II) chloride, $SnCl_2$, is a compound with a structure similar to carbon dioxide, so it will act as a **Lewis acid** to form an additional bond to the tin.
d) Oxygen difluoride, OF_2, is a **Lewis base** with a structure similar to water, where the oxygen has lone pairs of electrons that it can donate to a Lewis acid.

18.138 a) **Lewis acid** b) **Lewis base** c) **Lewis base** d) **Lewis acid**

18.139 a) The boron atom in boron trifluoride, BF_3, is electron deficient (has 6 electrons instead of 8) and can accept an electron pair; it is a **Lewis acid**.
b) The sulfide ion, S^{2-}, can donate any of four electron pairs and is a **Lewis base**.
c) The Lewis dot structure for the sulfite ion, SO_3^{2-} shows lone pairs on the sulfur and on the oxygens. The sulfur atom has a lone electron pair that it can donate more easily than the electronegative oxygen in the formation of an adduct. The sulfite ion is a **Lewis base**.
d) Sulfur trioxide, SO_3, acts as a **Lewis acid**.

18.140 a) **Lewis acid** b) **Lewis base** c) **Lewis acid** d) **Lewis acid**

18.141 a) Sodium ion is the Lewis acid because it is accepting electron pairs from water, the Lewis base.

$$\begin{array}{lclcl} Na^+ & + & 6\ H_2O & \leftrightarrows & Na(H_2O)_6^+ \\ \text{Lewis acid} & & \text{Lewis base} & & \text{adduct} \end{array}$$

b) The oxygen from water donates a lone pair to the carbon in carbon dioxide. Water is the Lewis base and carbon dioxide the Lewis acid.

$$\begin{array}{lclcl} CO_2 & + & H_2O & \leftrightarrows & H_2CO_3 \\ \text{Lewis acid} & & \text{Lewis base} & & \text{adduct} \end{array}$$

c) Fluoride ion donates an electron pair to form a bond with boron in BF_4^-. The fluoride ion is the Lewis base and the boron trifluoride is the Lewis acid.

$$\begin{array}{lclcl} F^- & + & BF_3 & \leftrightarrows & BF_4^- \\ \text{Lewis base} & & \text{Lewis acid} & & \text{adduct} \end{array}$$

18.142

$$\begin{array}{llclcl} \text{a) } Fe^{3+} & + & 2\ H_2O & \leftrightarrows & FeOH^{2+} & + & H_3O^+ \\ \text{Lewis acid} & & \text{Lewis base} & & & & \\ \text{b) } H_2O & + & H^- & \leftrightarrows & OH^- & + & H_2 \\ \text{Lewis acid} & & \text{Lewis base} & & & & \\ \text{c) } 4\ CO & + & Ni & \leftrightarrows & Ni(CO)_4 & & \\ \text{Lewis base} & & \text{Lewis acid} & & & & \end{array}$$

18.143 a) Since neither H^+ nor OH^- is involved, this is not an Arrhenius acid-base reaction. Since there is no exchange of protons, this is not a Brønsted-Lowry reaction. This reaction is only classified as **Lewis acid-base reaction**, where Ag^+ is the acid and NH_3 is the base.
b) Again, no OH^- is involved, so this is not an Arrhenius acid-base reaction. This is an exchange of a proton, from H_2SO_4 to NH_3, so it is a **Brønsted-Lowry acid-base reaction**. Since the Lewis definition is most inclusive, anything that is classified as a Brønsted-Lowry (or Arrhenius) reaction is automatically classified as a **Lewis acid-base reaction**.
c) This is not an acid-base reaction.

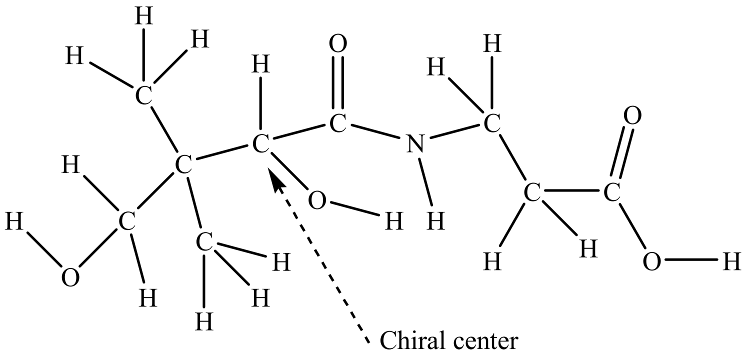
d) For the same reasons listed in (a), this reaction is only classified as **Lewis acid-base reaction**, where $AlCl_3$ is the acid and Cl^- is the base.

18.144 a) **Lewis acid-base reaction** b) **Brønsted-Lowry, Arrhenius, and Lewis acid-base reaction**
c) **This is not an acid-base reaction**. d) **Brønsted-Lowry and Lewis acid-base reaction**

18.145 a) $C_8H_{16}NO_3COOH(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + C_8H_{16}NO_3COO^-\,(aq)$

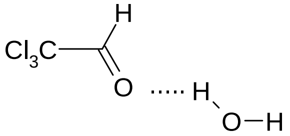
$$K_a = \frac{[H_3O^+][C_8H_{16}NO_3COO^-]}{[C_8H_{16}NO_3COOH]}$$

b)

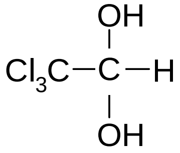


Chiral center

18.146 a) The hydrogen-bonded form would be:



The product of a Lewis acid-base reaction is:



$$Cl_3C-\overset{\displaystyle OH}{\underset{\displaystyle OH}{C}}-H$$

The O atom of water (Lewis base) donates a lone pair to the C of the carbonyl group, which functions as a Lewis acid. The π bond is broken and a C-O bond is formed. The O atom of the carbonyl (Lewis base) accepts a proton from water (Lewis acid) to complete the reaction.

b) Infrared spectroscopy could be used. Infrared spectroscopy is very good at identifying functional groups. C=O bonds have a characteristic range of absorption wavelengths. The hydrogen-bonded structure would have a carbonyl group and the second structure would not.

18.147 Calculate the $[H_3O^+]$ using the pH values given. Determine the value of K_w from the pK_w given. The $[H_3O^+]$ is combined with the K_w value at 37°C to find $[OH^-]$ using $K_w = [H_3O^+][OH^-]$.

$K_w = 10^{-pK_w} = 10^{-13.63} = 2.3442 \times 10^{-14}$ (unrounded)

$K_w = [H_3O^+]\,[OH^-] = 2.3442 \times 10^{-14}$ at 37°C

$[H_3O^+]$ range

High value (low pH) $= 10^{-pH} = 10^{-7.35} = 4.4668 \times 10^{-8} = 4.5 \times 10^{-8}\ M\ H_3O^+$

Low value (high pH) $= 10^{-pH} = 10^{-7.45} = 3.5481 \times 10^{-8} = 3.5 \times 10^{-8}\ M\ H_3O^+$

Range: **3.5×10^{-8} to $4.5 \times 10^{-8}\ M\ H_3O^+$**

$[OH^-]$ range

$K_w = [H_3O^+]\,[OH^-] = 2.3442 \text{ x } 10^{-14}$ at 37°C

$$[OH^-] = \frac{K_w}{[H_3O]^+}$$

$$\text{High value (high pH)} = \frac{2.3442 \text{ x } 10^{-14}}{3.5481 \text{ x } 10^{-8}} = 6.6069 \text{ x } 10^{-7} = 6.6 \text{ x } 10^{-7}\ M\ OH^-$$

$$\text{Low value (low pH)} = \frac{2.3442 \text{ x } 10^{-14}}{4.4668 \text{ x } 10^{-8}} = 5.24805 \text{ x } 10^{-7} = 5.2 \text{ x } 10^{-7}\ M\ OH^-$$

Range: **$5.2 \text{ x } 10^{-7}$ to $6.6 \text{ x } 10^{-7}$ M OH^-**

18.148 a) Acids will vary in the amount they dissociate (acid strength) depending on the acid-base character of the solvent. Water and methanol have different acid-base characters.

b) The K_a is the measure of an acid's strength. A stronger acid has a smaller pK_a. Therefore, phenol is a stronger acid in water than it is in methanol. In other words, water more readily accepts a proton from phenol than does methanol, i.e., methanol is a weaker base than water.

c) $C_6H_5OH(\mathit{solvated}) + CH_3OH(l) \leftrightarrows CH_3OH_2^+(\mathit{solvated}) + C_6H_5O^-\ (\mathit{solvated})$

The term "*solvated*" is analogous to "*aqueous*." "*Aqueous*" would be incorrect in this case because the reaction does not take place in water.

d) In the autoionization process, one methanol molecule is the proton donor while another methanol molecule is the proton acceptor.

$CH_3OH(l) + CH_3OH(l) \leftrightarrows CH_3O^-\ (\mathit{solvated}) + CH_3OH_2^+(\mathit{solvated})$

In this equation "(*solvated*)" indicates that the molecules are solvated by methanol.

The equilibrium constant for this reaction is the autoionization constant of methanol:

$$K = [CH_3O^-]\,[CH_3OH_2^+]$$

18.149 a) step (1): $CO_2(g) + H_2O(l) \leftrightarrows H_2CO_3(aq)$ **Lewis**

step (2): $H_2CO_3(aq) + H_2O(l) \leftrightarrows HCO_3^-(aq) + H_3O^+(aq)$ **Brønsted-Lowry and Lewis**

b) Molarity $CO_2 = k_{Henry}\,P_{\text{carbon dioxide}} = (0.033 \text{ mol/L•atm})\,(3.2 \text{ x } 10^{-4} \text{ atm})$

$= 1.056 \text{ x } 10^{-5}\ M\ CO_2$ (unrounded)

$CO_2(g) + 2\,H_2O(l) \leftrightarrows HCO_3^-(aq) + H_3O^+(aq)$ $K_{\text{overall}} = 4.5 \text{ x } 10^{-7}$

$$K_{\text{overall}} = 4.5 \text{ x } 10^{-7} = \frac{[H_3O^+][HCO_3^-]}{[CO_2]}$$

$$K_{\text{overall}} = 4.5 \text{ x } 10^{-7} = \frac{[x][x]}{[1.056 \text{ x } 10^{-5} - x]}$$

The problem will need to be solved as a quadratic.

$x^2 = (4.5 \text{ x } 10^{-7})\,(1.056 \text{ x } 10^{-5} - x) = 4.752 \text{ x } 10^{-12} - 4.5 \text{ x } 10^{-7}\,x$

$x^2 + 4.5 \text{ x } 10^{-7}\,x - 4.752 \text{ x } 10^{-12} = 0$

$a = 1 \quad b = 4.5 \text{ x } 10^{-7} \quad c = -4.752 \text{ x } 10^{-12}$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-4.5 \text{ x } 10^{-7} \pm \sqrt{\left(4.5 \text{ x } 10^{-7}\right)^2 - 4(1)\left(-4.752 \text{ x } 10^{-12}\right)}}{2(1)}$$

$x = 1.966489 \text{ x } 10^{-6}\ M\ H_3O^+$ (unrounded)

$pH = -\log\,[H_3O^+] = -\log\,(1.966489 \text{ x } 10^{-6}) = 5.7063 =$ **5.71**

c) $HCO_3^-(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CO_3^{2-}(aq)$

$$K_a = 4.7 \text{ x } 10^{-11} = \frac{[H_3O^+][CO_3^{2-}]}{[HCO_3^-]}$$

Use the unrounded x from part b.

$$K_{\text{overall}} = 4.5 \text{ x } 10^{-11} = \frac{\left[1.966489 \text{ x } 10^{-6} + \text{x}\right]\left[\text{x}\right]}{\left[1.966489 \text{ x } 10^{-6} - \text{x}\right]}$$ Assume x is small compared to 2 x 10^{-6}

$$K_{\text{overall}} = 4.5 \text{ x } 10^{-11} = \frac{\left[1.966489 \text{ x } 10^{-6}\right]\left[\text{x}\right]}{\left[1.966489 \text{ x } 10^{-6}\right]}$$

$[CO_3^{2-}]$ = **$4.5 \text{ x } 10^{-11}$ M CO_3^{2-}**

d) New molarity CO_2 = 2 k_{Henry} $P_{\text{carbon dioxide}}$ = 2 (0.033 mol/L•atm) (3.2 x 10^{-4} atm)
= 2.112 x 10^{-5} M CO_2 (unrounded)

$$K_{\text{overall}} = 4.5 \text{ x } 10^{-7} = \frac{\left[H_3O^+\right]\left[HCO_3^-\right]}{\left[CO_2\right]}$$

$$K_{\text{overall}} = 4.5 \text{ x } 10^{-7} = \frac{\left[\text{x}\right]\left[\text{x}\right]}{\left[2.112 \text{ x } 10^{-5} - \text{x}\right]}$$

The problem will need to be solved as a quadratic.

x^2 =(4.5 x 10^{-7}) (2.112 x 10^{-5} – x) = 9.504 x 10^{-12} – 4.5 x 10^{-7} x

x^2 + 4.5 x 10^{-7} x – 9.504 x 10^{-12} = 0

a = 1 b = 4.5 x 10^{-7} c = – 9.504 x 10^{-12}

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-4.5 \text{ x } 10^{-7} \pm \sqrt{\left(4.5 \text{ x } 10^{-7}\right)^2 - 4\left(1\right)\left(-9.504 \text{ x } 10^{-12}\right)}}{2\left(1\right)}$$

x = 2.866 x 10^{-6} M H_3O^+ (unrounded)

pH = –log $[H_3O^+]$ = –log (2.866 x 10^{-6}) = 5.5427 = **5.54**

18.150 At great depths, the higher pressure increases the concentration of H_3O^+ and the effect is to shift the dissolving reaction to the right, so seashells dissolve more rapidly.

18.151 a) $SnCl_4$ is the Lewis acid accepting an electron pair from $(CH_3)_3N$, the Lewis base.

b) Tin is the element in the Lewis acid accepting the electron pair. The electron configuration of tin is $[Kr]5s^24d^{10}5p^2$. The four bonds to tin are formed by sp^3 hybrid orbitals, which completely fill the 5*s* and 5*p* orbitals. The **5*d*** orbitals are empty and available for the bond with trimethylamine.

18.152 Hydrochloric acid is a strong acid that completely dissociates in water. Therefore, the concentration of H_3O^+ is the same as the starting acid concentration: $[H_3O^+]$ = [HCl]. The original solution pH:

pH = –log (1.0 x 10^{-5}) = **5.00 = pH**.

A 1:10 dilution means that the chemist takes 1 mL of the 1.0 x 10^{-5} M solution and dilutes it to 10 mL (or dilute 10 mL to 100 mL). The chemist then dilutes the diluted solution in a 1:10 ratio, and repeats this process for the next two successive dilutions. $M_1V_1 = M_2V_2$ can be used to find the molarity after each dilution:

Dilution 1: $M_1V_1 = M_2V_2$

(1.0 x 10^{-5} M) (1.0 mL) = (x)(10. mL)

$[H_3O^+]_{HCl}$ = 1.0 x 10^{-6} M H_3O^+

pH = –log (1.0 x 10^{-6}) = **6.00**.

Dilution 2:

(1.0 x 10^{-6} M) (1.0 mL) = (x)(10. mL)

$[H_3O^+]_{HCl}$ = 1.0 x 10^{-7} M H_3O^+

Once the concentration of strong acid is close to the concentration of H_3O^+ from water autoionization, the $[H_3O^+]$ in the solution does not equal the initial concentration of the strong acid. The calculation of $[H_3O^+]$ must be based on the water ionization equilibrium:

$H_2O(l) + H_2O(l) \leftrightarrows H_3O^+(aq) + OH^-(aq)$ with $K_w = 1.0 \text{ x } 10^{-14}$ at 25°C.

The dilution gives an initial [H_3O^+] of 1.0×10^{-7} *M*. Assuming that the initial concentration of hydroxide ions is zero, a reaction table is set up.

Concentration (*M*)	$2\ H_2O(l)$	$\leftrightarrows$	$H_3O^+(aq)$	+	$OH^-(aq)$
Initial	—		1×10^{-7}		0
Change	—		+x		+x
Equilibrium	—		$1 \times 10^{-7} + x$		x

$K_w = [H_3O^+]\,[OH^-] = (1 \times 10^{-7} + x)\,(x) = 1.0 \times 10^{-14}$

Set up as a quadratic equation: $x^2 + 1.0 \times 10^{-7}\,x - 1.0 \times 10^{-14} = 0$

$a = 1 \qquad b = 1.0 \times 10^{-7} \qquad c = -1.0 \times 10^{-14}$

$$x = \frac{-1.0 \times 10^{-7} \pm \sqrt{\left(1.0 \times 10^{-7}\right)^2 - 4(1)\left(-1.0 \times 10^{-14}\right)}}{2(1)}$$

$x = 6.1803 \times 10^{-8}$ (unrounded)

$[H_3O^+] = (1.0 \times 10^{-7} + x)\ M = (1.0 \times 10^{-7} + 6.1803 \times 10^{-8})\ M = 1.61803 \times 10^{-7}\ M\ H_3O^+$ (unrounded)

$\text{pH} = -\log\,[H_3O^+] = -\log\,(1.61803 \times 10^{-7}) = 6.79101 = \mathbf{6.79}$

Dilution 3:

$(1.0 \times 10^{-7}\ M)\ (1.0\ \text{mL}) = (x)(10.\ \text{mL})$

$[H_3O^+]_{HCl} = 1.0 \times 10^{-8}\ M\ H_3O^+$

The dilution gives an initial [H_3O^+] of 1.0×10^{-8} *M*. Assuming that the initial concentration of hydroxide ions is zero, a reaction table is set up.

Concentration (*M*)	$2\ H_2O(l)$	$\leftrightarrows$	$H_3O^+(aq)$	+	$OH^-(aq)$
Initial	—		1×10^{-8}		0
Change	—		+x		+x
Equilibrium	—		$1 \times 10^{-8} + x$		x

$K_w = [H_3O^+]\,[OH^-] = (1 \times 10^{-8} + x)\,(x) = 1.0 \times 10^{-14}$

Set up as a quadratic equation: $x^2 + 1.0 \times 10^{-8}\,x - 1.0 \times 10^{-14} = 0$

$a = 1 \qquad b = 1.0 \times 10^{-8} \qquad c = -1.0 \times 10^{-14}$

$$x = \frac{-1.0 \times 10^{-8} \pm \sqrt{\left(1.0 \times 10^{-8}\right)^2 - 4(1)\left(-1.0 \times 10^{-14}\right)}}{2(1)}$$

$x = 9.51249 \times 10^{-8}$ (unrounded)

$[H_3O^+] = (1.0 \times 10^{-8} + x)\ M = (1.0 \times 10^{-8} + 9.51249 \times 10^{-8})\ M = 1.051249 \times 10^{-7}\ M\ H_3O^+$ (unrounded)

$\text{pH} = -\log\,[H_3O^+] = -\log\,(1.051249 \times 10^{-7}) = 6.97829 = \mathbf{6.98}$

Dilution 4:

$(1.0 \times 10^{-8}\ M)\ (1.0\ \text{mL}) = (x)(10.\ \text{mL})$

$[H_3O^+]_{HCl} = 1.0 \times 10^{-9}\ M\ H_3O^+$

The dilution gives an initial [H_3O^+] of 1.0×10^{-9} *M*. Assuming that the initial concentration of hydroxide ions is zero, a reaction table is set up.

Concentration (*M*)	$2\ H_2O(l)$	$\leftrightarrows$	$H_3O^+(aq)$	+	$OH^-(aq)$
Initial	—		1×10^{-9}		0
Change	—		+x		+x
Equilibrium	—		$1 \times 10^{-9} + x$		x

$K_w = [H_3O^+]\,[OH^-] = (1 \times 10^{-9} + x)\,(x) = 1.0 \times 10^{-14}$

Set up as a quadratic equation: $x^2 + 1.0 \times 10^{-9}\,x - 1.0 \times 10^{-14} = 0$

$a = 1 \qquad b = 1.0 \times 10^{-9} \qquad c = -1.0 \times 10^{-14}$

$$x = \frac{-1.0 \times 10^{-9} \pm \sqrt{\left(1.0 \times 10^{-9}\right)^2 - 4(1)\left(-1.0 \times 10^{-14}\right)}}{2(1)}$$

$x = 9.95012 \times 10^{-8}$ (unrounded)

$[H_3O^+] = (1.0 \times 10^{-9} + x)\ M = (1.0 \times 10^{-9} + 9.95012 \times 10^{-8})\ M = 1.00512 \times 10^{-7}\ M\ H_3O^+$ (unrounded)

$\text{pH} = -\log\,[H_3O^+] = -\log\,(1.00512 \times 10^{-7}) = 6.99778 = \mathbf{7.00}$

As the HCl solution is diluted, the pH of the solution becomes closer to 7.0. Continued dilutions will not significantly change the pH from 7.0. Thus, a solution with a basic pH cannot be made by adding acid to water.

18.153 a) **Steps 1, 2, and 4** are Lewis acid-base reactions.

b) step 1: $Cl_2 + FeCl_3 \leftrightarrows FeCl_5$ (or $Cl^+FeCl_4^-$)

Lewis acid = $FeCl_3$ **Lewis base = Cl_2**

step 2: $C_6H_6 + Cl^+FeCl_4^- \leftrightarrows C_6H_6Cl^+ + FeCl_4^-$

Lewis acid = C_6H_6 **Lewis base = $Cl^+FeCl_4^-$**

step 4: $H^+ + FeCl_4^- \leftrightarrows HCl + FeCl_3$

Lewis acid = H^+ **Lewis base = $FeCl_4^-$**

18.154 a) $HY(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + Y^-(aq)$

$$K_a = \frac{\left[H_3O^+\right]\left[Y^-\right]}{\left[HY\right]}$$

Concentrations in Beaker A:

$$[HY] = \left(8 \text{ particles}\right)\left(\frac{0.010 \text{ mol}}{1 \text{ particle}}\right)\left(\frac{1}{0.300 \text{ L}}\right) = 0.266667 \text{ M}$$

$$[H_3O^+] = [Y^-] = \left(4 \text{ particles}\right)\left(\frac{0.010 \text{ mol}}{1 \text{ particle}}\right)\left(\frac{1}{0.300 \text{ L}}\right) = 0.133333 \text{ M}$$

$$K_a = \frac{\left[H_3O^+\right]\left[Y^-\right]}{\left[HY\right]} = \frac{\left[0.133333\right]\left[0.133333\right]}{\left[0.266667\right]} = 0.066667 = 0.067$$

Calculate the concentrations in Beakers B-D, then calculate Q to determine which are at equilibrium.

Concentrations in Beaker B:

$$[HY] = \left(6 \text{ particles}\right)\left(\frac{0.010 \text{ mol}}{1 \text{ particle}}\right)\left(\frac{1}{0.300 \text{ L}}\right) = 0.20 \text{ M}$$

$$[H_3O^+] = [Y^-] = \left(2 \text{ particles}\right)\left(\frac{0.010 \text{ mol}}{1 \text{ particle}}\right)\left(\frac{1}{0.300 \text{ L}}\right) = 0.066667 \text{ M}$$

$$Q = \frac{\left[H_3O^+\right]\left[Y^-\right]}{\left[HY\right]} = \frac{\left[0.066667\right]\left[0.066667\right]}{\left[0.20\right]} = 0.0222222 = 0.022$$

Beaker B is not at equilibrium.

Concentrations in Beaker C:

$$[HY] = \left(4 \text{ particles}\right)\left(\frac{0.010 \text{ mol}}{1 \text{ particle}}\right)\left(\frac{1}{0.300 \text{ L}}\right) = 0.133333 \text{ M}$$

$$[H_3O^+] = [Y^-] = \left(2 \text{ particles}\right)\left(\frac{0.010 \text{ mol}}{1 \text{ particle}}\right)\left(\frac{1}{0.300 \text{ L}}\right) = 0.066667 \text{ M}$$

$$Q = \frac{\left[H_3O^+\right]\left[Y^-\right]}{\left[HY\right]} = \frac{\left[0.066667\right]\left[0.066667\right]}{\left[0.13333\right]} = 0.0333345 = 0.033$$

Beaker C is not at equilibrium.

Concentrations in Beaker D:

$$[HY] = \left(2 \text{ particles}\right)\left(\frac{0.010 \text{ mol}}{1 \text{ particle}}\right)\left(\frac{1}{0.300 \text{ L}}\right) = 0.066667 \text{ M}$$

$$[H_3O^+] = [Y^-] = \left(2 \text{ particles}\right)\left(\frac{0.010 \text{ mol}}{1 \text{ particle}}\right)\left(\frac{1}{0.300 \text{ L}}\right) = 0.066667 \text{ M}$$

$$Q = \frac{\left[H_3O^+\right]\left[Y^-\right]}{\left[HY\right]} = \frac{\left[0.066667\right]\left[0.066667\right]}{\left[0.066667\right]} = 0.066667 = 0.067$$

Beaker D is at equilibrium.

b) For both beakers B and C, Q < Ka. Therefore, the reaction is proceeding to the **right** to produce more products.
c) Yes, dilution affects the extent of dissociation of a weak acid. Dilution increases the degree of dissociation. For example, in Beaker A, 4 of 12 HY molecules have dissociated for a (4/12)100 = 33% dissociation. In Beaker D, 2 of 4 HY molecules have dissociated for a (2/4)100 = 50% dissociation.

18.155 Compare the contribution of each acid by calculating the concentration of H_3O^+ produced by each.
For 3% hydrogen peroxide, first find initial molarity of H_2O_2, assuming the density is 1.00 g/mL (the density of water).

$$M\ H_2O_2 = \left(\frac{1.00\ g}{mL}\right)\left(\frac{3\%\ H_2O_2}{100\%}\right)\left(\frac{1\ mol\ H_2O_2}{34.02\ g\ H_2O_2}\right)\left(\frac{1\ mL}{10^{-3}\ L}\right) = 0.881834\ M\ H_2O_2 \text{ (unrounded)}$$

Find K_a from pK_a: $K_a = 10^{-pKa} = 10^{-11.75} = 1.778279 \times 10^{-12}$ (unrounded)

	H_2O_2	$+\ H_2O \leftrightarrows$	H_3O+	$+\ HO_2^-$
Initial	0.881834	—	0	0
Change	−x	—	+x	+x
Equilibrium	0.881834 − x	—	x	x

$$K_a = 1.778279 \times 10^{-12} = \frac{[H_3O^+][HO_2^-]}{[H_2O_2]}$$

$$K_a = 1.778279 \times 10^{-12} = \frac{(x)(x)}{(0.881834 - x)}$$ Assume x is small compared to 0.881834.

$$K_a = 1.778279 \times 10^{-12} = \frac{(x)(x)}{(0.881834)}$$

$[H_3O^+] = x = 1.2522567 \times 10^{-6}$ (unrounded)

Check assumption: $(1.2522567 \times 10^{-6} / 0.881834) \times 100\% = 0.0001\%$ error, so the assumption is valid.

$$M\ H_3PO_4 = \left(\frac{1.00\ g}{mL}\right)\left(\frac{0.001\%\ H_3PO_4}{100\%}\right)\left(\frac{1\ mol\ H_3PO_4}{97.99\ g\ H_3PO_4}\right)\left(\frac{1\ mL}{10^{-3}\ L}\right)$$

$= 1.0205 \times 10^{-4}\ M\ H_3PO_4$ (unrounded)

From the Appendix, K_a for phosphoric acid is 7.2×10^{-3}. The subsequent K_a values may be ignored. In this calculation x is not negligible since the initial concentration of acid is less than the K_a.

	H_3PO_4	$+\ H_2O \leftrightarrows$	H_3O^+	$+\ H_2PO_4^-$
Initial	1.0205×10^{-4}	—	0	0
Change	−x	—	+x	+x
Equilibrium	1.0205×10^{-4}	—	x	x

$$K_a = 7.2 \times 10^{-3} = \frac{[H_3O^+][H_2PO_4^-]}{[H_3PO_4]}$$

$$K_a = 7.2 \times 10^{-3} = \frac{[x][x]}{[1.0205 \times 10^{-4} - x]}$$

The problem will need to be solved as a quadratic.

$x^2 = (7.2 \times 10^{-3})(1.0205 \times 10^{-4} - x) = 7.3476 \times 10^{-7} - 7.2 \times 10^{-3}\ x$

$x^2 + 7.2 \times 10^{-3}\ x - 7.3476 \times 10^{-7} = 0$

$a = 1 \quad b = 7.2 \times 10^{-3} \quad c = -7.3476 \times 10^{-7}$

$$x = \frac{-7.2 \times 10^{-3} \pm \sqrt{\left(7.2 \times 10^{-3}\right)^2 - 4(1)\left(-7.3476 \times 10^{-7}\right)}}{2(1)}$$

$x = 1.00643 \times 10^{-4}\ M\ H_3O^+$ (unrounded)

The concentration of hydronium ion produced by the phosphoric acid, 1 x 10^{-4} *M*, is greater than the concentration produced by the hydrogen peroxide, 1 x 10^{-6} *M*. Therefore, the **phosphoric acid** contributes more H_3O^+ to the solution.

18.156 a) Electrical conductivity of 0.1 *M* HCl is **higher** than that of 0.1 *M* CH_3COOH. Conductivity is proportional to the concentration of charge in the solution. Since HCl dissociates to a greater extent than CH_3COOH, the concentration of ions, and thus the charge, is greater in 0.1 *M* HCl than in 0.1 *M* CH_3COOH.
b) The electrical conductivity of the two solutions will be **approximately the same** because at low concentrations the autoionization of water is significant causing the concentration of ions, and thus the charge, to be about the same in the two solutions. In addition, the percent dissociation of a weak electrolyte such as acetic acid increases with decreasing concentration.

18.157 In step (1), the RCOOH is the Lewis base and the H^+ is the Lewis acid. In step (2), the $RC(OH)_2^+$ is the Lewis acid and the R'OH is the Lewis base.

18.158 a) pH = $-\log [H_3O^+]$
HCl is a strong acid so $[H_3O^+]$ = *M* HCl
pH = $-\log (0.10)$ = **1.00**
$HClO_2$ and HClO are weak acids requiring a K_a from the Appendix.

$$HClO(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + ClO^-(aq)$$
$$0.10 - x \qquad\qquad x \qquad\qquad x$$

$$K_a = 2.9 \text{ x } 10^{-8} = \frac{[H_3O^+][ClO^-]}{[HClO]}$$

$$K_a = 2.9 \text{ x } 10^{-8} = \frac{(x)(x)}{(0.10 - x)}$$ Assume x is small compared to 0.10.

$$K_a = 2.9 \text{ x } 10^{-8} = \frac{(x)(x)}{(0.10)}$$

$[H_3O^+]$ = x = 5.38516 x 10^{-5} (unrounded)
Check assumption: (5.38516 x 10^{-5} / 0.10) x 100% = 0.05%. The assumption is good.
pH = $-\log [H_3O^+]$ = $-\log$ (5.38516 x 10^{-5}) = 4.2688 = **4.27**

$$HClO_2(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + ClO_2^-(aq)$$
$$0.10 - x \qquad\qquad x \qquad\qquad x$$

$$K_a = 1.1 \text{ x } 10^{-2} = \frac{[H_3O^+][ClO_2^-]}{[HClO_2]}$$

$$K_a = 1.1 \text{ x } 10^{-2} = \frac{[x][x]}{[0.10 - x]}$$

The problem will need to be solved as a quadratic.
$x^2 = K_a (0.10 - x) = (1.1 \text{ x } 10^{-2})(0.10 - x) = 1.1 \text{ x } 10^{-3} - 1.1 \text{ x } 10^{-2}\, x$
$x^2 + 1.1 \text{ x } 10^{-2}\, x - 1.1 \text{ x } 10^{-3} = 0$
a = 1 b = 1.1 x 10^{-2} c = – 1.1 x 10^{-3}

$$x = \frac{-1.1 \text{ x } 10^{-2} \pm \sqrt{(1.1 \text{ x } 10^{-2})^2 - 4(1)(-1.1 \text{ x } 10^{-3})}}{2(1)}$$

x = 2.8119 x 10^{-2} *M* H_3O^+ (unrounded)
pH = $-\log [H_3O^+]$ = $-\log$ (2.8119 x 10^{-2}) = 1.550997 = **1.55**

b) The lowest H_3O^+ concentration is from the HClO. Leave the HClO beaker alone, and dilute the other acids until they yield the same H_3O^+ concentration. A dilution calculation is needed to calculate the amount of water added.

HCl $M_i = 0.10\ M$ $V_i = 100.\text{ mL}$ $M_f = 5.38516 \text{ x } 10^{-5}\ M$ $V_f = ?$

$M_iV_i = M_fV_f$

$V_f = M_iV_i / M_f = [(0.10\ M)\ (100.\text{ mL})] / (5.38516 \text{ x } 10^{-5}\ M) = 1.85695 \text{ x } 10^5\text{ mL}$

Volume water added = $(1.85695 \text{ x } 10^5\text{ mL}) - 100.\text{ mL} = 1.85595 \text{ x } 10^5 =$ **$1.9 \text{ x } 10^5$ mL H_2O added**

$HClO_2$ requires the K_a for the acid with the ClO_2^- concentration equal to the H_3O^+ concentration. The final molarity of the acid will be M_f, which may be used in the dilution equation.

$$\begin{array}{lllll} HClO_2(aq) & + \quad H_2O(l) & \leftrightarrows & H_3O^+(aq) & + \quad ClO_2^-(aq) \\ x - 5.38516 \text{ x } 10^{-5} & & & 5.38516 \text{ x } 10^{-5} & \quad 5.38516 \text{ x } 10^{-5} \end{array}$$

$$K_a = 1.1 \text{ x } 10^{-2} = \frac{\left[H_3O^+\right]\left[ClO_2^-\right]}{\left[HClO_2\right]}$$

$$K_a = 1.1 \text{ x } 10^{-2} = \frac{\left[5.38516 \text{ x } 10^{-5}\right]\left[5.38516 \text{ x } 10^{-5}\right]}{\left[x - 5.38516 \text{ x } 10^{-5}\right]}$$

$x = M_f = 5.41152 \text{ x } 10^{-5}\ M$ (unrounded)

$M_i = 0.10\ M$ $V_i = 100.\text{ mL}$ $M_f = 5.41152 \text{ x } 10^{-5}\ M$ $V_f = ?$

$M_iV_i = M_fV_f$

$V_f = M_iV_i / M_f = [(0.10\ M)\ (100.\text{ mL})] / (5.41152 \text{ x } 10^{-5}\ M) = 1.8479 \text{ x } 10^5\text{ mL}$

Volume water added = $(1.8479 \text{ x } 10^5\text{ mL}) - 100.\text{ mL} = 1.846 \text{ x } 10^5 =$ **$1.8 \text{ x } 10^5$ mL H_2O added**

18.159 Determine the hydrogen ion concentration from the pH. The molarity and the volume will give the number of moles, and with the aid of Avogadro's number, the number of ions may be found.

$M\ H_3O^+ = 10^{-pH} = 10^{-6.2} = 6.30957 \text{ x } 10^{-7}\ M$ (unrounded)

$$\left(\frac{6.30957 \text{ x } 10^{-7}\text{ mol } H_3O^+}{L}\right)\left(\frac{10^{-3}\text{ L}}{1\text{ mL}}\right)\left(\frac{1250.\text{mL}}{d}\right)\left(\frac{7\text{ d}}{1\text{ wk}}\right)\left(\frac{6.022 \text{ x } 10^{23}\ H_3O^+}{1\text{ mol } H_3O^+}\right) = 3.32467 \text{ x } 10^{18} = \mathbf{3 \text{ x } 10^{18}\ H_3O^+}$$

The pH has only one significant figure, and limits the significant figures in the final answer.

18.160 a) $2\ NH_3(l) \leftrightarrows NH_4^+(am) + NH_2^-(am)$

In this equilibrium "(*am*)" indicated ammoniated, solvated by ammonia, instead of "(*aq*)" to indicate aqueous, solvated by water.

Initially, based on the equilibrium: $K_c = \dfrac{\left[NH_4^+\right]\left[NH_2^-\right]}{\left[NH_3\right]^2}$

Since NH_3 is a liquid and a solvent:

$K_c\ [NH_3]^2 = \mathbf{K_{am} = [NH_4^+]\ [NH_2^-]}$

b) **Strongest acid = NH_4^+** **Strongest base = NH_2^-**

c) $NH_2^- > NH_4^+$: basic $NH_4^+ > NH_2^-$: acidic

$HNO_3\ (am) + NH_3(l) \rightarrow NH_4^+\ (am) + NO_3^-\ (am)$

$HCOOH\ (am) + NH_3(l) \rightarrow NH_4^+\ (am) + HCOO^-\ (am)$

HNO_3 is a strong acid in water while HCOOH is a weak acid in water. However, both acids are equally strong (i.e., their strengths are leveled) in NH_3 because they dissociate completely to form NH_4^+.

d) $K_{am} = [NH_4^+]\ [NH_2^-] = 5.1 \text{ x } 10^{-27}$

$[NH_4^+] = [NH_2^-] = x$

$K_{am} = [x]\ [x] = 5.1 \text{ x } 10^{-27}$

$x = 7.1414 \text{ x } 10^{-14} =$ **$7.1 \text{ x } 10^{-14}\ M\ NH_4^+$**

e) $2\ H_2SO_4(l) \leftrightarrows H_3SO_4^+(sa) + HSO_4^-(sa)$ (*sa*) = solvated by sulfuric acid (sulf)

$K_{sulf} = [H_3SO_4^+]\ [HSO_4^-] = 2.7 \text{ x } 10^{-4}$

$[H_3SO_4^+] = [HSO_4^-] = x$

$K_{sulf} = [x]\ [x] = 2.7 \text{ x } 10^{-4}$

$x = 1.643 \text{ x } 10^{-2} =$ **$1.6 \text{ x } 10^{-2}\ M\ HSO_4^-$**

18.161 Autoionization involves the transfer of an ion, usually H^+, from one molecule to another. This produces a solvated cation and anion characteristic of the liquid.

a) $CH_3OH(l) + CH_3OH(l) \leftrightarrows CH_3OH_2^+(solvated) + CH_3O^-\ (solvated)$

$K_{met} = [CH_3OH_2^+]\ [CH_3O^-] = (x)\ (x) = 2 \text{ x } 10^{-17}$

$x = [CH_3O^-] = \sqrt{2 \text{ x } 10^{-17}} = 4.4721 \text{ x } 10^{-9} = \mathbf{4 \text{ x } 10^{-9}}\ \boldsymbol{M}\ \mathbf{CH_3O^-}$

b) $2\ NH_2CH_2CH_2NH_2(l) \leftrightarrows NH_2CH_2CH_2NH_3^+(solvated) + NH_2CH_2CH_2NH^-\ (solvated)$

$[NH_2CH_2CH_2NH_3^+] = x = 2 \text{ x } 10^{-8}\ M$

$K_{ed} = [NH_2CH_2CH_2NH_3^+]\ [NH_2CH_2CH_2NH^-] = (x)\ (x)$

$K_{ed} = (2 \text{ x } 10^{-8})\ (2 \text{ x } 10^{-8}) = \mathbf{4 \text{ x } 10^{-16}}$

18.162 M is the unknown molarity of the thiamine.

$C_{12}H_{18}ON_4SCl_2(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + C_{12}H_{17}ON_4SCl_2^-(aq)$

$M - x$ x x

pH = 3.50

$[H_3O^+] = 10^{-3.50} = 3.162 \text{ x } 10^{-4}\ M$ (unrounded) = x

$$K_a = 3.37 \text{ x } 10^{-7} = \frac{\left[H_3O^+\right]\left[C_{12}H_{17}ON_4SCl_2^-\right]}{\left[C_{12}H_{18}ON_4SCl_2\right]}$$

$$K_a = 3.37 \text{ x } 10^{-7} = \frac{(x)(x)}{(M - x)}$$

$$K_a = 3.37 \text{ x } 10^{-7} = \frac{\left(3.162 \text{ x } 10^{-4}\right)\left(3.162 \text{ x } 10^{-4}\right)}{\left(M - 3.162 \text{ x } 10^{-4}\right)}$$

$M = 0.296999998\ M$ (unrounded)

$$\text{Mass} = \left(\frac{0.296999998 \text{ mol Thiamine HCl}}{\text{L}}\right)\left(\frac{10^{-3}\text{ L}}{1 \text{ mL}}\right)\left(10.00 \text{ mL}\right)\left(\frac{337.27 \text{ g Thiamine HCl}}{1 \text{ mol Thiamine HCl}}\right)$$

= 1.00169 = 1.0 g thiamine hydrochloride

18.163 Determine the K_b using the relationship: $K_b = 10^{pK} = 10^{-5.91} = 1.23027 \text{ x } 10^{-6}$

	TRIS(*aq*)	+ $H_2O(l)$	$\leftrightarrows$ $OH^-(aq)$	+ $HTRIS^+(aq)$
Initial	0.075	—	0	0
Change	–x	—	+x	+x
Equilibrium	0.075 – x	—	x	x

$$K_b = 1.23027 \text{ x } 10^{-6} = \frac{\left[HTRIS^+\right]\left[OH^-\right]}{[TRIS]}$$

$$K_b = 1.23027 \text{ x } 10^{-6} = \frac{[x][x]}{[0.075 - x]}$$ Assume x is small compared to 0.075.

$$K_b = 1.23027 \text{ x } 10^{-6} = \frac{[x][x]}{[0.075]}$$

$x = [OH^-] = 3.03760 \text{ x } 10^{-4}\ M\ OH^-$ (unrounded)

Check assumption: $[3.03760 \text{ x } 10^{-4} / 0.075] \text{ x } 100\% = 0.40\%$, therefore the assumption is good.

$[H_3O^+] = K_w / [OH^-] = (1.0 \text{ x } 10^{-14}) / (3.03760 \text{ x } 10^{-4}) = 3.292073 \text{ x } 10^{-11}\ M$ (unrounded)

$pH = -\log[H_3O^+] = -\log(3.292073 \text{ x } 10^{-11}) = 10.4825 = \mathbf{10.48}$

18.164 $Fe^{3+}(aq) + 6H_2O(l) \leftrightarrows Fe(H_2O)_6^{3+}(aq)$ Lewis acid-base reaction

$Fe(H_2O)_6^{3+}(aq) + H_2O(l) \leftrightarrows Fe(H_2O)_5OH^{2+}(aq) + H_3O^+(aq)$ Brønsted-Lowry acid-base reaction

18.165 The pH is dependent on the *molar* concentration of H_3O^+. Convert % w/v to molarity, and use the K_a of acetic acid to determine $[H_3O^+]$ from the equilibrium expression.

Convert % w/v to molarity using the molecular weight of acetic acid (CH_3COOH):

$$\text{Molarity} = \left(\frac{5.0\text{ g }CH_3COOH}{100\text{ mL Solution}}\right)\left(\frac{1\text{ mol }CH_3COOH}{60.05\text{ g }CH_3COOH}\right)\left(\frac{1\text{ mL}}{10^{-3}\text{ L}}\right) = 0.832639\ M\ CH_3COOH \text{ (unrounded)}$$

Acetic acid dissociates in water according to the following equation and equilibrium expression:

	$CH_3COOH(aq)$	$+ H_2O(l) \leftrightarrows$	$CH_3COO^-(aq)$	$+ H_3O^+(aq)$
Initial	0.832639	—	0	0
Change	–x	—	+x	+x
Equilibrium	0.832639 – x	—	x	x

$$K_a = 1.8 \times 10^{-5} = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

$$K_a = 1.8 \times 10^{-5} = \frac{[x][x]}{[0.832639 - x]}$$ Assume x is small compared to 0.832639.

$$K_a = 1.8 \times 10^{-5} = \frac{[x][x]}{[0.832639]}$$

$x = 3.871 \times 10^{-3} = [H_3O^+]$ (unrounded)

Check assumption: $[3.871 \times 10^{-3} / 0.832639] \times 100\% = 0.46\%$, therefore the assumption is good.

$pH = -\log [H_3O^+] = -\log (3.871 \times 10^{-3}) = 2.4121768 = \mathbf{2.41}$

18.166 a) The strong acid solution would have a larger electrical conductivity.

b) The strong acid solution would have a lower pH.

c) The strong acid solution would bubble more vigorously.

18.167 a) $K_w = [H_3O^+][OH^-] = (x)(x) = 5.19 \times 10^{-14}$

$x = [H_3O^+] = 2.278 \times 10^{-7} = \mathbf{2.28 \times 10^{-7}\ M\ H_3O^+}$

b) $K_w = [H_3O^+][OH^-] = (x)(0.010) = 5.19 \times 10^{-14}$

$[H_3O^+] = K_w / [OH^-] = (5.19 \times 10^{-14}) / (0.010) = 5.19 \times 10^{-12} = \mathbf{5.2 \times 10^{-12}\ M\ H_3O^+}$

c) $K_w = [H_3O^+][OH^-] = (0.0010)(x) = 5.19 \times 10^{-14}$

$[OH^-] = K_w / [H_3O^+] = (5.19 \times 10^{-14}) / (0.0010) = 5.19 \times 10^{-11} = \mathbf{5.2 \times 10^{-11}\ M\ OH^-}$

d) $K_w = [H_3O^+][OH^-] = (x)(0.0100) = 1.10 \times 10^{-12}$

$[H_3O^+] = K_w / [OH^-] = (1.10 \times 10^{-12}) / (0.0100) = \mathbf{1.10 \times 10^{-10}\ M\ H_3O^+}$

e) $[H_3O^+][OH^-] = K_w = 1.10 \times 10^{-12}$

$[H_3O^+] = [OH^-] = x$

$x = [H_3O^+] = 1.0488 \times 10^{-6}\ M\ H_3O^+$

$pH = -\log [H_3O^+] = -\log (1.0488 \times 10^{-6}) = 5.979307 = \mathbf{5.979}$

18.168 Assuming that the pH in the specific cellular environment is equal to the optimum pH for the enzyme, the hydronium ion concentrations are $[H_3O^+] = 10^{-pH}$

Salivary amylase, mouth: $[H_3O^+] = 10^{-6.8} = 1.58489 \times 10^{-7} = \mathbf{2 \times 10^{-7}\ M}$

Pepsin, stomach: $[H_3O^+] = 10^{-2.0} = \mathbf{1 \times 10^{-2}\ M}$

Trypsin, pancreas: $[H_3O^+] = 10^{-9.5} = 3.162 \times 10^{-10} = \mathbf{3 \times 10^{-10}\ M}$

18.169 a) $CH_3COOH(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CH_3COO^-(aq)$

0.240 – x x x

$$K_a = 1.8 \times 10^{-5} = \frac{(H_3O^+)(CH_3COO^-)}{(CH_3COOH)}$$

$$K_a = 1.8 \times 10^{-5} = \frac{(x)(x)}{(0.240 - x)}$$ Assume x is small compared to 0.240.

$K_a = 1.8 \times 10^{-5} = \dfrac{(x)(x)}{(0.240)}$

$x = 2.07846 \times 10^{-3}$ (unrounded)

Check assumption: $[2.07846 \times 10^{-3} / 0.240] \times 100\% = 0.9\%$, therefore the assumption is good.

$x = [H_3O^+] = 2.07846 \times 10^{-3} =$ **2.1×10^{-3} *M* H_3O^+**

$[OH^-] = K_w / [H_3O^+] = (1.0 \times 10^{-14}) / (2.07846 \times 10^{-3}) = 4.81125 \times 10^{-12} =$ **4.8×10^{-12} *M* OH^-**

$pH = -\log [H_3O^+] = -\log (2.07846 \times 10^{-3}) = 2.682258 =$ **2.68**

$pOH = -\log [OH^-] = -\log (4.81125 \times 10^{-12}) = 11.317742 =$ **11.32**

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

$0.240 - x \qquad x \qquad x$

$K_b = 1.8 \times 10^{-5} = \dfrac{(NH_4^+)(OH^-)}{(NH_3)}$

$K_b = 1.8 \times 10^{-5} = \dfrac{(x)(x)}{(0.240 - x)}$ Assume x is small compared to 0.240.

$K_b = 1.8 \times 10^{-5} = \dfrac{(x)(x)}{(0.240)}$

$x = 2.07846 \times 10^{-3}$ (unrounded)

Check assumption: $[2.07846 \times 10^{-3} / 0.240] \times 100\% = 0.9\%$, therefore the assumption is good.

$x = [OH^-] = 2.07846 \times 10^{-3} =$ **2.1×10^{-3} *M* OH^-**

$[H_3O^+] = K_w / [OH^-] = (1.0 \times 10^{-14}) / (2.07846 \times 10^{-3}) = 4.81125 \times 10^{-12} =$ **4.8×10^{-12} *M* H_3O^+**

$pOH = -\log [OH^-] = -\log (2.07846 \times 10^{-3}) = 2.682258 =$ **2.68**

$pH = -\log [H_3O^+] = -\log (4.81125 \times 10^{-12}) = 11.317742 =$ **11.32**

18.170 Concentration $= M = \left(\dfrac{33\text{ g Na}_3\text{PO}_4}{1\text{ L}}\right)\left(\dfrac{1\text{ mol Na}_3\text{PO}_4}{163.94\text{ g Na}_3\text{PO}_4}\right)\left(\dfrac{1\text{ mol PO}_4^{3-}}{1\text{ mol Na}_3\text{PO}_4}\right) = 0.20129\ M\ PO_4^{3-}$ (unrounded)

$PO_4^{3-}(aq) + H_2O(l) \leftrightarrows OH^-(aq) + HPO_4^{2-}(aq)$ (Use K_{a3} for H_3PO_4)

$K_b = K_w / K_a = (1.0 \times 10^{-14}) / (4.2 \times 10^{-13}) = 0.0238095$ (unrounded)

$K_b = 0.0238095 = \dfrac{(HPO_4^{2-})(OH^-)}{(PO_4^{3-})}$

$K_b = 0.0238095 = \dfrac{(x)(x)}{(0.20129 - x)}$

A quadratic is required.

$x^2 + 0.0238095\,x - 0.00479261 = 0$

$a = 1 \qquad b = 0.0238095 \qquad c = -0.00479261$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-0.0238095 \pm \sqrt{(0.0238095)^2 - 4(1)(-0.00479261)}}{2(1)}$$

$x = 0.058340 =$ **0.058 *M* OH^-**

$[H_3O]^+ = K_w / [OH^-] = (1.0 \times 10^{-14}) / (0.058340) = 1.7140898 \times 10^{-13}\ M\ H_3O^+$ (unrounded)

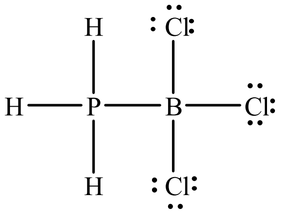
$pH = -\log [H_3O^+] = -\log (1.7140898 \times 10^{-13}) = 12.765966 =$ **12.77**

18.171 a) $PH_3BCl_3(s) \leftrightarrows PH_3(g) + BCl_3(g)$

$x = [PH_3] = [BCl_3]$

$K_c = [PH_3][BCl_3] = (x)(x) = x^2 = [8.4 \times 10^{-3} / 3.0\text{ L}]^2 = 7.84 \times 10^{-6} =$ **7.8×10^{-6}**

b)



18.172 The freezing point depression equation is required to determine the molality of the solution.

$\Delta T = [0.00 - (-1.93°C)] = 1.93°C = = iK_f m$

Temporarily assume i = 1.

$$m = \frac{\Delta T}{iK_f} = \frac{1.93^\circ C}{(1)(1.86^\circ C/m)} = 1.037634\ m = 1.037634\ M \text{ (unrounded)}$$

This molality is the total molality of all species in the solution, and is equal to their molarity.

From the equilibrium:

	$ClCH_2COOH(aq) + H_2O(l) \leftrightarrows$	$H_3O^+(aq)$	$+ ClCH_2COO^-(aq)$
Initial	1.000 M	x	x
Change	–x	+x	+x
Equilibrium	1.000 – x	x	x

The total concentration of all species is:

$[ClCH_2COOH] + [H_3O^+] + [ClCH_2COO^-] = 1.037634\ M$

$[1.000 - x] + [x] + [x] = 1.000 + x = 1.037634\ M$

$x = 0.037634\ M$ (unrounded)

$$K_a = \frac{\left[H_3O^+\right]\left[CH_3COO^-\right]}{\left[CH_3COOH\right]}$$

$$K_a = \frac{(0.037634)(0.037634)}{(1.000 - 0.037634)} = 0.0014717 = \mathbf{0.00147}$$

18.173 $$\text{Molarity} = \left(\frac{0.42\text{ g } C_{17}H_{35}COONa}{10.0\text{ mL}}\right)\left(\frac{1\text{ mL}}{10^{-3}\text{ L}}\right)\left(\frac{1\text{ mol } C_{17}H_{35}COONa}{306.45\text{ g } C_{17}H_{35}COONa}\right)\left(\frac{1\text{ mol } C_{17}H_{35}COO^-}{1\text{ mol } C_{17}H_{35}COONa}\right)$$

$= 0.137053\ M\ C_{17}H_{35}COO^-$ (unrounded)

$K_b = K_w / K_a = (1.0 \times 10^{-14}) / (1.3 \times 10^{-5}) = 7.6923 \times 10^{-10}$ (unrounded)

$$K_b = 7.6923 \times 10^{-10} = \frac{\left[C_{17}H_{35}COOH\right]\left[OH^-\right]}{\left[C_{17}H_{35}COO^-\right]}$$

$$K_b = 7.6923 \times 10^{-10} = \frac{(x)(x)}{(0.137053 - x)}$$ Assume x is small compared to 0.137053.

$$K_b = 7.6923 \times 10^{-10} = \frac{(x)(x)}{(0.137053)}$$

$x = 1.026768 \times 10^{-5} = [OH^-]$ (unrounded)

Check assumption: $[1.026768 \times 10^{-5} / 0.137053] \times 100\% = 0.007\%$, therefore the assumption is good.

$[H_3O]^+ = K_w / [OH^-] = (1.0 \times 10^{-14}) / (1.026768 \times 10^{-5}) = 9.739298 \times 10^{-10}\ M\ H_3O^+$ (unrounded)

$pH = -\log [H_3O^+] = -\log (9.739298 \times 10^{-10}) = 9.01147 = \mathbf{9.01}$

18.174 a) The two ions that comprise this salt are Ca^{2+} (derived from the strong base $Ca(OH)_2$) and $CH_3CH_2COO^-$ (derived from the weak acid, propionic acid, CH_3CH_2COOH). A salt derived from a strong base and weak acid produces a **basic** solution.

Ca^{2+} does not react with water.

$CH_3CH_2COO^-(aq) + H_2O(l) \leftrightarrows CH_3CH_2COOH(aq) + OH^-(aq)$

b) Calcium propionate is a soluble salt and dissolves in water to yield two propionate ions:

$Ca(CH_3CH_2COO)_2(s) + H_2O(l) \rightarrow Ca^{2+}(aq) + 2\ CH_3CH_2COO^-(aq)$

The molarity of the solution is:

$$\text{Molarity} = \left(\frac{8.75\text{ g Ca(CH}_3\text{CH}_2\text{COO)}_2}{0.500\text{ L}}\right)\left(\frac{1\text{ mol Ca(CH}_3\text{CH}_2\text{COO)}_2}{186.22\text{ g Ca(CH}_3\text{CH}_2\text{COO)}_2}\right)\left(\frac{2\text{ mol CH}_3\text{CH}_2\text{COO}^-}{1\text{ mol Ca(CH}_3\text{CH}_2\text{COO)}_2}\right)$$

$= 0.1879497\ M\ CH_3CH_2COO^-$ (unrounded)

	$CH_3CH_2COO^-$	+ H_2O $\leftrightarrows$	CH_3CH_2COOH	+ OH^-
Initial	0.1879497 M		0	0
Change	–x		+x	+x
Equilibrium	0.1879497 – x		x	x

$K_b = K_w / K_a = (1.0 \times 10^{-14}) / (1.3 \times 10^{-5}) = 7.6923 \times 10^{-10}$ (unrounded)

$$K_b = 7.6923 \times 10^{-10} = \frac{[CH_3CH_2COOH][OH^-]}{[CH_3CH_2COO^-]}$$

$$K_b = 7.6923 \times 10^{-10} = \frac{(x)(x)}{(0.1879497 - x)} \qquad \text{Assume x is small compared to 0.1879497.}$$

$$K_b = 7.6923 \times 10^{-10} = \frac{(x)(x)}{(0.1879497)}$$

$x = 1.20239988 \times 10^{-5} = [OH^-]$ (unrounded)

Check assumption: $[1.20239988 \times 10^{-5} / 0.1879497] \times 100\% = 0.006\%$, therefore the assumption is good.

$[H_3O]^+ = K_w / [OH^-] = (1.0 \times 10^{-14}) / (1.20239988 \times 10^{-5}) = 8.31671 \times 10^{-10}\ M\ H_3O^+$ (unrounded)

$pH = -\log [H_3O^+] = -\log (8.31671 \times 10^{-10}) = 9.0800 = \mathbf{9.08}$

18.175 a) Annual depositions:

$$(NH_4)_2SO_4\text{:} \quad \left(\frac{3.0\ (NH_4)_2SO_4}{9.5\text{ total}}\right)(2.688\text{ g/m}^2) = 0.8488421 = 0.85\text{ g/m}^2$$

$$NH_4HSO_4\text{:} \quad \left(\frac{5.5\ NH_4HSO_4}{9.5\text{ total}}\right)(2.688\text{ g/m}^2) = 1.55621 = 1.56\text{ g/m}^2$$

$$H_2SO_4\text{:} \quad \left(\frac{1.0\ H_2SO_4}{9.5\text{ total}}\right)(2.688\text{ g/m}^2) = 0.282947 = 0.28\text{ g/m}^2$$

$(NH_4)_2SO_4$ is a weak acid; NH_4HSO_4 has half the acidity per mole as H_2SO_4 so the equivalent amount of sulfuric acid deposition would be:

$$\left(\frac{1.56\text{ g NH}_4\text{HSO}_4}{\text{m}^2}\right)\left(\frac{0.50\text{ M NH}_4\text{HSO}_4}{1\text{ M H}_2\text{SO}_4}\right)\left(\frac{98.1\text{ g H}_2\text{SO}_4}{115.1\text{ g NH}_4\text{HSO}_4}\right) = 0.664796\text{ g/m}^2$$

Total as sulfuric acid = 0.66 g/m^2 + 0.28 g/m^2 = 0.94 g/m^2

$$\left(\frac{0.94\text{ g H}_2\text{SO}_4}{\text{m}^2}\right)(10.\text{ km}^2)\left(\frac{1000\text{ m}}{1\text{ km}}\right)^2\left(\frac{1\text{ kg}}{1000\text{ g}}\right) = \mathbf{9.4 \times 10^3\ kg}$$

b) $H_2SO_4(aq) + CaCO_3(s) \rightarrow H_2O(l) + CO_2(g) + CaSO_4(s)$

There is a 1:1 mole ratio between H_2SO_4 and $CaCO_3$.

$$(9.4 \times 10^3\text{ kg H}_2\text{SO}_4)\left(\frac{1000\text{ g}}{1\text{ kg}}\right)\left(\frac{1\text{ mol H}_2\text{SO}_4}{98.1\text{ g H}_2\text{SO}_4}\right)\left(\frac{1\text{ mol CaCO}_3}{1\text{ mol H}_2\text{SO}_4}\right)\left(\frac{100.1\text{ g CaCO3}}{1\text{ mol CaCO3}}\right)\left(\frac{2.205\text{ lb}}{1000\text{ g}}\right)$$

$= 2.1150 \times 10^4 = \mathbf{2.1 \times 10^4\ lb\ CaCO_3}$

c) Moles of H^+= $$\left(9.4 \text{ x } 10^3 \text{ kg } H_2SO_4\right)\left(\frac{1000 \text{ g}}{1 \text{ kg}}\right)\left(\frac{1 \text{ mol } H_2SO_4}{98.1 \text{ g } H_2SO_4}\right)\left(\frac{2 \text{ mol } H^+}{1 \text{ mol } H_2SO_4}\right) = 1.91641 \text{ x } 10^5 \text{ mol } H^+$$

Volume of lake = $$\left(10.\text{ km}^2\right)\left(\frac{1000 \text{ m}}{1 \text{ km}}\right)^2 \left(3 \text{ m}\right)\left(\frac{1 \text{ L}}{10^{-3} \text{ m}^3}\right) = 3.0 \text{ x } 10^{10} \text{ L}$$

Molarity of H^+ = $$\frac{1.91641 \text{ x } 10^5 \text{ mol } H^+}{3.0 \text{ x } 10^{10} \text{ L}} = 6.3880 \text{ x } 10^{-6} \text{ M}$$

pH = –log [H^+] = –log (6.3880 x 10^{-6}) = 5.1946 = **5.19**

18.176 a) 0°C $K_w = [H_3O^+] [OH^-]$ = (x) (x) = 1.139 x 10^{-15}
x = $[H_3O^+]$ = 3.374907 x 10^{-8} = **3.375 x 10^{-8} *M* H_3O^+**
pH = –log $[H_3O^+]$ = –log (3.374907 x 10^{-8}) = 7.471730 = **7.4717**
50°C $K_w = [H_3O^+] [OH^-]$ = (x) (x) = 5.474 x 10^{-14}
x = $[H_3O^+]$ = 2.339658 x 10^{-7} = **2.340 x 10^{-7} *M* H_3O^+**
pH = –log $[H_3O^+]$ = –log (2.339658 x 10^{-7}) = 6.6308476 = **6.6308**
b) 0°C $K_w = [D_3O^+] [OD^-]$ = (x) (x) = 3.64 x 10^{-16}
x = $[D_3O^+]$ = 1.907878 x 10^{-8} = **1.91 x 10^{-8} *M* D_3O^+**
pH = –log $[D_3O^+]$ = –log (1.907878 x 10^{-8}) = 7.719449 = **7.719**
50°C $K_w = [D_3O^+] [OD^-]$ = (x) (x) = 7.89 x 10^{-15}
x = $[D_3O^+]$ = 8.882567 x 10^{-8} = **8.88 x 10^{-8} *M* D_3O^+**
pH = –log $[D_3O^+]$ = –log (8.882567 x 10^{-8}) = 7.0514615 = **7.051**
c) The deuterium atom has twice the mass of a normal hydrogen atom. The deuterium atom is held more strongly to the oxygen atom, so the degree of ionization is decreased.

18.177 Molarity of HX = $$\left(\frac{12.0 \text{ g HX}}{\text{L}}\right)\left(\frac{1 \text{ mol HX}}{150. \text{ g HX}}\right) = 0.0800\ M \text{ HX}$$

Molarity of HY = $$\left(\frac{6.00 \text{ g HY}}{\text{L}}\right)\left(\frac{1 \text{ mol HY}}{50.0 \text{ g HY}}\right) = 0.120\ M \text{ HY}$$

HX must be the stronger acid because lower concentration of HX has the same pH (it produces the same number of H^+ ions) as a higher concentration of HY.

18.178 Acid HA: $HA(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + A^-(aq)$

$$K_a = \frac{\left[\frac{0.010 \text{ mol}}{0.50 \text{ L}}\right]\left[\frac{0.010 \text{ mol}}{0.50 \text{ L}}\right]}{\left[\frac{0.050 \text{ mol}}{0.50 \text{ L}}\right]} = \mathbf{4.0 \text{ x } 10^{-3}}$$

Acid HB: $HB(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + B^-(aq)$

$$K_a = \frac{\left[\frac{0.010 \text{ mol}}{0.25 \text{ L}}\right]\left[\frac{0.010 \text{ mol}}{0.25 \text{ L}}\right]}{\left[\frac{0.040 \text{ mol}}{0.25 \text{ L}}\right]} = \mathbf{1.0 \text{ x } 10^{-2}}$$

Acid HB, with the larger K_a value, is the stronger acid.

18.179 Treat $H_3O^+(aq)$ as $H^+(aq)$ because this corresponds to the listing in the Appendix.
a) $K^+(aq) + OH^-(aq) + H^+(aq) + NO_3^-(aq) \rightarrow K^+(aq) + NO_3^-(aq) + H_2O(l)$
Net ionic equation: $OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$
$Na^+(aq) + OH^-(aq) + H^+(aq) + Cl^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$
Net ionic equation: $OH^-(aq) + H^+(aq) \rightarrow H_2O(l)$
ΔH°_{neut} = [1 mol (ΔH_f°, $H_2O(l)$)] – [1 mol (ΔH_f°, $H^+(aq)$) + 1 mol (ΔH_f°, OH^- (aq))]
= [1 mol (–285.840 kJ/mol)] – [1 mol (0 kJ/mol) + 1 mol (–229.94 kJ/mol)]
= **– 55.90 kJ**

b) The neutralization reaction of a strong acid and a strong base is essentially the reaction between $H^+(aq)$ and $OH^-(aq)$ to form $H_2O(l)$. Therefore, $\Delta H°_{neut}$ for KOH and HCl would be expected to be **-55.90 kJ**.

18.180 Putrescine can be abbreviated to $NH_2(CH_2)_4NH_2$. Its reaction in water is written as follows:

$$NH_2(CH_2)_4NH_2(aq) + H_2O(l) \leftrightarrows NH_2(CH_2)_4NH_3^+(aq) + OH^-(aq)$$

0.10 – x x x

$x = [OH^-] = 2.1 \times 10^{-3}$

$$K_b = \frac{[NH_2(CH_2)_4NH_3^+][OH^-]}{[NH_2(CH_2)_4NH_2]} = \frac{[2.1 \times 10^{-3}][2.1 \times 10^{-3}]}{[0.10 - 2.1 \times 10^{-3}]} = 4.5045965 \times 10^{-5} = \mathbf{4.5 \times 10^{-5}}$$

18.181 a) There are 20 OH^- ions for every 2 H_3O^+ ions; in other words, $[OH^-] = 10 \times [H_3O^+]$

$Kw = 1.0 \times 10^{-14} = [H_3O^+][OH^-]$

$1.0 \times 10^{-14} = [H_3O^+](10)[H_3O^+]$

$[H_3O^+] = 3.16 \times 10^{-8}$ M

$pH = -\log [H_3O^+] = -\log (3.16 \times 10^{-8}) = \mathbf{7.5}$

b) For a pH of 4, $[H_3O^+] = 10^{-pH} = 10^{-4} = 1.0 \times 10^{-4}$ M

$[OH^-] = K_w / [H_3O^+] = (1.0 \times 10^{-14}) / (1.0 \times 10^{-4}) = 1.0 \times 10^{-10}$ *M* OH^-

$[H_3O^+]/[OH^-] = 1.0 \times 10^{-4}/1.0 \times 10^{-10} = 1.0 \times 10^6$

The H_3O^+ concentration is 1 million times greater than that of OH^-. You would have to draw one million H_3O^+ ions for every one OH^-.

18.182 a) As the pH of a water solution containing casein increases, the H^+ ions from the carboxyl groups on casein will be removed. This will increase the number of charged groups, and the solubility of the casein will increase.

b) As the pH of a water solution containing histones decreases, $-NH_2$ and =NH groups will accept H^+ ions from solution. This will increase the number of charged groups, and the solubility of the histones will increase.

18.183 a) The concentration of oxygen is higher in the lungs so the equilibrium shifts to the right.

b) In an oxygen deficient environment, the equilibrium would shift to the left to release oxygen.

c) A decrease in the $[H_3O^+]$ concentration would shift the equilibrium to the right. More oxygen is absorbed, but it will be more difficult to remove the O_2.

d) An increase in the $[H_3O^+]$ concentration would shift the equilibrium to the left. Less oxygen is absorbed, but it will be easier to remove the O_2.

18.184 a) Convert the w/v % to molarity:

$$\left(\frac{5.0 \text{ g } H_2C_6H_6O_6}{100 \text{ mL Solution}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\frac{1 \text{ mol } H_2C_6H_6O_6}{176.12 \text{ g } H_2C_6H_6O_6}\right) = 0.283897\ M\ H_2C_6H_6O_6 \text{ (unrounded)}$$

$$H_2C_6H_6O_6(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + HC_6H_6O_6^-(aq)$$

0.283897 – x x x

Assuming all the H_3O^+ comes from this equilibrium:

$x = [H_3O^+] = 10^{-pH} = 10^{-2.77} = 1.69824 \times 10^{-3}$ *M* H_3O^+ (unrounded)

$$K_{a1} = \frac{[H_3O^+][HC_6H_6O_6^-]}{[H_2C_6H_6O_6]}$$

$$K_{a1} = \frac{(1.69824 \times 10^{-3})(1.69824 \times 10^{-3})}{(0.283897 - 1.69824 \times 10^{-3})} = 1.02198 \times 10^{-5} = \mathbf{1.0 \times 10^{-5}}$$

b) $K_b = K_w / K_a = (1.0 \times 10^{-14}) / (1.02198 \times 10^{-5}) = 9.7849 \times 10^{-10}$ (unrounded)

$$\left(\frac{10.0 \text{ g } NaHC_6H_6O_6}{1 \text{ L Solution}}\right)\left(\frac{1 \text{ mol } NaHC_6H_6O_6}{198.10 \text{ g } NaHC_6H_6O_6}\right)\left(\frac{1 \text{ mol } HC_6H_6O_6^-}{1 \text{ mol } NaHC_6H_6O_6}\right)$$

$= 0.050479555$ *M* $H_2C_6H_6O_6$ (unrounded)

$$K_b = 9.7849 \text{ x } 10^{-10} = \frac{\left[H_2C_6H_6O_6\right]\left[OH^-\right]}{\left[HC_6H_6O_6^{\ -}\right]}$$

$$K_b = 9.7849 \text{ x } 10^{-10} = \frac{(x)(x)}{(0.050479555 \ - \ x)}$$ Assume x is small compared to 0.050479555.

$$K_b = 9.7849 \text{ x } 10^{-10} = \frac{(x)(x)}{(0.050479555)} = 7.028068 \text{ x } 10^{-6} = [OH^-] \text{ (unrounded)}$$

Check assumption: [7.028068 x 10^{-6} / 0.050479555] x 100% = 0.01%, therefore, the assumption is good.

$[H_3O]^+ = K_w / [OH^-] = (1.0 \text{ x } 10^{-14}) / (7.028068 \text{ x } 10^{-6}) = 1.422866 \text{ x } 10^{-9}$ M H_3O^+ (unrounded)

pH = –log $[H_3O^+]$ = –log (1.422866 x 10^{-9}) = 8.8468 = **8.85**

18.185 a) The amine acts as a Lewis base as the unshared pair of electrons on the nitrogen atom is donated to the electron deficient carbon atom in the acid chloride. The acid chloride behaves as the Lewis acid.

b) Ammonia is a stronger base than water so ammonia would react faster.

18.186 a) Calculate the molarity of the solution

$$M = \left(\frac{7.500 \text{ g } CH_3CH_2COOH}{100.0 \text{ mL solution}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\frac{1 \text{ mol } CH_3CH_2COOH}{74.08 \text{ g } CH_3CH_2COOH}\right)$$

= 1.012419 = **1.012 M CH_3CH_2COOH**

b) The freezing point depression equation is required to determine the molality of the solution.

$\Delta T = iK_fm$ = [0.000 – (–1.890°C)] = 1.890°C

Temporarily assume i = 1.

$m = \Delta T / iK_f$ = (1.890°C) / [(1) (1.86°C/m] = 1.016129032 m = 1.016129032 M (unrounded)

This molality is the total molality of all species in the solution, and is equal to their molarity.

From the equilibrium:

$$CH_3CH_2COOH(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + CH_3CH_2COO^-(aq)$$

1.012419 – x   x   x

The total concentration of all species is:

$[ClCH_2COOH] + [H_3O^+] + [ClCH_2COO^-] = 1.016129032$ M

[1.012419 - x] + [x] + [x] = 1.012419 + x = 1.016129032 M

x = 0.00371003 = **0.004 M $CH_3CH_2COO^-$**

c) The percent dissociation is the amount dissociated (x from part b) divided by the original concentration from part a.

$$\text{Percent dissociation} = \frac{(0.00371003 \text{ M})}{(1.012419 \text{ M})} \text{ x } 100\% = 0.366452 = \mathbf{0.4\%}$$

18.187 Note that both pK_b values only have one significant figure. This will limit the final answers.

$K_{b \text{ (tertiary amine N)}} = 10^{-pK_b} = 10^{-5.1} = 7.94328 \text{ x } 10^{-6}$ (unrounded)

$K_{b \text{ (aromatic ring N)}} = 10^{-pK_b} = 10^{-9.7} = 1.995262 \text{ x } 10^{-10}$ (unrounded)

a) Ignoring the smaller K_b:

	$C_{20}H_{24}N_2O_2(aq) + H_2O(l) \leftrightarrows$	$OH^-(aq)$ +	$HC_{20}H_{24}N_2O_2^+(aq)$
Initial	1.6 x 10^{-3} M	0	0
Change	–x	+x	+x
Equilibrium	1.6 x 10^{-3} – x	x	x

$$K_b = \frac{\left[HC_{20}H_{24}N_2O_2^{\ +}\right]\left[OH^-\right]}{\left[H_2C_{20}H_{24}N_2O_2\right]} = 7.94328 \text{ x } 10^{-6}$$

$$K_b = \frac{[x][x]}{\left[1.6 \text{ x } 10^{-3} \ - \ x\right]} = 7.94328 \text{ x } 10^{-6}$$

The problem will need to be solved as a quadratic.

$x^2 = (7.94328 \text{ x } 10^{-6})\ (1.6 \text{ x } 10^{-3} - x) = 1.27092 \text{ x } 10^{-8} - 7.94328 \text{ x } 10^{-6}\ x$

$x^2 + 7.94328 \text{ x } 10^{-6}\ x - 1.27092 \text{ x } 10^{-8} = 0$

$a = 1 \quad b = 7.94328 \text{ x } 10^{-6} \quad c = -1.27092 \text{ x } 10^{-8}$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-7.94328 \text{ x } 10^{-6} \pm \sqrt{\left(7.94328 \text{ x } 10^{-6}\right)^2 - 4(1)\left(-1.27092 \text{ x } 10^{-8}\right)}}{2(1)} = 1.08833 \text{ x } 10^{-4}\ M\ OH^-$$

$$[H_3O]^+ = \frac{K_w}{[OH^-]} = \frac{1.0 \text{ x } 10^{-14}}{1.08833 \text{ x } 10^{-4}} = 9.18838955 \text{ x } 10^{-11}\ M\ H_3O^+ \text{ (unrounded)}$$

$pH = -\log [H_3O^+] = -\log (9.18838955 \text{ x } 10^{-11}) = 10.03676 = \mathbf{10.0}$

b) (Assume the aromatic N is unaffected by the tertiary amine N.) Use the K_b value for the aromatic nitrogen.

$C_{20}H_{24}N_2O_2(aq) + H_2O(l) \leftrightarrows OH^-(aq) + HC_{20}H_{24}N_2O_2^+(aq)$

$1.6 \text{ x } 10^{-3} - x \qquad\qquad x \qquad\qquad x$

$$K_b = \frac{\left[HC_{20}H_{24}N_2O_2^+\right]\left[OH^-\right]}{\left[C_{20}H_{24}N_2O_2\right]} = 1.995262 \text{ x } 10^{-10}$$

$$K_b = \frac{[x][x]}{\left[1.6 \text{ x } 10^{-3} - x\right]} = 1.995262 \text{ x } 10^{-10}$$ Assume x is small compared to $1.6 \text{ x } 10^{-3}$.

$$K_b = \frac{[x][x]}{\left[1.6 \text{ x } 10^{-3}\right]} = 1.995262 \text{ x } 10^{-10}$$

$x = 5.6501 \text{ x } 10^{-7}\ M\ OH^-$ (unrounded)

The hydroxide ion from the smaller K_b is much smaller than the hydroxide ion from the larger K_b (compare the powers of ten in the concentration).

c) $HC_{20}H_{24}N_2O_2^+(aq) + H_2O(l) \leftrightarrows H_3O^+(aq) + C_{20}H_{24}N_2O_2(aq)$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \text{ x } 10^{-14}}{7.94328 \text{ x } 10^{-6}} = 1.2589 \text{ x } 10^{-9} \text{ (unrounded)}$$

$$K_a = 1.2589 \text{ x } 10^{-9} = \frac{\left[H_3O^+\right]\left[C_{20}H_{24}N_2O_2\right]}{\left[HC_{20}H_{24}N_2O_2^+\right]}$$

$$K_a = 1.2589 \text{ x } 10^{-9} = \frac{(x)(x)}{(0.33 - x)}$$ Assume x is small compared to 0.33.

$$K_a = 1.2589 \text{ x } 10^{-9} = \frac{(x)(x)}{(0.33)}$$

$[H_3O^+] = x = 2.038248 \text{ x } 10^{-5}$ (unrounded)

Check assumption: $(2.038248 \text{ x } 10^{-5} / 0.33) \text{ x } 100\% = 0.006\%$. The assumption is good.

$pH = -\log [H_3O^+] = -\log (2.038248 \text{ x } 10^{-5}) = 4.69074 = \mathbf{4.7}$

d) Quinine hydrochloride will be indicated as QHCl.

$$M = \left(\frac{1.5\%}{100\%}\right)\left(\frac{1.0 \text{ g}}{\text{mL}}\right)\left(\frac{1 \text{ mL}}{10^{-3} \text{ L}}\right)\left(\frac{1 \text{ mol QHCl}}{360.87 \text{ g QHCl}}\right) = 0.041566\ M \text{ (unrounded)}$$

$$K_a = 1.2589 \text{ x } 10^{-9} = \frac{\left[H_3O^+\right]\left[C_{20}H_{24}N_2O_2\right]}{\left[HC_{20}H_{24}N_2O_2^+\right]}$$

$$K_a = 1.2589 \text{ x } 10^{-9} = \frac{(x)(x)}{(0.041566 - x)}$$ Assume x is small compared to 0.041566.

$$K_a = 1.2589 \text{ x } 10^{-9} = \frac{(x)(x)}{(0.041566)}$$

$[H_3O^+] = x = 7.23377 \text{ x } 10^{-6}$ (unrounded)

Check assumption: $(7.23377 \text{ x } 10^{-6} / 0.041566) \text{ x } 100\% = 0.02\%$. The assumption is good.

$\text{pH} = -\log [H_3O^+] = -\log (7.23377 \text{ x } 10^{-6}) = 5.1406 = \mathbf{5.1}$

18.188 a) At pH = 7.00, $[H_3O^+] = 10^{-pH} = 10^{-7.00} = 1.0 \text{ x } 10^{-7}\ M$

$$\frac{[HOCl]}{[HOCl] + [OCl^-]} = \frac{K_a}{[H_3O^+] + K_a}$$

$$\frac{[HOCl]}{[HOCl] + [OCl^-]} = \frac{2.9 \text{ x} 1\,0^{-8}}{1.0 \text{ x } 10^{-7} + 2.9 \text{ x } 10^{-8}} = 0.224806 = \mathbf{0.22}$$

b) At pH = 10.00, $[H_3O^+] = 10^{-pH} = 10^{-10.00} = 1.0 \text{ x } 10^{-10}\ M$

$$\frac{[HOCl]}{[HOCl] + [OCl^-]} = \frac{K_a}{[H_3O^+] + K_a}$$

$$\frac{[HOCl]}{[HOCl] + [OCl^-]} = \frac{2.9 \text{ x } 10^{-8}}{1.0 \text{ x } 10^{-10} + 2.9 \text{ x } 10^{-8}} = 0.99656 = \mathbf{1.0}$$

18.189 a) All boxes indicate equal initial amounts of each acid. The more H_3O^+ present, the stronger the acid is (greater K_a).

Increasing K_a: **HX < HZ < HY**

b) The pK_a values increase in order of decreasing K_a values.

Increasing pK_a: **HY < HZ < HX**

c) The order of pK_b is always the reverse of pK_a values:

Increasing pK_b: **HX < HZ < HY**

d) Percent dissociation = (2/8) x 100% = **25%**

e) **NaY**, the weakest base, will give the highest pOH and the smallest pH.

18.190 $NH_3(aq) + H_2O(l) \leftrightarrows NH_4^+(aq) + OH^-(aq)$

Convert to a K_a relationship:

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

$K_a = K_w / K_b = (1.0 \text{ x } 10^{-14}) / (1.76 \text{ x } 10^{-5}) = 5.6818 \text{ x } 10^{-10}$ (unrounded)

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

$$\frac{[NH_3]}{[NH_4^+]+[NH_3]} = \frac{K_a}{[H_3O^+]+K_a}$$

a) $[H_3O^+] = 10^{-pH} = 10^{-7.00} = 1.0 \text{ x } 10^{-7}\ M\ H_3O^+$

$$\frac{[NH_3]}{[NH_4^+]+[NH_3]} = \frac{5.6818 \text{ x } 10^{-10}}{1.0 \text{ x } 10^{-7} + 5.6818 \text{ x } 10^{-10}} = 5.6496995 \text{ x } 10^{-3} = \mathbf{5.6 \text{ x } 10^{-3}}$$

b) $[H_3O^+] = 10^{-pH} = 10^{-10.00} = 1.0 \text{ x } 10^{-10}\ M\ H_3O^+$

$$\frac{[NH_3]}{[NH_4^+]+[NH_3]} = \frac{5.6818 \text{ x } 10^{-10}}{1.0 \text{ x } 10^{-10} + 5.6818 \text{ x } 10^{-10}} = 0.8503397 = \mathbf{0.85}$$

c) Increasing the pH shifts the equilibria towards NH_3. Ammonia is able to escape the solution as a gas.